Fluktuations-Dissipationstheorem

$$\boxed{C(\omega) = \frac{2k_BT}{\omega}\chi''(\omega)} \quad (7.15)$$

d) Kramers-Kronig-Relation:

- Motivation: FD-Theorem: $C(\omega) \longrightarrow \chi''(\omega) \xrightarrow{\text{KK-Rel.}} \chi'(\omega)$

$$\boxed{\text{Kausalität} \longrightarrow \chi'(\omega) \leftrightarrow \chi''(\omega)} \quad (7.20)$$

- Herleitung:

(1) Definiere: $\chi(z) = \int_{-\infty}^{\infty} e^{izt}\chi(t)\,dt = \int_{0}^{\infty} e^{izt}\chi(t)\,dt$, $\operatorname{Im} z \geq 0$! (7.21a)

Fortsetzung von $\chi(\omega)$ ins Komplexe

$\longrightarrow$ $\chi(z)$ ist analytisch in $\operatorname{Im} z \geq 0$

Grund: Kausalität

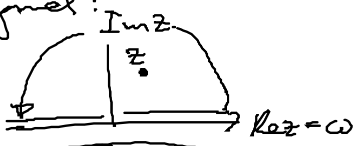
Eigenschaften: $\chi^*(z) = \chi(-z^*)$ (7.21)

andere Darstellung:

$$\boxed{\chi(z) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,\frac{\chi(\omega)}{\omega - z}} \quad (7.22)$$

(i) Grund: Cauchysche Integralformel:

$$f(z) = \oint \frac{dz'}{2\pi i}\,\frac{f(z')}{z'-z}$$



(ii) Beweis:

$$\chi(z) \overset{(7.21a)}{=} \int_{-\infty}^{\infty}\chi(t)\,e^{izt}\,dt = \int_{-\infty}^{\infty}dt\,\chi(t)\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,\frac{e^{i\omega t}}{\omega - z} \quad \chi(\omega)$$

(2) (7.22) $\longrightarrow$ $\chi(z) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,\chi(\omega)\left[\frac{1}{\omega - z} \pm \underbrace{\frac{1}{\omega - z^*}}\right]$

$\oint \frac{\chi(z')dz'}{z'-z^*} = 0$, weil $\frac{\chi(z')}{z'-z^*}$ analytisch für $\operatorname{Im} z > 0$

$$\overset{(+)}{=} \underbrace{\int_{-\infty}^{\infty}\frac{d\omega}{\pi i}\,\chi(\omega)\operatorname{Re}\frac{1}{\omega - z}}_{\text{lese ab: } \longrightarrow \operatorname{Re}\chi(z)} \overset{(-)}{=} \underbrace{\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\,\chi(\omega)\operatorname{Im}\frac{1}{\omega - z}}_{\longrightarrow \operatorname{Im}\chi(z)}$$

also: $\chi(z) = \int_{-\infty}^{\infty}\frac{d\omega}{\pi}\operatorname{Im}\chi(\omega)\left[\operatorname{Re}\frac{1}{\omega - z} + i\operatorname{Im}\frac{1}{\omega - z}\right]$ (7.23)

$$\longrightarrow \boxed{\chi(z) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \, \frac{\chi''(\omega)}{\omega - z}} \qquad (7.24)$$

... $\chi(z)$ aus $\chi''(\omega)$!

$$\longrightarrow \chi(\omega) = \lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \, \frac{\chi''(\omega')}{\omega' - (\omega + i\varepsilon)}$$

mit $\lim_{\varepsilon \to 0} \frac{1}{x - i\varepsilon} = \lim_{\varepsilon \to 0} \frac{x + i\varepsilon}{x^2 + \varepsilon^2} = P\frac{1}{x} + \pi i \, \delta(x)$ (7.25)

$$\boxed{P\int_{-\infty}^{\infty} \frac{1}{x} \dots dx = \lim_{\varepsilon \to 0} \int_{-\infty}^{-\varepsilon} \dots + \int_{+\varepsilon}^{\infty} \frac{1}{x} \dots dx} \qquad (7.26)$$

$$\longrightarrow \chi(\omega) = P\int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \, \frac{\chi''(\omega')}{\omega' - \omega} + i \, \chi''(\omega)$$

$$\longrightarrow \boxed{\chi'(\omega) = P\int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \, \frac{\chi''(\omega')}{\omega' - \omega}} \qquad (a)$$

(7.27)

$$\xrightarrow{\text{analog}} \boxed{\chi''(\omega) = P\int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \, \frac{\chi'(\omega')}{\omega' - \omega}} \qquad (b) \longleftarrow (7.23) \text{ mit } \mathrm{Re}\,\chi(\omega)$$

... Kramers-Kronig-Relationen

• Wegen (7.21) $\chi(-z^*) = \chi^*(z) \xrightarrow[\mathrm{Im}]{z=\omega} \boxed{\chi''(\omega) = -\chi''(-\omega)}$ (7.28)

$$(7.27)(a) \longrightarrow \chi'(\omega) = P\int_{0}^{\infty} \frac{d\omega'}{\pi} \, \frac{\chi''(\omega')}{\omega' - \omega} + P\int_{0}^{\infty} \frac{d\omega'}{\pi} \, \frac{\chi''(\omega')}{\omega' + \omega}$$

verwende (7.28) in $\int_{-\infty}^{0} \dots$

$$\longrightarrow \boxed{\chi'(\omega) = 2P\int_{0}^{\infty} \frac{d\omega'}{\pi} \, \frac{\omega' \chi''(\omega')}{\omega'^2 - \omega^2}} \qquad (7.29)$$

... nur $\chi''(\omega)$ für $\omega > 0$ nötig!

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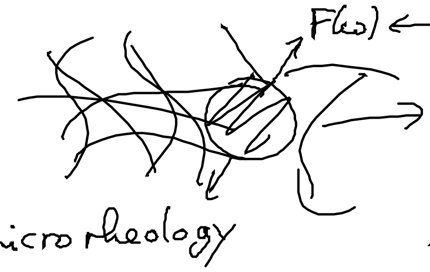
$F(\omega) \longleftrightarrow \chi(\omega)$



$C(t) = \langle x(0) x(t) \rangle$

... Brown. Fluktuation von ● im Netzwerk

$\longrightarrow C(\omega) \xrightarrow[\text{Theorem}]{\text{FD}} \chi''(\omega)$

$\xrightarrow[\text{Relation}]{\text{KK}} \chi'(\omega)$

microrheology

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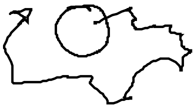
7.4 Beispiel: Brownsches Teilchen

• System: Brownsche Bewegg in viskoser Flüssigkeit (Wärmebad)



• mögliche dynamische Variable: $\langle \underline{x} \rangle = 0$

$$\boxed{\begin{aligned} \langle |\underline{x}(t) - \underline{x}(0)|^2 \rangle &= 2\left[\langle \underline{x}^2 \rangle - \langle \underline{x}(0) \cdot \underline{x}(t) \rangle \right] \\ &= 2\left[C(0) - C(t) \right] \end{aligned}} \quad (7.30)$$

... mittlere quadratische Verschiebung

NB: $\langle \underline{x}(0) - \underline{x}(t) \rangle = 0$

• dynamische Suszeptibilität:
vernachlässige Trägheitseffekte von Teilchen und Flüssigkeit

$$\longrightarrow \quad \underline{v}(t) = \mu\, \underline{F}(t) \quad \longrightarrow \quad \frac{d\underline{x}(t)}{dt} = \mu\, \underline{F}(t)$$

$$\xrightarrow{FT} -i\omega\, \underline{x}(\omega) = \mu\, \underline{F}(\omega)$$

Mobilität
$\frac{1}{6\pi\eta a}$ für Kugel
Viskosität, Kugelradius

$$\longrightarrow \quad \boxed{\underline{x}(\omega) = i \underbrace{\frac{\mu}{\omega}}_{\chi''(\omega)} \underline{F}(\omega)} \quad (7.31)$$

[gültig für „kleines" ω]

• FD-Theorem:

$$C(\omega) = \int \langle \underline{x}(0) \cdot \underline{x}(t) \rangle e^{i\omega t} dt$$

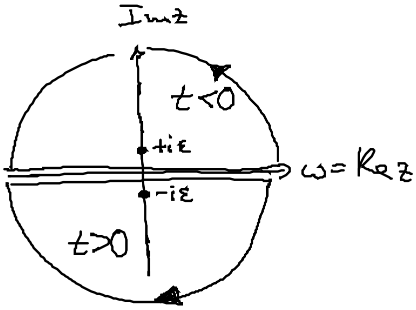
$$= 3 \times \frac{2k_B T}{\omega} \chi''(\omega) = \frac{6\mu\, k_B T}{\omega^2}$$

für jede Raumdimension!

Berechne:

$$C(0)-C(t) = \int C(\omega)\left(1-e^{-i\omega t}\right)\frac{d\omega}{2\pi}$$

$$= 6\mu k_B T \int_{-\infty}^{\infty} \frac{1}{\omega^2}\left(1-e^{-i\omega t}\right)\frac{d\omega}{2\pi}$$



$$\lim_{\varepsilon\to 0}\frac{1}{(\omega+i\varepsilon)(\omega-i\varepsilon)} \qquad \underbrace{1-\varepsilon t}$$

$$\overset{\text{Residuensatz}}{=} \lim_{\varepsilon\to 0} 6\mu k_B T \begin{cases} -\frac{\cancel{2\pi} i}{\cancel{2\pi}}\,\frac{1-e^{-\varepsilon t}}{-2i\varepsilon} = 3\mu k_B T\, t, & t>0 \\ \frac{\cancel{2\pi} i}{\cancel{2\pi}}\,\frac{1-e^{\varepsilon t}}{2i\varepsilon} = -3\mu k_B T\, t, & t<0 \end{cases}$$

(7.30) ⟶

$$\boxed{\begin{aligned} \langle |x(t)-x(0)|^2\rangle &= 2\left[C(0)-C(t)\right] \\ &= 6\,D\,|t| \ \ldots \text{ Diffusion!} \\ \text{mit } D &= \mu k_B T \ \ldots \text{ Einstein-Relation} \end{aligned}}$$

Fluktuation (→ D) Dissipation (→ μ)