d) Kramers-Kronig-Relation:

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

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

- Herleitung:

(1) Definiere: $\chi(z) = \int_{-\infty}^{\infty} e^{izt}\chi(t)\,dt = \int_0^{\infty} e^{izt}\chi(t)\,dt \;, \quad \operatorname{Im} z \geq 0$

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

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

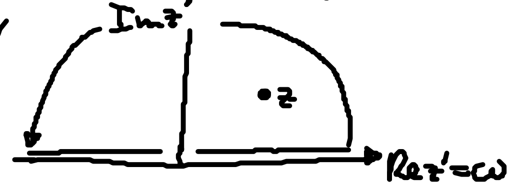
andere Darstellung

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

Beweis: $\chi(z) = \int_{-\infty}^{\infty}\chi(t)\,dt \underbrace{\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,\frac{e^{i\omega t}}{\omega - z}}_{e^{izt}}$

Grund: Cauchysche Integralformel

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



$\chi(z) = (7.22) + \underbrace{\int \frac{dz'}{2\pi i}\,\frac{\chi(z')}{z'-z}}_{=0}$, falls $\chi(\omega) \sim \frac{1}{|\omega|^{1+\varepsilon}}$ für $\omega \to \infty$

(2) (7.22) $\longrightarrow \chi(z) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}\,\chi(\omega)\left[\frac{1}{\omega - z} \pm \underbrace{\frac{1}{\omega - z^*}}_{0 = \oint \frac{\chi(z)}{z - z^*}}\right]$, weil $\chi(z)$ analytisch für $\operatorname{Im} z > 0$

$$\overset{(+)}{=} \underbrace{\int_{-\infty}^{\infty}\frac{d\omega}{\pi i}\,\chi(\omega)\,\mathrm{Re}\,\frac{1}{\omega - z}}_{} \overset{(-)}{=} \underbrace{\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\,\chi(\omega)\,\mathrm{Im}\,\frac{1}{\omega - z}}_{}$$

lese ab: $\longrightarrow \mathrm{Re}\,\chi(z)$ $\qquad \longrightarrow \mathrm{Im}\,\chi(z)$

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

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

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

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

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

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

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

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

(7.27)

$$\text{analog: } \boxed{\chi''(\omega) = P\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\,\frac{\chi'(\omega')}{\omega'-\omega}} \quad (b)$$

[(7.23) mit $\mathrm{Re}\,\chi(\omega)$]

... Kramers-Kronig-Relationen

• wegen: $\chi(-z^*) = \chi^*(z) \xrightarrow{z=\omega} \boxed{\chi''(\omega) = -\chi''(-\omega)}$ (7.28)

... Antisymmetrie

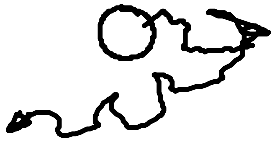
$$(7.27)(a) \xrightarrow{(7.28)} \chi'(\omega) = P\int_{0}^{\infty}\frac{d\omega'}{\pi}\,\frac{\chi''(\omega')}{\omega'-\omega} + P\int_{0}^{\infty}\frac{d\omega'}{\pi}\,\frac{\chi''(\omega')}{\omega'+\omega}$$

$$\xrightarrow[\omega'+\omega+\omega'-\omega = 2\omega']{} \boxed{\chi'(\omega) = 2P\int_{0}^{\infty}\frac{d\omega'}{\pi}\,\frac{\omega'\chi''(\omega')}{\omega'^2-\omega^2}} \quad (7.29)$$

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

7.4 Beispiel: Brownsches Teilchen

• System: thermische Bewegung in viskoser Flüssigkeit (Wärmebad!)



• mögliche dynamische Variable:

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

... mittlere quadratische Verschiebung

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

• dynamische Suszeptibilität:

vernachlässige Trägheitseffekte von Teilchen und Flüssigkeit:

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

Mobilität:
$\frac{1}{6\pi\eta a}$ für Kugel

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

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

[gültig für „kleines" ω]

• FD-Theorem:

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

$$= 3\cdot\frac{2k_BT}{\omega}\chi''(\omega) = \frac{6\mu\,k_BT}{\omega^2}$$

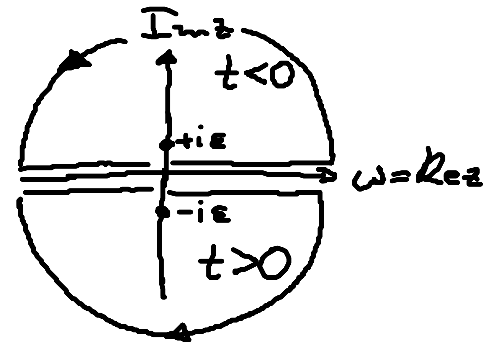
für jede Raumdimension

Berechne:

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

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

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



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

(7.30) ⟶

$$\boxed{\begin{aligned}\langle|x(t)-x(0)|^2\rangle&=2\left[C(0)-C(t)\right]\\&=6D|t|\quad\ldots\text{ Diffusion}\\ \text{mit } \underbrace{D}_{\text{Fluktuation}}&=\underbrace{\mu}_{\text{Dissipation}} k_B T\quad\ldots\text{ Einstein-Relation}\end{aligned}}\qquad(7.32)$$