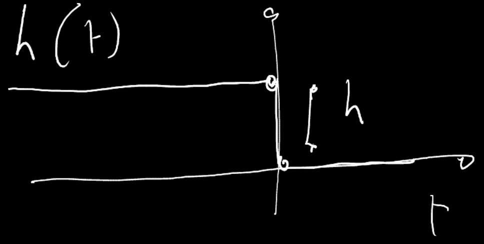
Linear response theory:

perturbed Hamiltonian $\mathcal{H}' = \mathcal{H} - hX$



non equilibrium average $\langle X(t) \rangle$

$\boxed{\beta h \ll 1}$ — $\langle X(t)\rangle - \langle X\rangle_0 = \beta h \left[\langle X(t) X(0)\rangle_0 - \langle X\rangle_0^2 \right]$

$\langle X \rangle_0 = 0$

$\langle X(t)\rangle = \beta h \left[\langle X(t) X(0) \rangle \right]$ ←

for a generic $h(t)$

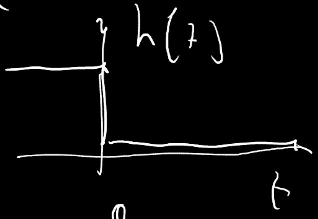
Response function $\Xi(t, t')$ defined by

$$\boxed{\langle X(t) \rangle = \int dt' \, \Xi(t, t') \, h(t')} \quad (*)$$

$$\Xi(t,t') = \begin{cases} \Xi(t - t') & \text{if } t' < t \\ 0 & \text{if } t' > t \end{cases}$$

↳ causality

(Green function)



$\tau = t - t'$

$$\int_{-\infty}^{0} dt' \, \Xi(t - t') = \int_t^{+\infty} d\tau \, \Xi(\tau) = \frac{\langle X(t) \rangle}{h} = \beta \langle X(t) X(0) \rangle_0$$

$$\int_t^{+\infty} \Xi(\tau) \, d\tau = \beta \langle X(t) X(0) \rangle_0$$

$$\Xi(t) = -\beta \, \theta(t) \frac{d}{dt} \langle X(t) X(0) \rangle_0 \quad (+)$$

↳ Heaviside step function

$$F(\omega) = \int_{-\infty}^{+\infty} dt \exp(-i\omega t)\, F(t)\, dt$$

$$F(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \exp(i\omega t)\, F(\omega)\, d\omega$$

(*) $\langle X(\omega) \rangle = h(\omega) \cdot F(\omega)$

(+) $F(\omega) = -\beta \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi}\, \theta(\omega - \omega')\, i\omega' C(\omega')$

$$C(t) = \langle X(t)\, X(0) \rangle_0 \xrightarrow{\text{F.T.}} C(\omega)$$

$C(\omega)$ = "power spectrum"

$$C(\omega) = \int_{-\infty}^{+\infty} dt \exp(-i\omega t)\, C(t)$$

$$= \lim_{T \to \infty} \frac{1}{T} \langle |X_T(\omega)|^2 \rangle_0$$

Wiener-Kinchin theorem

$$X_T(\omega) = \int_{-T/2}^{+T/2} dt \exp(-i\omega t)\, X(t)$$

$\langle X(t) \rangle_0 \not\to$ FT

$C(\omega) \in \mathbb{R}$; $C(\omega) \geq 0 \;\; \forall \omega$

$$C(t) = \frac{1}{\tau} \exp\left(-\frac{|t|}{\tau}\right) \quad \forall t$$

$$\to C(\omega) = \frac{1}{1+i\omega\tau} + \frac{1}{1-i\omega\tau} = \frac{2}{1+\omega^2\tau^2}$$

Lorentzian

$$C(t) = C(-t) \longrightarrow C(\omega) = C(-\omega)$$

$$\langle X(t)\, X(0)\rangle_0 = \langle X(0)\, X(-t)\rangle_0 = C(-t)$$

time translation invariance at equilibrium

$$\Gamma(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \, \exp(i\omega t)\, \Gamma(\omega) \qquad z = \omega - i\varepsilon$$

$\Gamma(t) = 0$ for $t < 0$ $\Rightarrow$ $\Gamma(z)$ analytic for $\mathrm{Im}(z) < 0$ ~ NO POLES

$$\vartheta(\omega) = \lim_{\varepsilon \to 0^+} \int_0^{\infty} dt \, \exp(-(\varepsilon + i\omega t)) = \lim_{\varepsilon \to 0^+} \frac{1}{\varepsilon + i\omega}$$

(APPENDIX F Livi & Politi) $= \pi\,\delta(\omega) - i\, PV\left(\frac{1}{\omega}\right)$ (×)

$$PV\left(\frac{1}{\omega}\right) = \lim_{\varepsilon \to 0^+}\left[\int_{-\infty}^{\varepsilon} \frac{\phi(\omega)}{\omega} d\omega + \int_{\varepsilon}^{+\infty} \frac{\phi(\omega)}{\omega} d\omega\right]$$

($\phi(\omega)$ test function)

$$(+) + (\times) \longrightarrow \Gamma(\omega) = -\beta\left[\frac{i\omega}{2} C(\omega) + PV\left[\int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \frac{\omega' C(\omega')}{\omega - \omega'}\right]\right]$$

imaginary part — real part

$C(\omega) \in \mathbb{R}$

$$\Gamma^I(\omega) = -\beta \frac{\omega}{2} C(\omega)$$ — odd function of ω

$$\Gamma^R(\omega) = PV\left[\int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{1}{\omega - \omega'} \Gamma^I(\omega')\right]$$ $\Leftarrow$ FL-DISS Theorem

KRAMERS - KRONIG relation

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

- Work done on a system by the perturbation (out-of-equilibrium → dissipation)

System energy $-h X$ ⇒ work done by the field on the system $\sim +h\dot{X}$

$$W = \int_{-\infty}^{+\infty} dt \, h(t) \left\langle \frac{d X(t)}{dt} \right\rangle$$

NON-EQUILIBRIUM AVERAGE

(periodic perturbation → integral over a period)

$$\langle X(t) \rangle = \int_{-\infty}^{+\infty} dt' \, \chi(t-t') \, h(t')$$

$h(t)$; $h(t')$; $\chi(t-t')$ → FT

$$W = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \, i\omega \, \chi(\omega) \, |h(\omega)|^2$$

($h(t) \in \mathbb{R}$ → $h^*(\omega) = h(-\omega)$)

$$W = -\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \, \omega \, \chi^I(\omega) \, |h(\omega)|^2$$

$$W = \frac{\beta}{2} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \, \omega^2 \, C(\omega) \, |h(\omega)|^2$$

DISSIPATION ↕ POWER SPECTRUM ↕ IMAGINARY PART RESPONSE FUNCTION

Susceptibility: $\langle X(\omega)\rangle = \Xi(\omega)\, h(\omega)$

$\Xi(\omega)$ = "dynamic" (frequence-dependent) susceptibility

"Static" thermodynamic susceptibility χ

$$\chi = \lim_{\omega\to 0} \Xi(\omega) = \left.\frac{\partial \langle X(\omega)\rangle}{\partial h(\omega)}\right|_{\omega=0}$$

$$\lim_{\omega\to 0}\Xi(\omega) = \lim_{\omega\to 0}\left[-\beta\int_0^{+\infty} dt\, \exp(-i\omega t)\frac{d}{dt}\left(\langle X(t)X(0)\rangle_0\right)\right]$$

regularization: $z = \omega - i\varepsilon$, $\lim_{\varepsilon\to 0^+}\lim_{\omega\to 0}$

$$= \lim_{\varepsilon\to 0^+}\left(-\beta\int_0^{+\infty} dt\, \exp(-\varepsilon t)\frac{d}{dt}\langle X(t)X(0)\rangle_0\right)$$

$$= \lim_{\varepsilon\to 0^+}\left[-\beta \exp(-\varepsilon t)\langle X(t)X(0)\rangle_0\right]_{0}^{+\infty} - \beta\varepsilon\int_0^{+\infty} dt\, \exp(-\varepsilon t)\langle X(t)X(0)\rangle_0$$

(the first bracket: 0 at $t=+\infty$, X_0 at $t=0$; the last term $\to 0$)

$$= \beta\langle X^2\rangle_0$$

$$\chi = \lim_{\omega\to 0}\Xi(\omega) = \beta\langle X^2\rangle_0 \qquad \left(\chi = \beta\left[\langle X^2\rangle_0 - \langle X\rangle_0^2\right]\right)$$

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

$$= -\lim_{\varepsilon\to 0^+}\int_{-\infty}^{+\infty}\frac{d\omega'}{\pi}\frac{\Xi^I(\omega')}{\omega'+i\varepsilon} \qquad \left(\Xi^I(\omega) = -\frac{\beta\omega}{2}C(\omega)\right)$$

$$= \frac{\beta}{2\pi}\int_{-\infty}^{+\infty} d\omega\, C(\omega)$$

$$\chi = -\lim_{\varepsilon \to 0^+} \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\Gamma''(\omega')}{\omega' + i\varepsilon} = \frac{\beta}{2\pi} \int_{-\infty}^{+\infty} d\omega\, C(\omega) > 0$$

Thermodynamic sum rule
↳ (integral over the response at all frequencies)

Example → damped harmonic oscillator

Hamilton equation: $m\ddot{x}(t) + \tilde{\gamma}\dot{x}(t) + k\,x(t) = F(t)$ ← external force

(energy term → $-x \cdot F$ — perturbing field; x: observable)

NO NOISE → NO THERMODYN. – NO STAT. MECH.

Linear Hamilton equation → Linear response theory is EXACT!!

$$\Gamma(t-t') = G(t-t')$$ ← exact Green function

$$x(t) = \int_{-\infty}^{+\infty} dt'\, G(t-t')\, F(t');$$

$$G(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega\, \exp(i\omega t)\, G(\omega)$$

$$x(t) = \int_{-\infty}^{+\infty} \frac{dt'}{2\pi} \int_{-\infty}^{+\infty} d\omega\, \exp(i\omega(t-t'))\, G(\omega)\, F(t')$$

$$F(t) = m\ddot{x}(t) + \tilde{\gamma}\dot{x}(t) + k\,x(t)$$

"1"

$$F(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \int_{-\infty}^{+\infty} dt' \left[-m\omega^2 + i\tilde{\gamma}\omega + k\right] F(t')\, G(\omega) \cdot \exp(i\omega(t-t'))$$

$$G(\omega) = -\frac{1}{m\omega^2 - i\tilde{\gamma}\omega - k}$$

$\int \frac{d\omega}{2\pi} \to \delta(t-t')$

$\int dt' \to F(t)$

$\omega_0 = \sqrt{k/m}$ $\quad \gamma = \tilde{\gamma}/m$

$$G(\omega) = -\frac{1}{m[\omega^2 - i\gamma\omega - \omega_0^2]}$$

static susceptibility

$$\chi = \lim_{\omega \to 0} G(\omega) = \frac{1}{m\omega_0^2} = \frac{1}{k} = \frac{1}{\frac{d^2U}{dx^2}}$$

$U(x) = \frac{1}{2}kx^2$

$F = kx \to x = F/k$

Poles of $G(\omega)$ in the complex plane

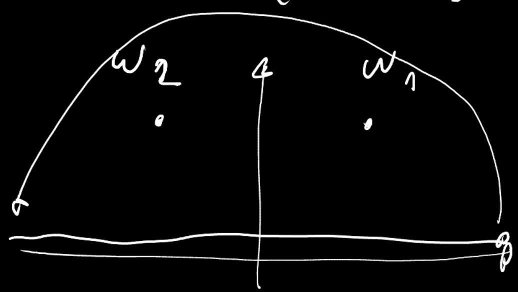
$\omega_1 = \Omega + i\gamma/2 \qquad \Omega^2 = \omega_0^2 - \gamma^2/4$

$\omega_2 = -\Omega + i\gamma/2$

$$G(\omega) = -\frac{1}{m(\omega - \omega_1)(\omega - \omega_2)}$$

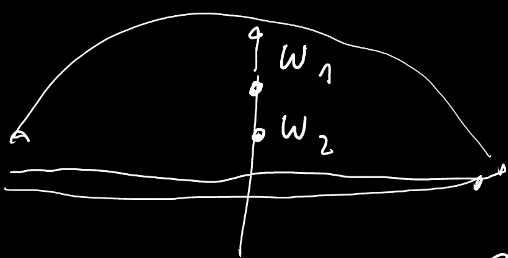
- $\Omega \in \mathbb{R}$ $(\omega_0^2 > \gamma^2/4)$

↳ underdamped case



- $i\Omega \in \mathbb{R}$ $(\omega_0^2 < \gamma^2/4)$

↳ overdamped case



[NO POLES in the lower half plane → CAUSALITY → $G(t) = 0$ for $t < 0$]

Explicit expression for $G(t)$:

$$G(t) = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} \frac{1}{m(\omega-\omega_1)(\omega-\omega_2)} \exp(i\omega t)$$

$$G(t) = -\frac{1}{2\pi m} 2\pi i \left[\frac{\exp(i\omega_1 t)}{\omega_1 - \omega_2} + \frac{\exp(i\omega_2 t)}{\omega_2 - \omega_1} \right]$$

↑ residue theorem

$$\boxed{G(t) = \frac{\sin(\Omega t)}{m\Omega} \exp\left(-\gamma t/2\right)}$$

$\omega_1 - \omega_2 = 2\Omega$

underdamped case ($\Omega \in \mathbb{R}$) → exponential decay (characteristic time $2/\gamma$) + oscillations (frequency Ω)

Poles of $G(\omega)$

- Imaginary part → exponential decay
- Real part → oscillations

Strongly overdamped regime: ($m = 0$ no inertial term)

$$G(\omega) \simeq \frac{1}{k + i\tilde{\gamma}\omega}$$

1 pole: $\omega_1 = ik/\tilde{\gamma}$ (→ exponential decay)

$$C(\omega) = -\frac{2}{\beta\omega} G^I(\omega) = -\frac{2}{\beta\omega} \frac{-\tilde{\gamma}\omega}{k^2 + \omega^2\tilde{\gamma}^2}$$

$$= \frac{2}{\beta} \frac{\tilde{\gamma}}{k^2 + \omega^2\tilde{\gamma}^2}$$

Lorentzian function width $k/\tilde{\gamma}$