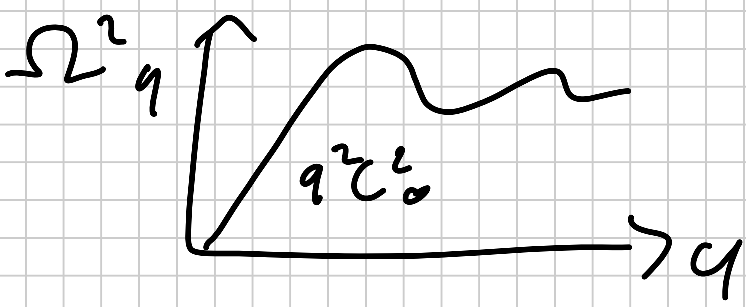
Mori-Zwanzig Projection-Operator Formalism for Liquid Dynamics

MZ-step 1: projection operator
MZ-step 2: frequency matrix
MZ-step 3: memory kernel
MZ-step 4: equation of motion

Hydrodynamic Limit of (*)

$q \to 0$



$\Omega_q^2 \to q^2 c_0^2$

$$c_0^2 = \lim_{q \to 0} \frac{v_{th}^2}{S_q} = \partial_\rho P\big|_T = \frac{1}{m n \kappa_T}$$

κ_T isothermal compressibility
c_0 isothermal sound velocity

for $q \to 0$, $z \to 0$, $\hat{\Gamma}(q,z) \to i\Gamma$, $\Gamma > 0$

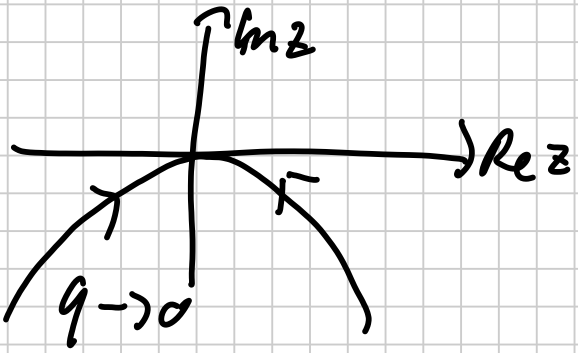
$$\boxed{\hat{S}(q,z) \to \frac{-v_{th}^2/c_0^2}{z - \dfrac{q^2 c_0^2}{z + iq^2\Gamma/mn}}}$$

singular for $q \to 0$, $z \to 0$
↳ look for pole structure

$$\hat{S}(q,z) = \frac{-(v_{th}^2/c_0^2)\,(z + iq^2\Gamma/mn)}{z^2 - q^2 c_0^2 + i z q^2 \Gamma/mn}$$

denominator vanishes for

$$\boxed{z = \pm c_0 q - i q^2 \Gamma/2mn + \mathcal{O}(q^3)}$$



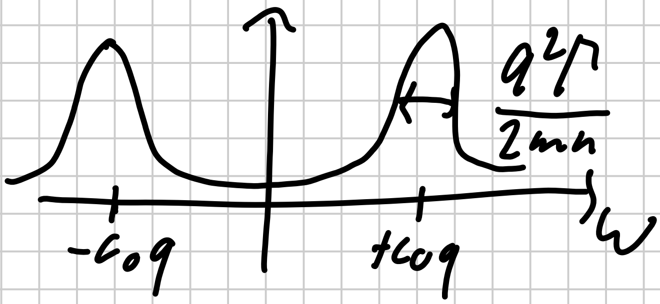
poles approach real axis for $q \to 0$

partial fraction decomposition

$$\boxed{\hat{S}(q,z) = \frac{-V_m^2/2c_0^2}{z - c_0 q + i q^2 \Gamma/2mn} + \frac{-V_m^2/2c_0^2}{z + c_0 q + i q^2 \Gamma/2mn}}$$

spectrum measured in scattering experiment

$$\boxed{\mathrm{Im}\, S(q, z=\omega+i0) = \frac{V_m^2}{c_0^2}\left[\frac{q^2\Gamma/4mn}{(\omega - c_0 q)^2 + (q^2\Gamma/2mn)^2} + \frac{q^2\Gamma/4mn}{(\omega + c_0 q)^2 + (q^2\Gamma/2mn)^2}\right]}$$



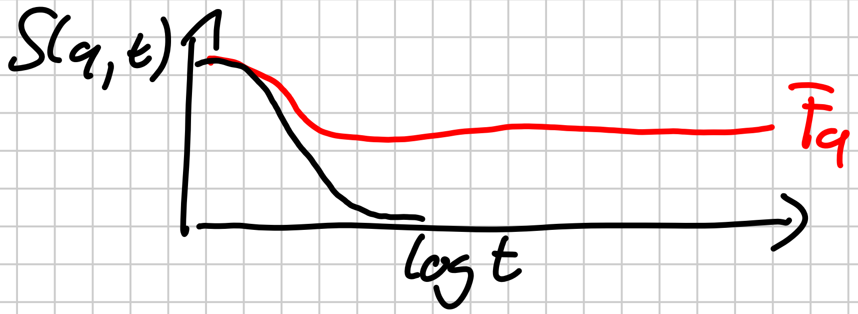
propagating damped sound waves

NB: inclusion of energy mode for $q \to 0$ plus MZ-procedure yields in addition thermal diffusion

II. 1. F Glass Transition

Definition of Glass state

$$F_q := \lim_{t\to\infty} S(q,t) > 0 \text{ , glass form factor}$$



$F_q = 0$, fluid

$F_q > 0$, glass

dynamic structure factor develops elastic peak $\hat{S}(q,z) = -\frac{F_q}{z} + \text{smooth contributions}$

exact dynamic structure factor in (*) with memory kernel $\hat{M}(q,z)$

$$\boxed{\hat{S}(q,z) = \frac{-S_q}{z - \frac{\Omega_q^2}{z + \Omega_q^2 \hat{M}(q,z)}} \qquad M(q,t) = \frac{S_q}{N v_{th}^2} \langle Q\sigma_q^L | R_Q(t) | Q\sigma_q^L \rangle}$$

finite correlator implies finite memory kernel

$$F_q = -\lim_{z\to 0} z\hat{S}(q,z)$$

$$= -\lim_{z\to 0} S_q z \frac{z + \Omega_q^2 \hat{M}(q,z)}{z[z + \Omega_q^2 \hat{M}(q,z)]} \overset{!}{\neq} 0$$

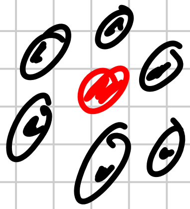
$$\Leftrightarrow -\lim_{z\to 0} z\hat{M}(q,z) =: \tilde{m}_q > 0$$

$$\boxed{\frac{F_q}{S_q} = \frac{\tilde{m}_q}{1+\tilde{m}_q} = 1/[1 + 1/\tilde{m}_q]} \quad **$$

Ansatz for closing Equations of Motion (mode-coupling theory)

$$\boxed{M(q,t) = \mathcal{F}[q; S(k,t)]}$$

physically motivated Ansatz: cage effect



memory kernel encoding stresses caused by density fluctuations $S(q,t)$

with this ansatz, (**) is closed set of equations, can be solved by iteration

ansatz implemented by projection onto density pairs

$$\boxed{P_2 := |\rho_k \rho_p\rangle \frac{1}{N^2 S_k S_p} \langle \rho_k \rho_p|}$$

summation over $\vec{k} < \vec{p}$

$$M(q,t) = \frac{S_q}{N v_{th}^2} \langle Q\sigma_q^L \underset{\uparrow P_2}{|} R_Q(t) \underset{\uparrow P_2}{|} Q\sigma_q^L\rangle$$

so-called uncontrolled approximation: factorization into pair modes

$$\langle \rho_k \rho_p | R_Q(t) | \rho_{k'} \rho_{p'}\rangle \approx \langle \rho_k | R(t) | \rho_{k'}\rangle \langle \rho_p | R(t) | \rho_{p'}\rangle$$

$$= \underbrace{\delta_{kk'} \delta_{pp'}}_{\text{translational invariance}} N^2 S(k,t) S(p,t)$$

$$\hookrightarrow \quad \boxed{M(q,t) \approx \sum_{k<p} V_{qkp} \, S(k,t) S(p,t)}$$

vertices $\boxed{V_{qkp} = n S_q \{\vec{q}\cdot[\vec{k} c_k + \vec{p} c_p]\}^2 / (2q^4)}$

direct correlation function c_q: $S_q = 1/(1 - \varrho c_q)$

nontrivial finding: fixed-point equations allow for solution $F_q > 0$ for realistic interaction potentials, say, hard-sphere exclusion or Lennard-Jones potential

normalization $F_q / S_q =: f_q$

illustration of transition in onedimensional model → fixed-point equation

$$\boxed{f = \frac{\mathcal{F}[f]}{1 + \mathcal{F}[f]} \Leftrightarrow \mathcal{F}[f] = \frac{f}{1-f}}$$

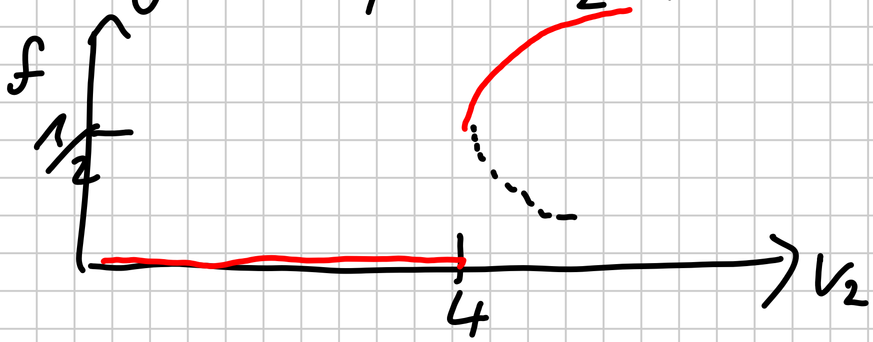
simplest (with severe defects) example: $\mathcal{F}[f] = V_2 f^2$

$$V_2 f^2 (1 - f) - f = 0 \quad \| : f \text{, for } f = 0 \text{, fluid state}$$

$$V_2 f (1 - f) - 1 = 0$$

roots $f = \dfrac{V_2 \pm \sqrt{V_2^2 - 4V_2}}{2V_2}$, real solution only if discriminant positive

singularity at $V_2^c = 4$



re-inserting solution at singularity
into eom (*) an asymptotic expansion
yields glassy dynamics correlation functions