Glassy Dynamics

recapitulation:

① Mori-Zwanzig projection for exact reformulation of eom into double fraction

$$\hat{S}(q,z) = \frac{-S_q}{z - \frac{\Omega_q^2}{z + \Omega_q^2 \hat{M}(q,z)}}$$

② closure of memory kernel via factorisation of memory kernel into pair modes

$$\mathcal{F}_q[S_k(t)] = M(q,t) \approx \sum_{k<p} V_{qkp} S(k,t) S(p,t)$$

with vertizes

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

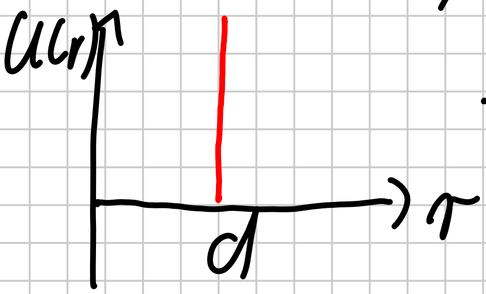
③ identification of bifurcations in long-time limits $f_q = \lim_{t\to\infty} \frac{S(q,t)}{S_q}$ in

$$\boxed{\mathcal{F}_q[f_k] = \frac{f_q}{1-f_q}}$$ also $$\partial_{f_q} \mathcal{F}_q[f_k] = \partial_{f_q} \frac{f_q}{1-f_q}$$

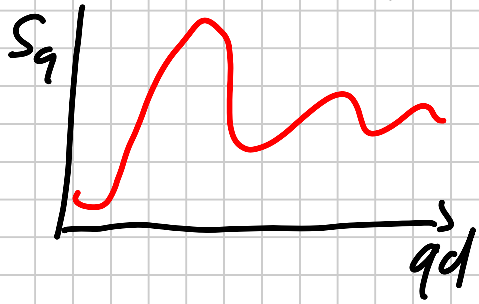
NB: - simplified schematic models as exercise: analytical solution possible
- full microscopic models to be solved by numerical methods

interaction potential $U(r) \rightarrow$ static structure factor $S_q \longrightarrow$ glass-transition diagram

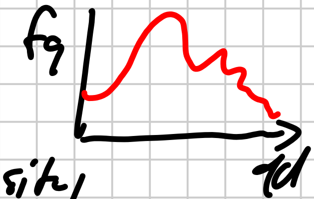
example for liquid-glass transition:
hard-sphere system (HSS), Bengtzelius et al (1984)



$\rightarrow$

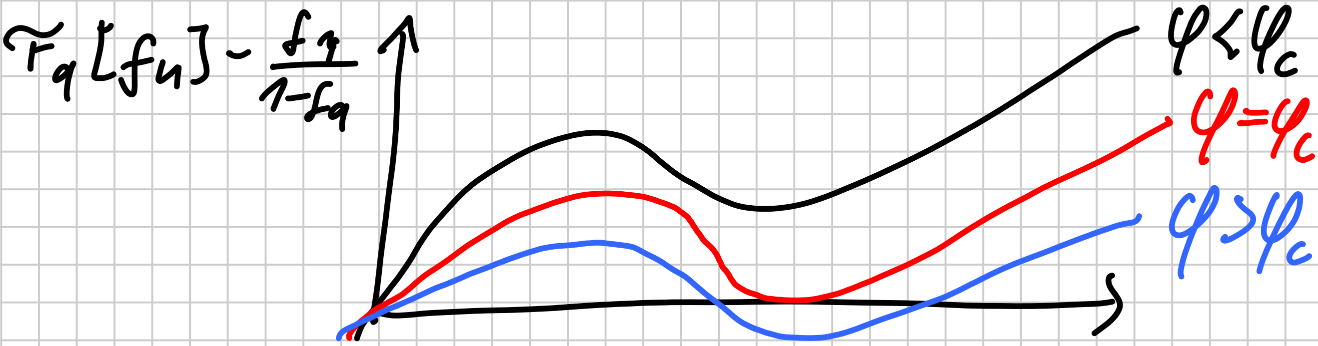


$\rightarrow$ $\varphi^c = 0.52$ glass transition



1 control parameter
packing fraction $\varphi = n\frac{\pi}{6}$; n, density

liquid-glass transition identified with simplest bifurcation A_2 or fold singularity



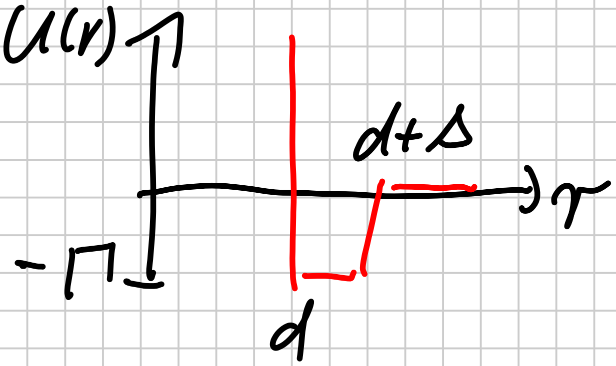
$\hookrightarrow$ for $\varphi > \varphi_c$: growth of plateau value f_q like

$$f_q = f_q^c + a_q\sqrt{\varphi - \varphi_c}$$

singularity of type A_l requires $l-1$ control parameters: A_2 needs 1, i.e. density or T

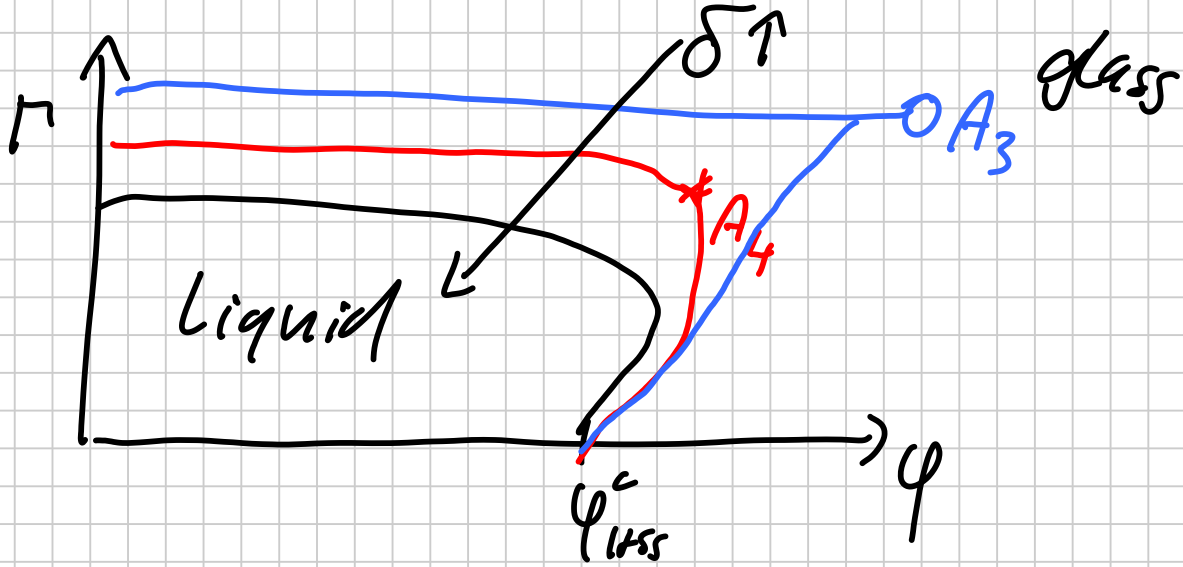
For $l > 2$, more control parameters need to be varied $\rightarrow$ endpoint singularities and glass-glass transitions

example: Square-Well System (SWS)



3 control parameters
- packing fraction φ
- well depth Γ
- well width $\delta = \frac{\Delta}{d}$

glass-transition diagram



predicted and found in computer simulation (2001 – 2003)

Dynamics close to Liquid-Glass Transition

eom
$$\boxed{\ddot{\phi}_q(t) + \Omega^2_q \phi_q(t) + \Omega^2_q \underbrace{\int_0^t dt' \, m_q(t') \dot{\phi}(t-t')}_{\frac{d}{dt}\int_0^t dt' \, m_q(t') \phi(t-t') - m_q(t) \underbrace{\phi(0)}_{=1}} = 0}$$

expansion around critical plateau value f^c:

$$\Phi_q(t) = f_q^c + G(t)$$

$$m_q(t) = \mathcal{F}_q[f_u^c] + \partial_{f_{q_1}} \mathcal{F}_q[f_u^c]\, G(t) + \frac{1}{2}\, \partial_{f_{q_1}} \partial_{f_{q_2}} \mathcal{F}_q[f_u^c]\, G(t)^2$$

neglect q-dependence in the following

$$\frac{1}{\Omega^2}\ddot{G}(t) + \underbrace{f^c - \mathcal{F}[f^c] + f^c \mathcal{F}[f^c]}_{①}$$
$$+ \underbrace{G(t) - \mathcal{F}'[f^c] G(t) + \mathcal{F}'[f^c] G(t) f^c + \mathcal{F}[f^c] G(t)}_{②}$$
$$- \frac{1}{2}\mathcal{F}''[f^c]\, G(t)^2 + \frac{1}{2}\mathcal{F}''[f^c]\, f^c\, G(t)^2$$
$$+ \mathcal{F}'[f^c] \frac{d}{dt} \int_0^t dt'\, G(t')\, G(t-t')$$
$$+ \frac{1}{2}\mathcal{F}''[f^c] \frac{d}{dt} \int_0^t dt'\, G(t')^2 G(t-t') = 0$$

① $f^c - \mathcal{F}[f^c] + f^c \mathcal{F}[f^c] = f^c - \mathcal{F}[f^c](1-f^c) = 0$

due to $\frac{f}{1-f} = \mathcal{F}[f]$

② $G(t)\left\{1 + \mathcal{F}[f^c] - \mathcal{F}'[f^c](1-f^c)\right\} =$

$$= G(t)\Big\{1 + \frac{f^c}{1-f^c} - \underbrace{\mathcal{F}'[f^c]}_{\frac{1}{(1-f)^2}}(1-f^c)\Big\} =$$

$$= G(t)\, \frac{1-f+f-1}{1-f} = 0$$

define $\lambda := \frac{1}{2}\mathcal{F}''[f^c](1-f^c)/\mathcal{F}'[f^c]$

exponent parameter

$$\Rightarrow \boxed{\lambda\, G(t)^2 - \frac{d}{dt}\int_0^t dt'\, G(t')G(t-t') = \frac{1}{\mathcal{F}'[f^c]}\left\{\frac{1}{\Omega^2}\ddot{G}(t) + \frac{d}{dt}\int_0^t dt'\, G(t')^2 G(t-t')\right\}} \quad (*)$$

Ansatz $\boxed{G(t) = (t/t_0)^{-a}}$

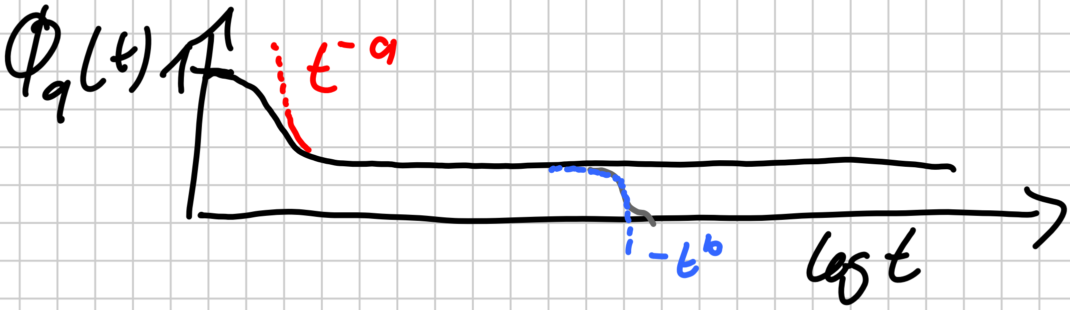
$$\int_0^t dt'\, t'^{-a}(t-t')^{-a} = \frac{t^{1-2a}}{1-2a}\,\frac{\Gamma(1-a)^2}{\Gamma(1-2a)}$$

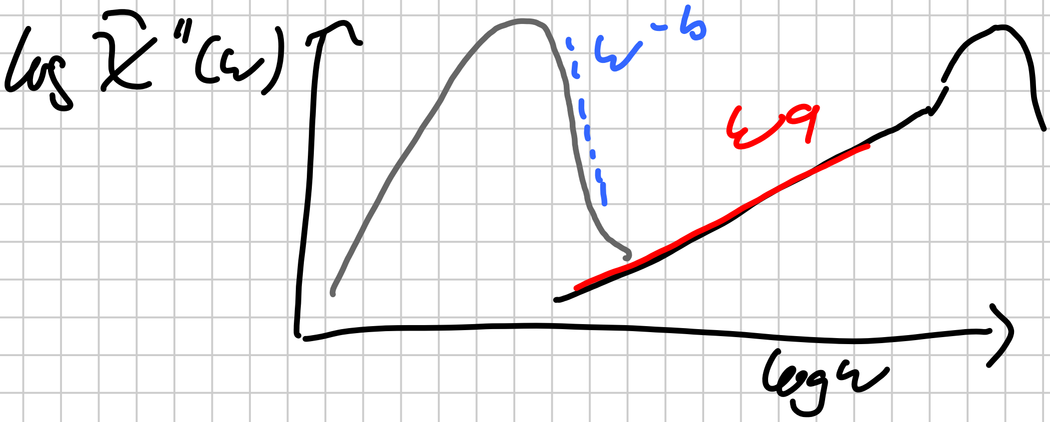
$$\hookrightarrow \boxed{\lambda = \frac{\Gamma(1-a)^2}{\Gamma(1-2a)}\,,\ a \le 1/2}$$

terms on rhs of (*) of higher order

↳ critical relaxation at transition point onto plateau

$$\boxed{\Phi_q(t) = f_q^c + h_q (t/t_0)^{-a} + K_q (t/t_0)^{-2a} + O(t^{-3a})}$$





Similar arguments for dynamics close to but not at the transition: decay from plateau, $\sigma<0$

$$\boxed{\Phi_q(t) = f_q^c - h_q\left(t/t_\sigma\right)^b + \kappa_q\left(t/t_\sigma\right)^{2b} + \mathcal{O}(t^{3b})}$$

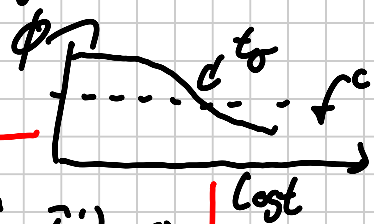
with exponent b again given by $\lambda = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}$

eom for transition (A_2)

$$\boxed{\sigma + \lambda\, G(t)^2 - \frac{d}{dt}\int_0^t dt'\, G(t')\, G(t-t') = 0}$$

allows for Master function in scaling limit

$$G(t) = \sqrt{|\sigma|}\; g_\pm(\hat{t}), \quad \hat{t} = t/t_\sigma$$



$$\boxed{\pm 1 + \lambda\, g_\pm(\hat{t})^2 - \frac{d}{d\hat{t}}\int_0^{\hat{t}} d\hat{t}'\, g_\pm(\hat{t}')\, g_\pm(\hat{t}-\hat{t}') = 0}$$

divergent time scale for crossing f

$$t_\sigma = t_0\, |\sigma|^{-1/2a}$$

validity of scaling law for $|G(t)| \ll 1$

↳ $\sqrt{|\sigma|}\,(t/t_\sigma)^b$ for large times and $\sigma<0$

↳ $t \ll t'_\sigma$ with $t'_\sigma = t_\sigma\, |\sigma|^{-1/2b} = t_0\, |\sigma|^{-1/2a - 1/2b}$

↳ second time scale t'_σ diverges faster than t_σ