Methoden moderner Röntgenphysik: Streuung und Abbildung

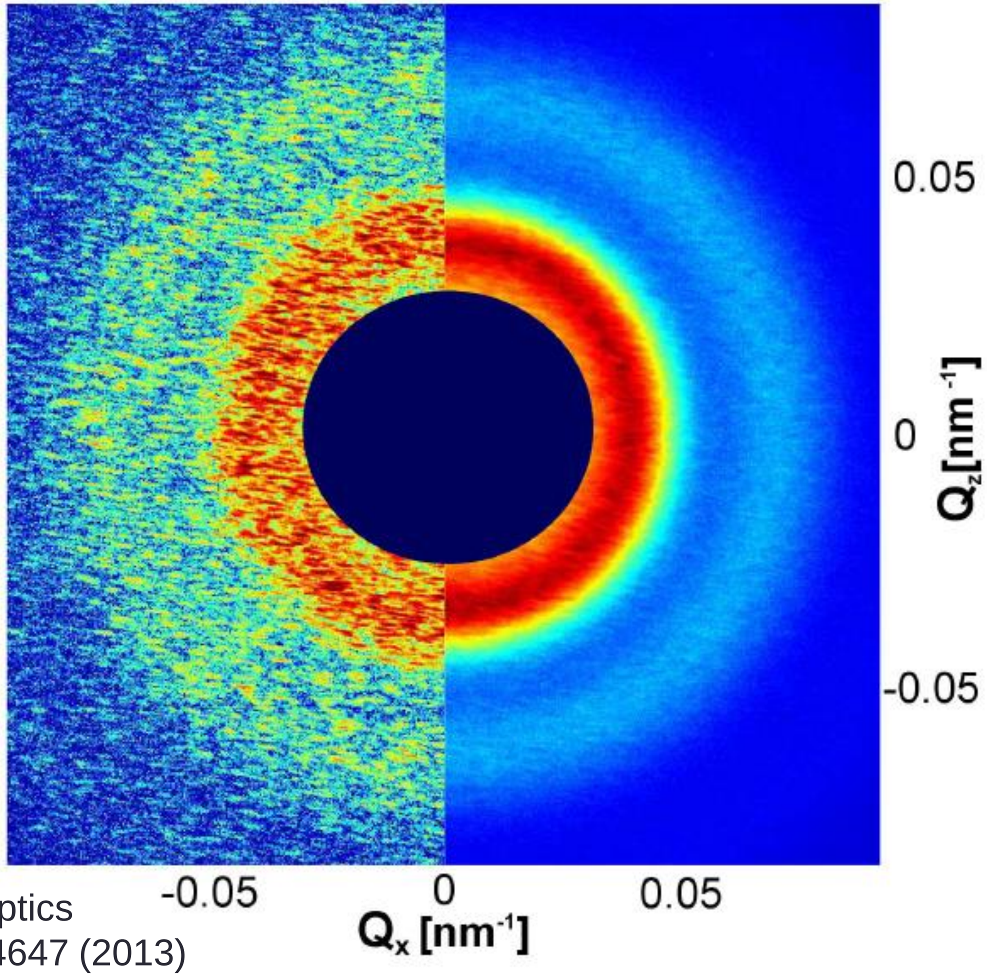
Lecture 19	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2021		
	G. Grübel, O. Seeck, F. Lehmkühler, A. Philippi-Kobs, V. Markmann, M. Martins		
Location	online		
Date	Tuesday	12:30 - 14:00	(starting 6.4.)
	Thursday	8:30 - 10:00	(until 8.7.)

Soft Matter – Timeline

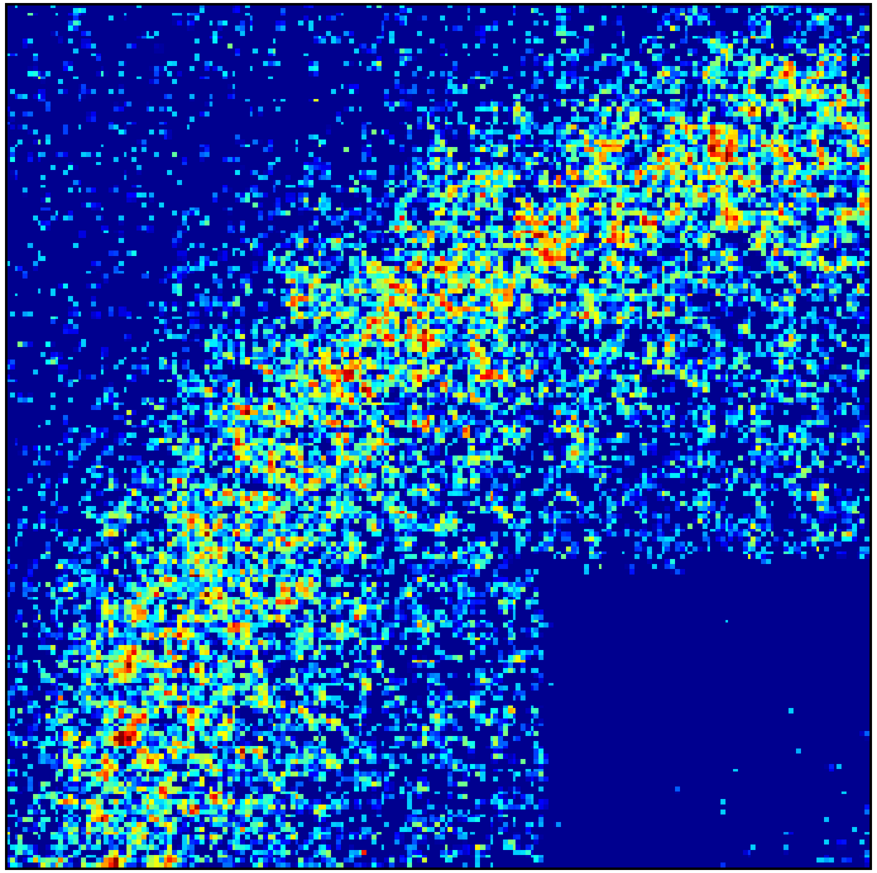
- Do 27.05.2021 Soft Matter studies I: Methods & experiments
  Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, **…**
- Di 01.06.2021 Soft Matter studies II: Structure
  SAXS & WAXS applications, X-ray cross correlations, **…**
- Do 03.06.2021 Soft Matter studies III: Dynamics
  XPCS applications, diffusion, dynamical heterogeneities, ...
- Di 08.06.2021 XPCS & XCCA simulations and modelling
- Do 10.06.2021 Case study I: Glass transition
  Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, ...
- Di 15.05.2021 Case study II: Water
  Phase diagram, anomalies, crystalline and glassy forms, FEL studies, ...
- Do 17.06.2021 Outlook: Opportunities at new facilities

Probing structure and dynamics with coherent X-rays: XPCS & XCCA

X-ray scattering from disordered samples: speckles → structure decoded



S. Lee et al. Optics Express 21, 24647 (2013)

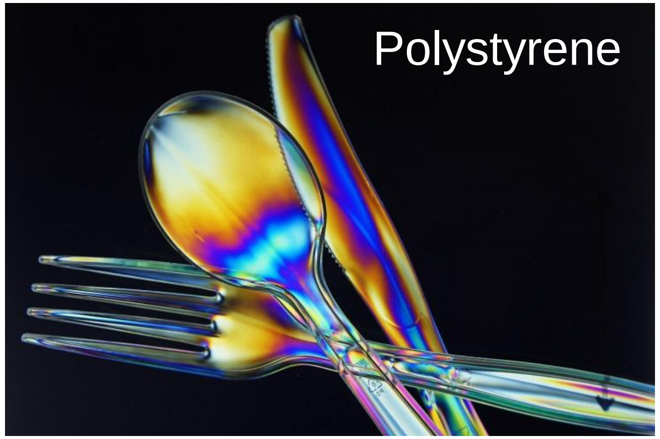


What is a glass?

- Disordered materials
  - Lack of periodicity (long-range order) as crystals
  - But: short-range order may exist
  - Behave mechanically like solids

- Glass is known since ancient times (e.g. silicate glass)

- Examples of glasses
  - Fused Silica (SiO_2)
  - Network glasses (phosphate glasses, borate glasses, …)
  - Obsidian
  - Glass fibres
  - Metallic glasses
  - Polymer glasses (plastics)
  - Colloidal glasses
  - Glassy water (→ lecture 20)



Roman glasses

Pictures: wikipedia

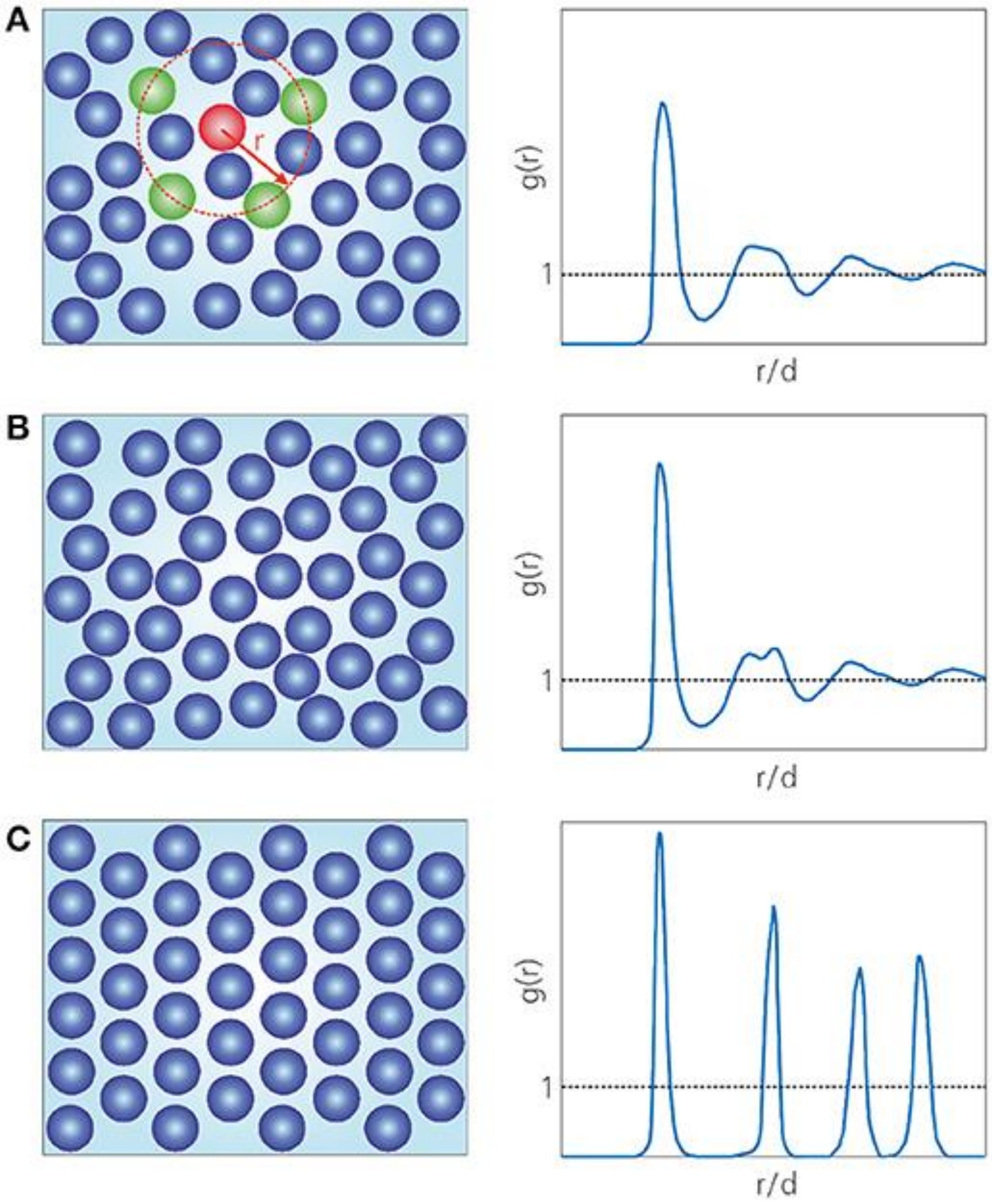
What is a glass?

Structure of

(A) a normal liquid

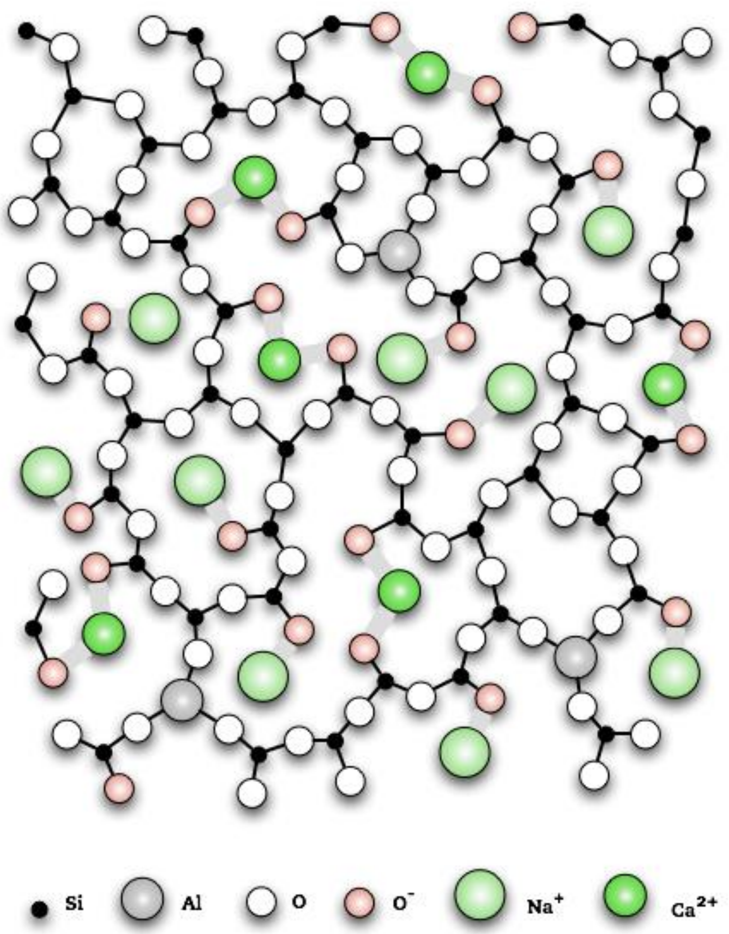
(B) an amorphous solid, i.e., a glass

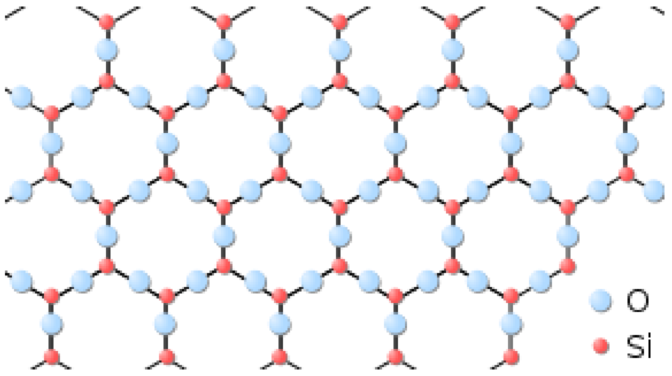
(C) a crystalline solid

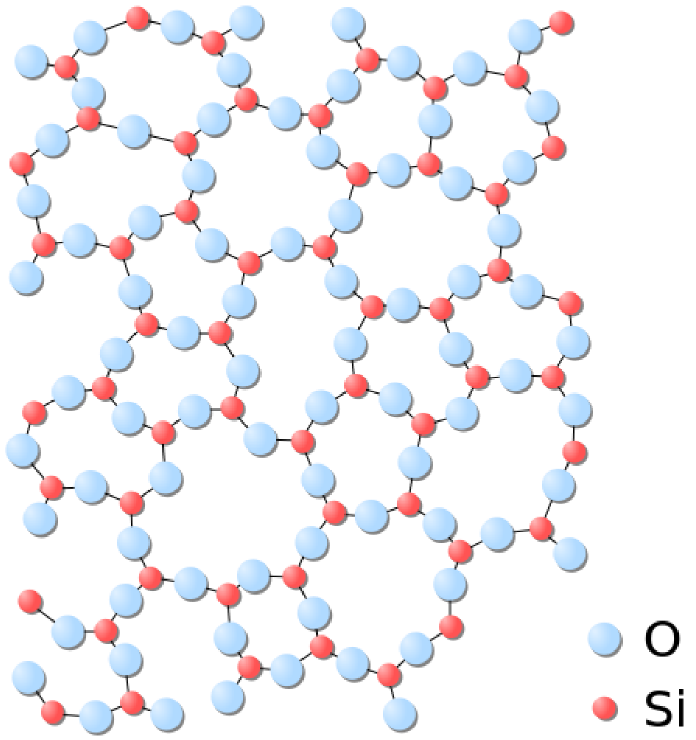


Frontiers in Physics 6, 97 (2018)
arXiv:1806.01369 (2018)

What is a glass?







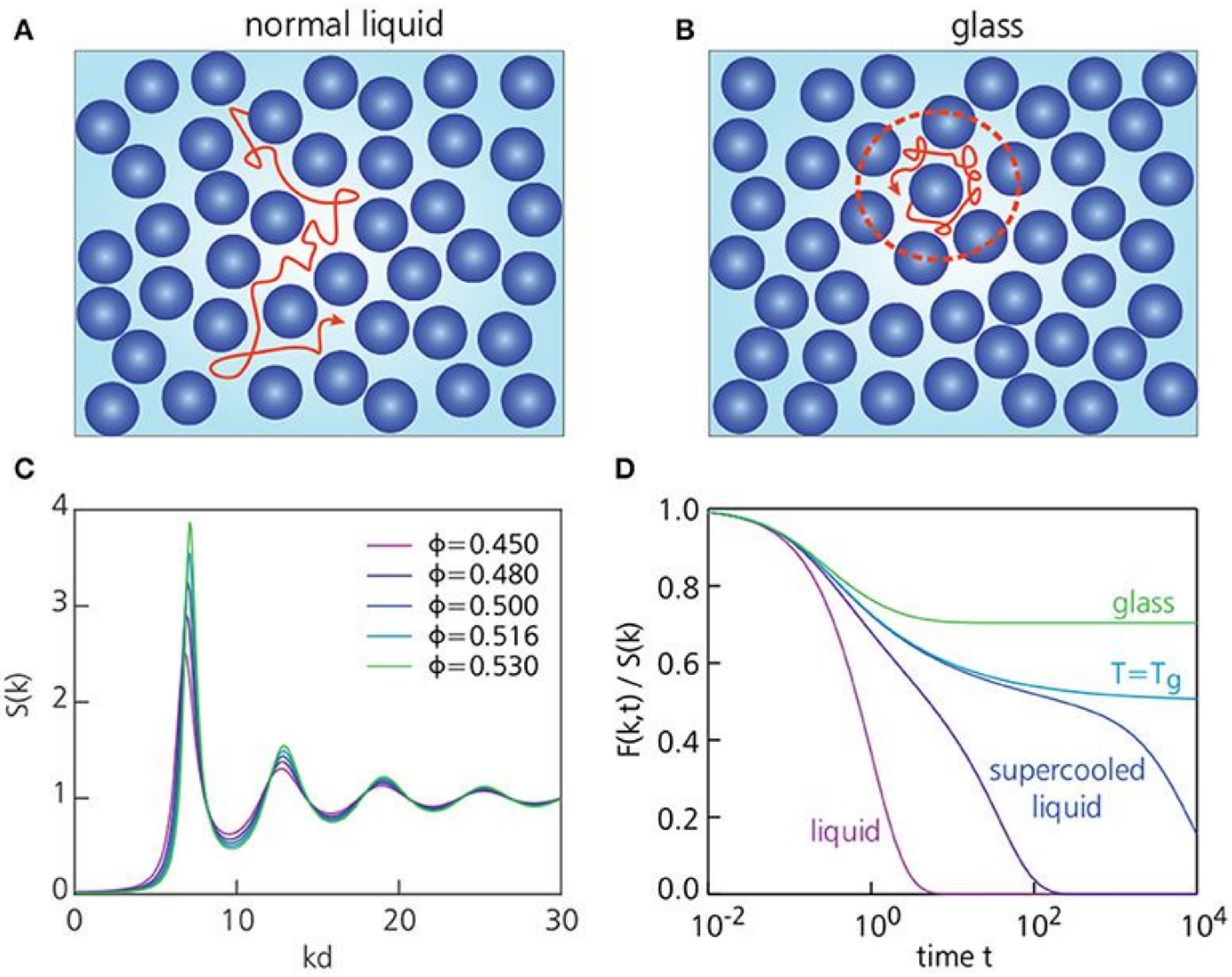
What is a glass?

Schematic dynamics of
(A) a normal liquid
(B) a glass

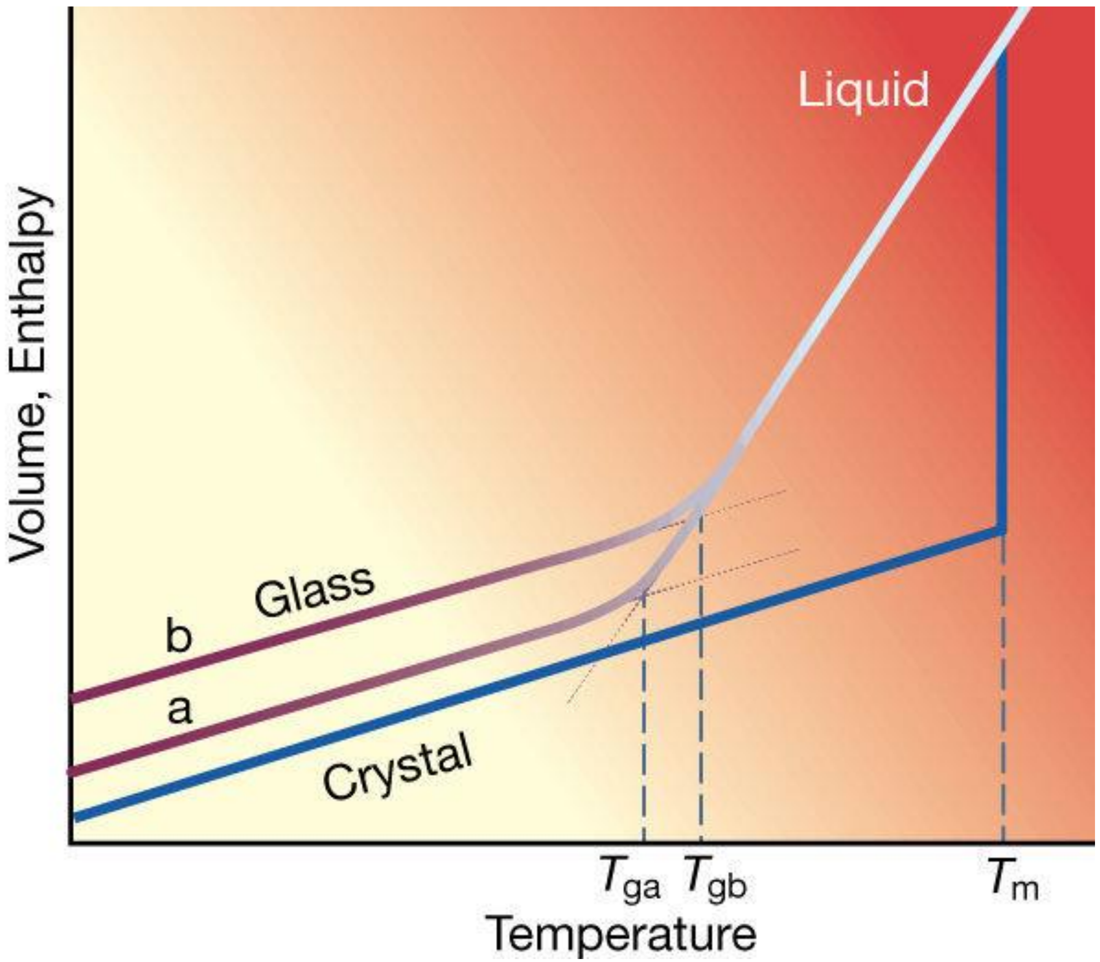
→Video

Hard spheres
(C) Structure factor of hard spheres.
(D) Corresponding Intermediate scattering functions

Frontiers in Physics 6, 97 (2018)
arXiv:1806.01369 (2018)



Supercooled liquids and glass transition



Nature 410, 259 (2001)

Cooling a liquid below its freezing point T_m
→ slow down of molecular motion

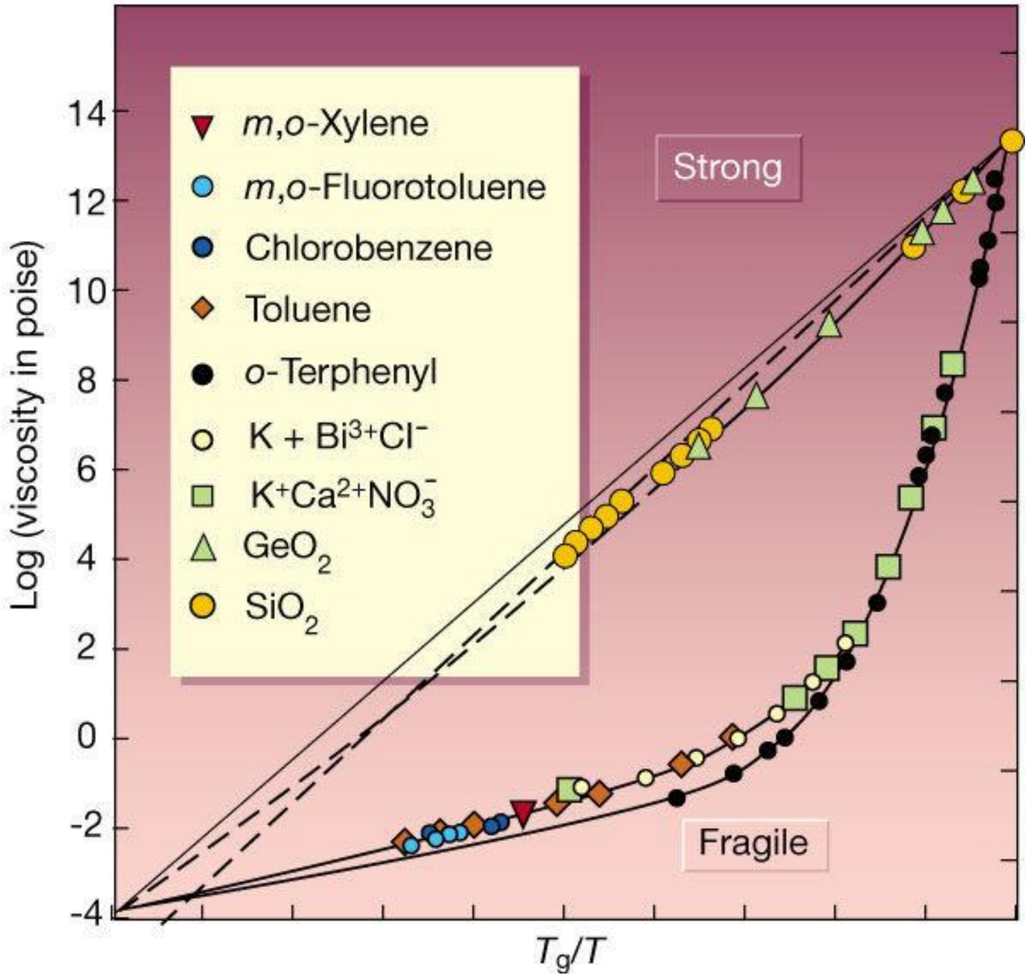
If cooled sufficiently fast
→ Crystallisation avoided
→ Molecules rearrange too slowly
→ Out-of-equilibrium
→ Liquid is "frozen" on experimental timescales
→ No phase transition!

Glass transition temperature: convention!
- Depends on cooling rate
- Molecular relaxation ~100 s
- Viscosity of 10^{12} Pa s
- Change of heat capacity, thermal expansion, …

Glass transition temperatures

Material	Glass transition T_g (°C)	Crystallisation T_m (°C)
Silica SiO_2	~1200	1713
Borosilicate glass	~500	
GeO_2	~700	~1000
Polystyrene	95	~240-270
Teflon	115	327
PMMA (Plexiglas)	105	
Glycerol	~ -70	18
$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	360	

Fragility



Science 267, 1927 (1995)

Nature 410, 259 (2001)

Viscosity towards T_g

- Arrhenius behaviour $\eta = A \exp\left(\frac{E}{k_B T}\right)$

→ "strong" glass former
→ Broad range of T_g

- Fragility: deviation from Arrhenius behaviour

→ More pronounced viscous slow-down

→ Described empirically by Vogel-Fulcher-Tamann law
$\eta = A \exp\left(\frac{B}{T - T_0}\right)$

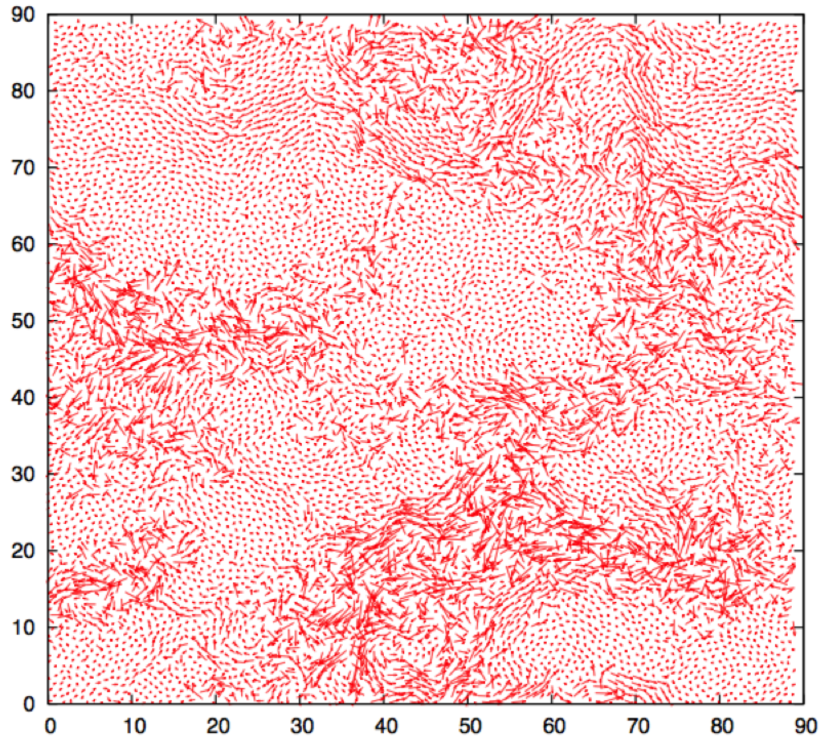
→ Fragility index: $m \coloneqq \left(\frac{\partial \log_{10} \eta}{\partial\left(\frac{T_g}{T}\right)}\right)_{T=T_g}$

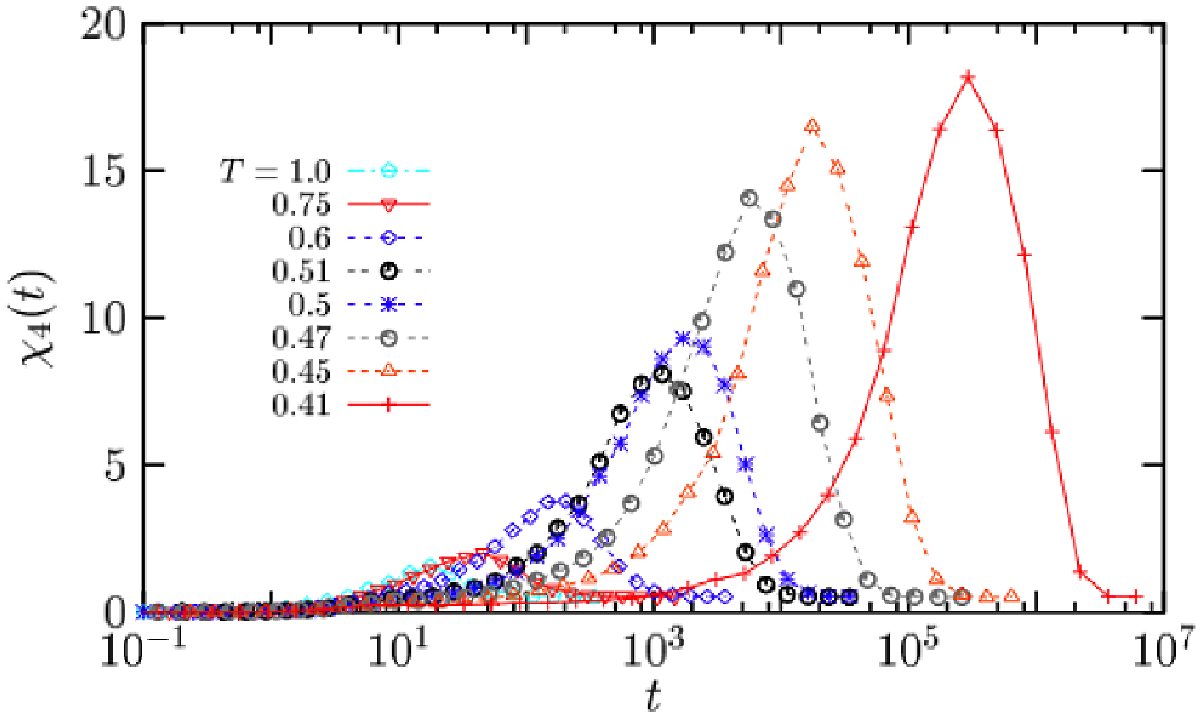
Non-exponential relaxation

- Close to T_g, temporal behaviour of response functions becomes non-exponential
  - E.g. stress response on deformation, polarization response on applied electric field, …
  - Likewise: particle dynamics
- Described by Kohlrausch-Williams-Watts function $F(t) = \exp(-\left(\frac{t}{\tau}\right)^{\gamma})$ with $\gamma < 1$ (cf. Lecture 18) → XPCS experiments
- Contrasts to liquids → exponential response
- Spatial & dynamic heterogeneity: growth of domains with distinct relaxation

Dynamic Heterogeneities

- Different dynamics at different regions of supercooled liquids
- Quantify via $\chi_4(t) = N[\langle C(t)^2 \rangle - \langle C(t) \rangle^2]$, with "total mobility" $C(t)$
- Dynamic susceptibility $\chi_4(t)$ ~ volume of correlated clusters
- Need higher-order correlations to be determined

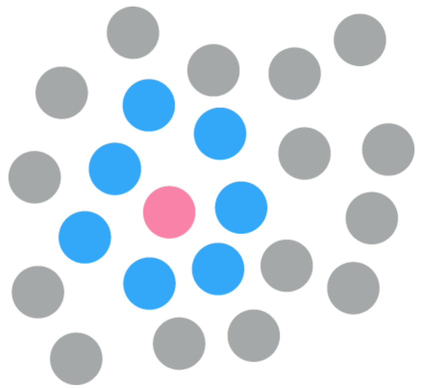


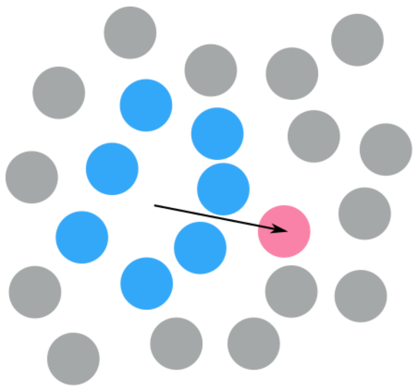


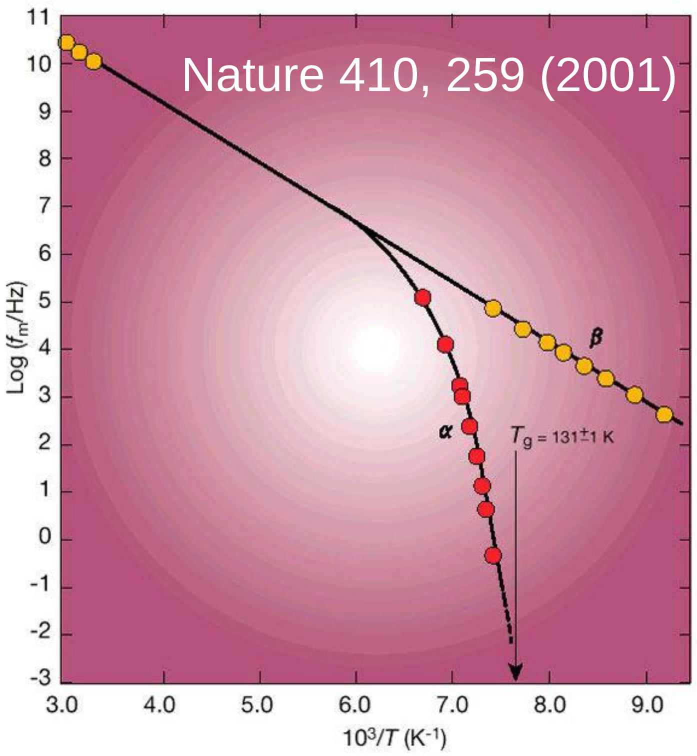
Physics 4, 42 (2011)

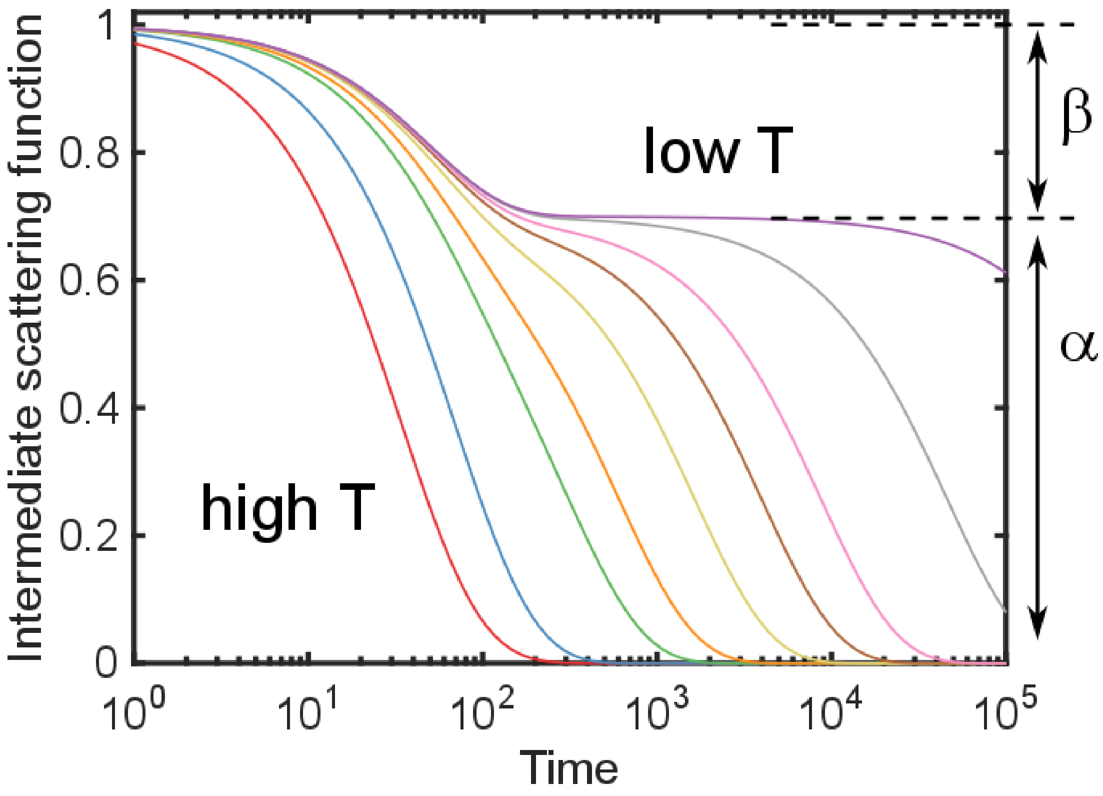
Alpha- & beta-relaxation

- Decoupling of dynamics near T_g: α- and β-relaxations



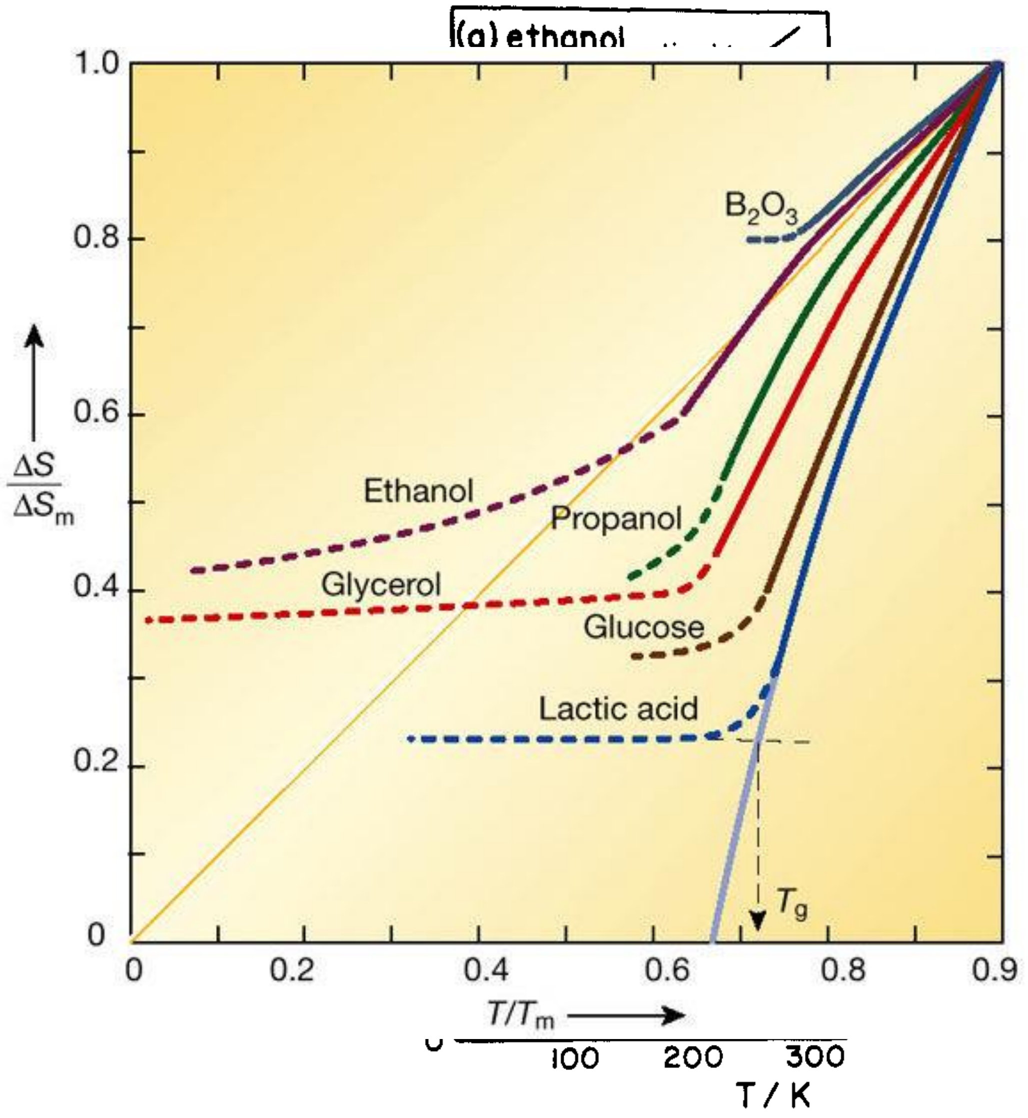






Thermodynamics: Adam-Gibbs model

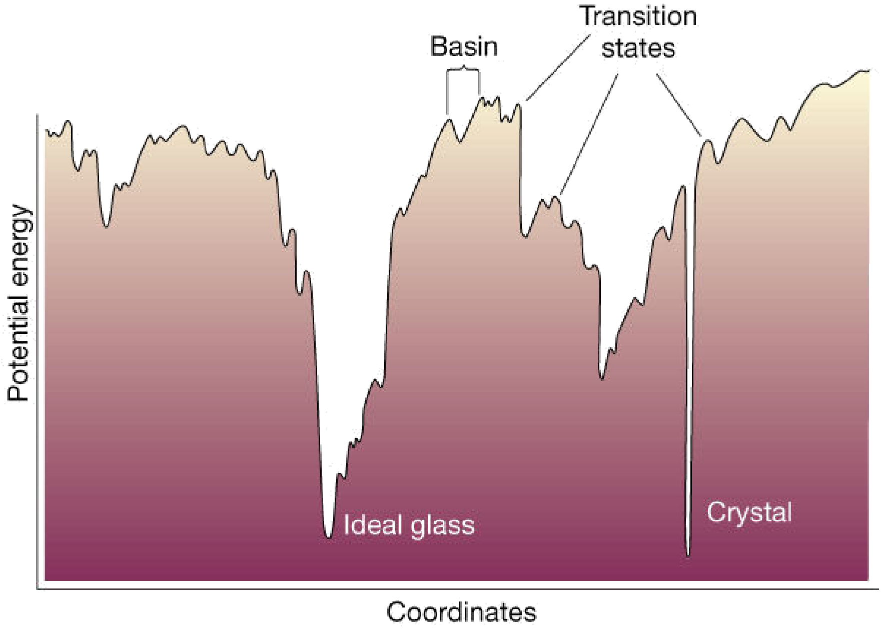
- Entropy difference liquid and crystal: glass transition before $\Delta S = 0$
- Entropy crisis: $S_{cryst}(T \to 0) \to 0$ → third law of thermodynamics
- Kauzmann temperature T_K: $S_{liquid} = S_{crystal}$ → ideal glass
- Glass transition: Kinetics vs. Thermodynamics?
- Adam-Gibbs model: $\tau = A \exp\left(\frac{B}{T s_c}\right)$
    - s_c configurational entropy
    - Slow down → decreasing number of configurations
    - Energy landscapes
    - Cooperatively rearranging regions

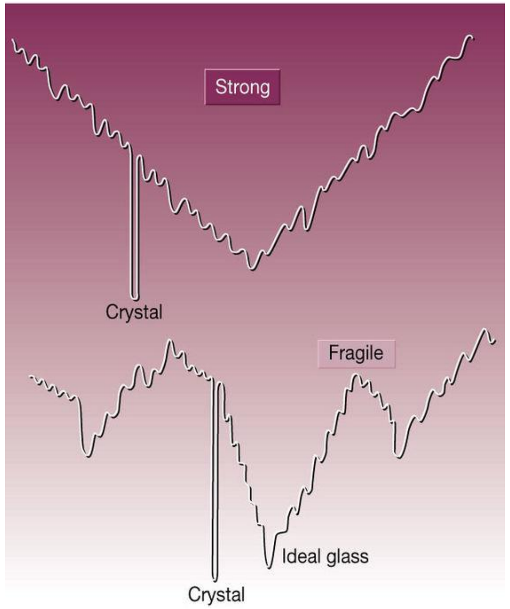


Pure & Appl. Chem. 63, 1387 (1991).

Energy landscapes

- Configurational entropy s_c ~ number of minima in potential energy surface





- At Kauzman temperature: non-crystalline state of lowest energy (ideal glass)
- Strong vs. Fragile – heterogeneous landscapes of fragile glass-formers → broad range of relaxation times → dynamical heterogeneity
- α-relaxations correspond to configurational sampling of neighbouring "megabasins", whereas β-processes are thought to correspond to elementary relaxations between contiguous basins

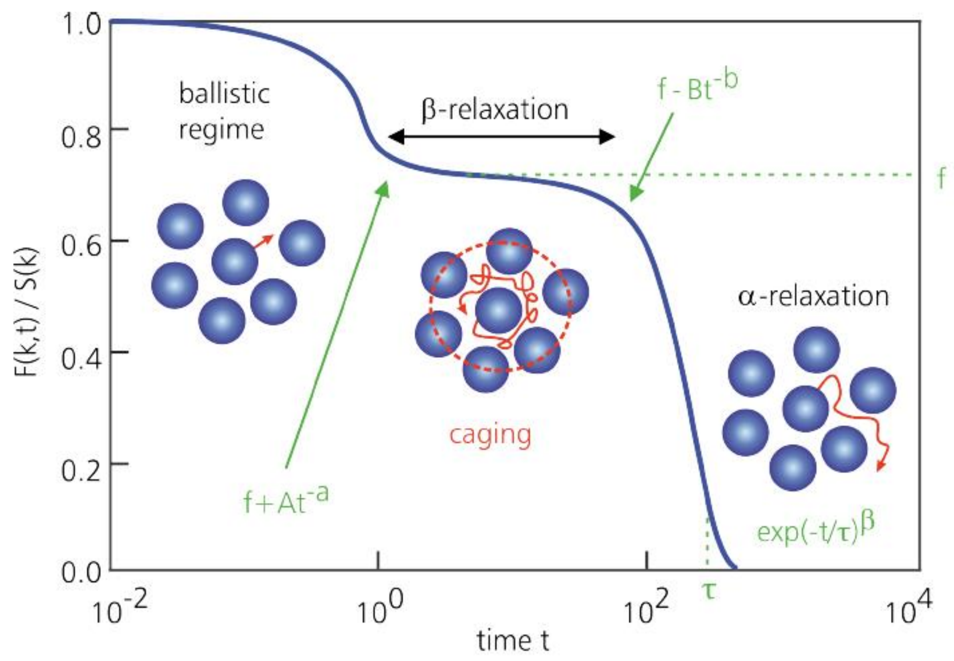
Mode coupling theory (MCT)

- Understanding dynamics of supercooled liquids
- Time evolution (dynamics) of intermediate scattering function (as density-density correlation function) from time-independent structural properties, such as $S(q)$

→ Dynamics of ISF: four-point correlation function

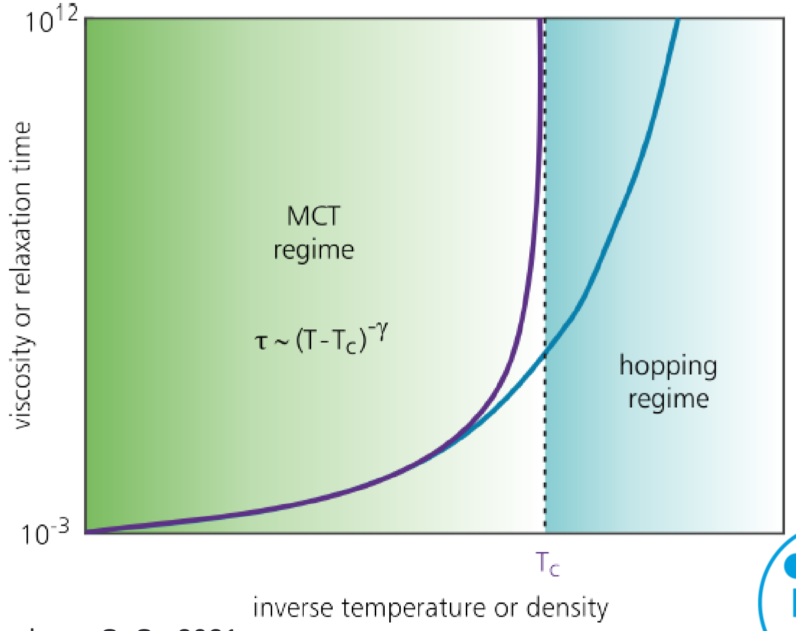
→ MCT: factorization of such four-point correlations to products of ISF's

→ Mode coupling equations whoses solutions provide the full time dependence of the ISF



Predictions from MCT

- Critical temperature T_c at which relaxation rate vanishes with a power law $\Gamma = \frac{1}{\tau_0} \propto (T - T_c)^{\delta}$ with $\delta > 1.5$
- Plateau regime of dynamics & scaling of α, β-relaxation
- Slow relaxation at longer times showing KWW type stretched exponential



Drawbacks:

- Ideal glass transition at relatively high temperature / low densities
- Fails to explain strong and fragile behaviour
- Currently approaches to overcome these shortcomings

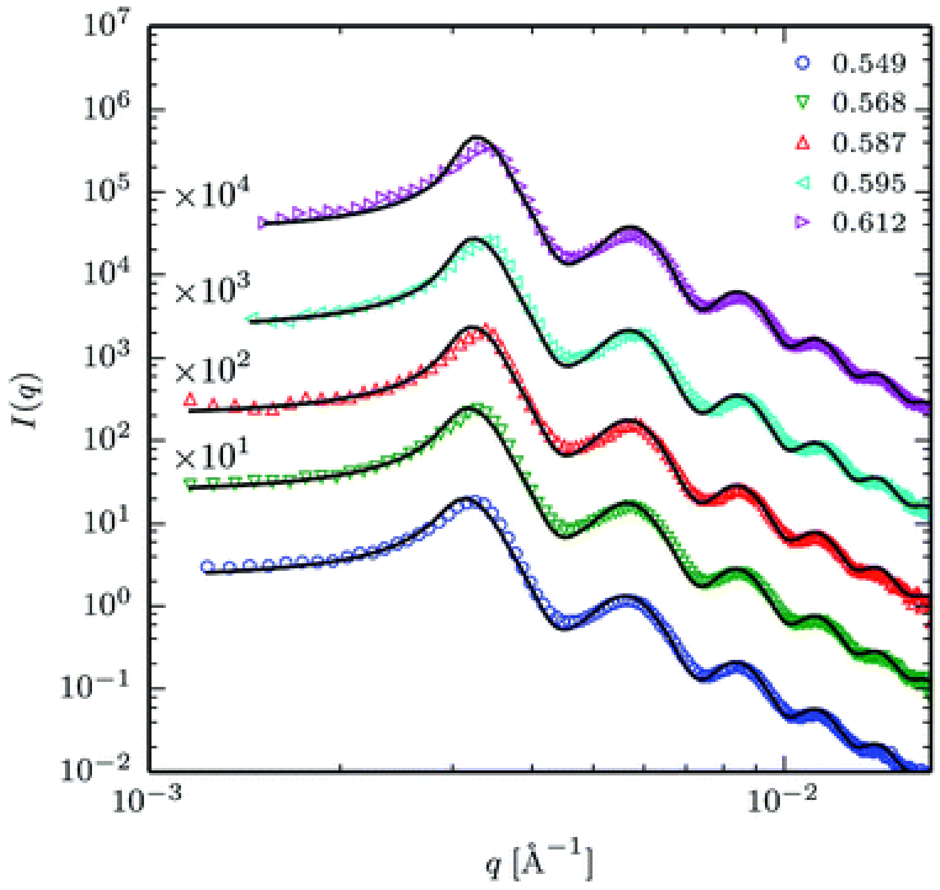
Frontiers in Physics 6, 97 (2018)
arXiv:1806.01369 (2018)

X-ray scattering studies of glass transition

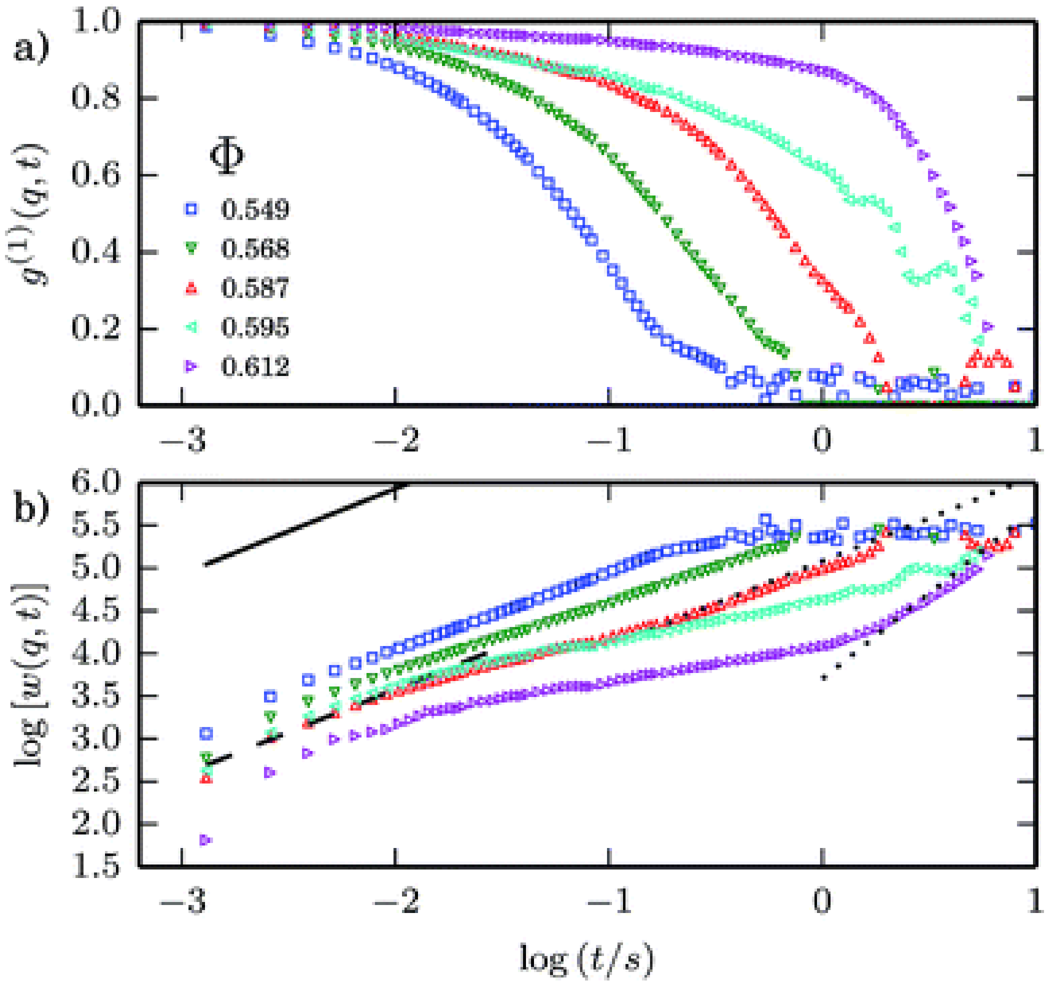
- Structure: Is there any difference to liquid state in $S(q)$ and $g(r)$?
  → X-ray diffraction (SAXS / WAXS)
- Is there any orientational/bond order?
  → higher order structural correlations (e.g. XCCA)
- Intermediate scattering function: Dynamics
  → XPCS

Example 1: Colloidal hard sphere glasses

Hard sphere colloidal glasses



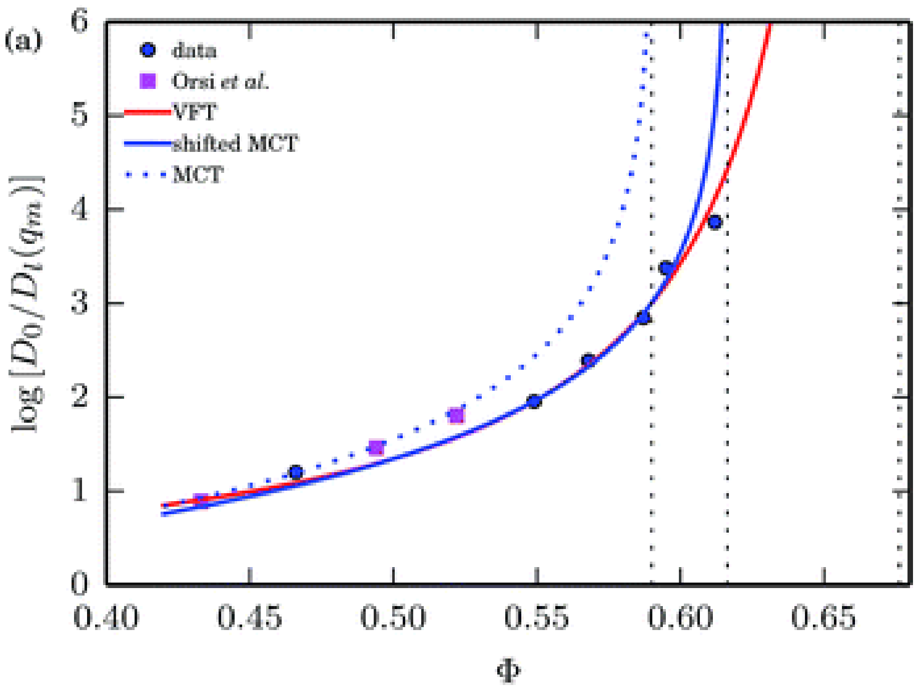
Soft Matter 10, 8698 (2014)

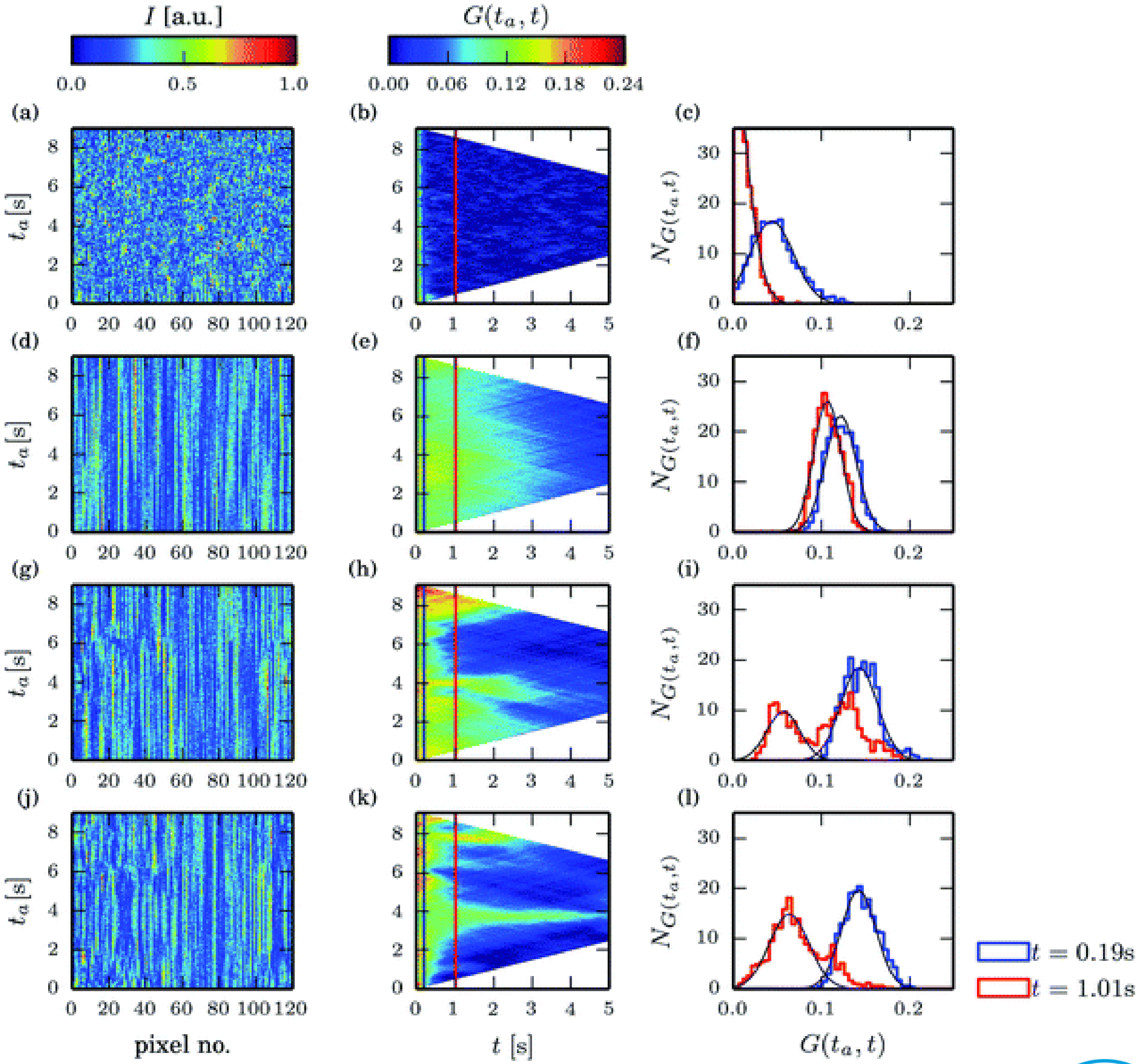


Intermediate scattering function $g^{(1)}(q,t)$

$w(q,t) = -\ln(g^{(1)}(q,t))/q^2$ analog to MSD

Example 1: Colloidal hard sphere glasses





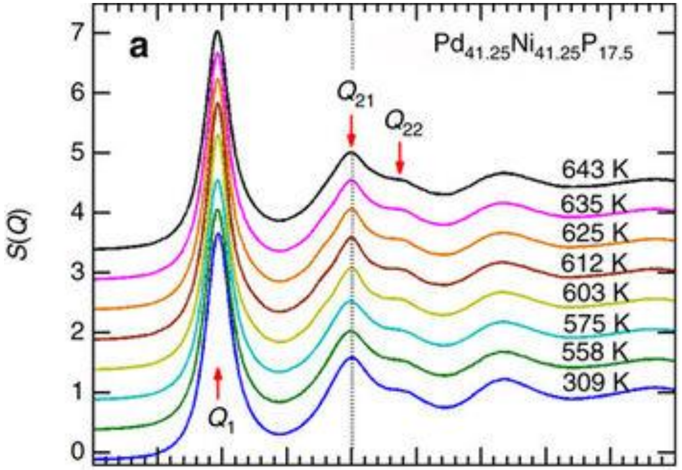
Long time diffusion → structural relaxation

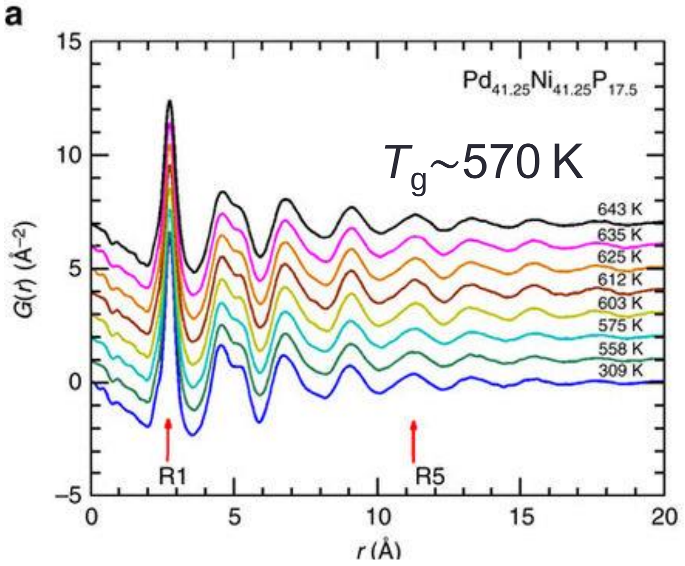
MCT & VFT modelling → 3% shift necessary

Soft Matter 10, 8698 (2014)

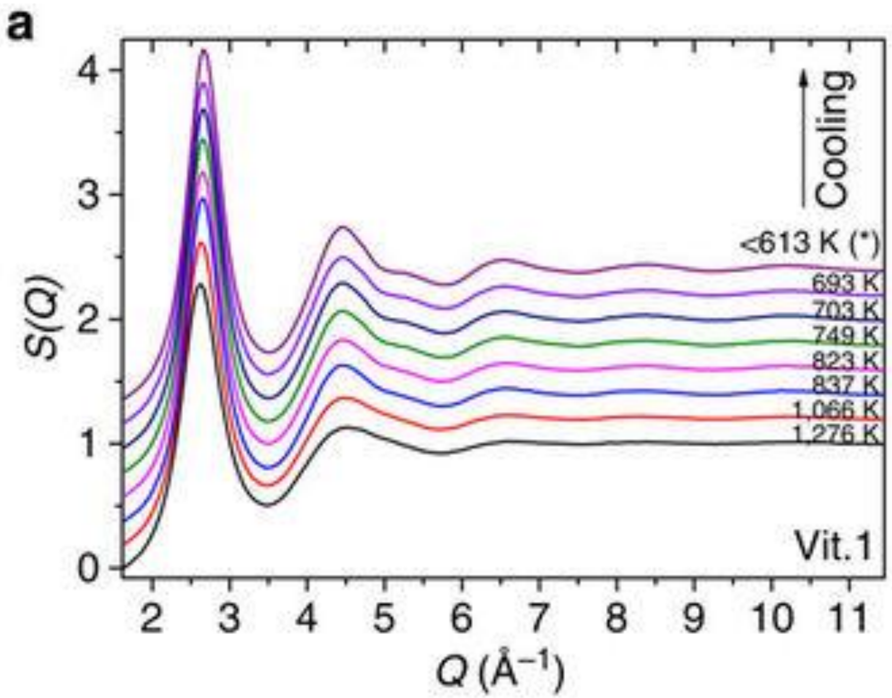
Example 2: Structure factors

Metallic glasses





Nat. Commun. 8, 14679 (2017)



$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$

Nat. Commun. 4, 2083 (2013)

- Similar results for other glass formers
- Pair-correlations do not change significantly crossing the glass transition
- Is there any structure-dynamics relation?
- Higher-order correlations?

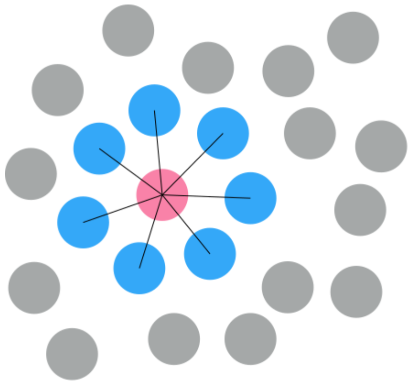
Higher-order structure in simulation and microscopy

- Steinhardt parameters: local bond order of l-fold symmetry with distance $\mathbf{r}$ and number of bonds N

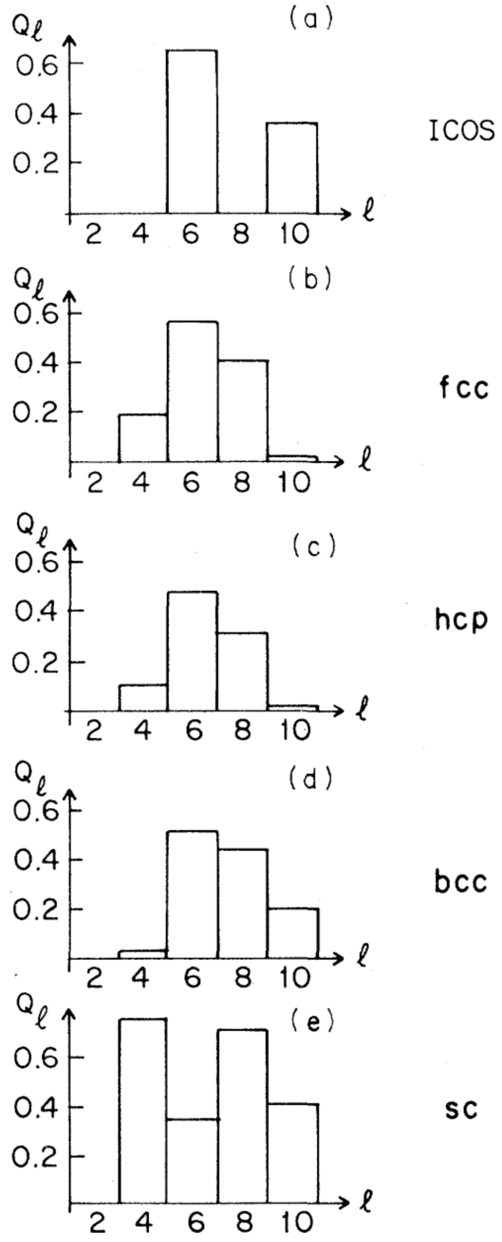
$$Q_{lm} = \frac{1}{N}\sum_{0}^{N} Y_{lm}(\theta(\mathbf{r}), \phi(\mathbf{r}))$$

- Rotationally invariant coordinate system

$$Q_l = \left(\frac{4\pi}{2l+1}\sum_{m=-l}^{l} |Q_{lm}|^2\right)^{\frac{1}{2}}$$

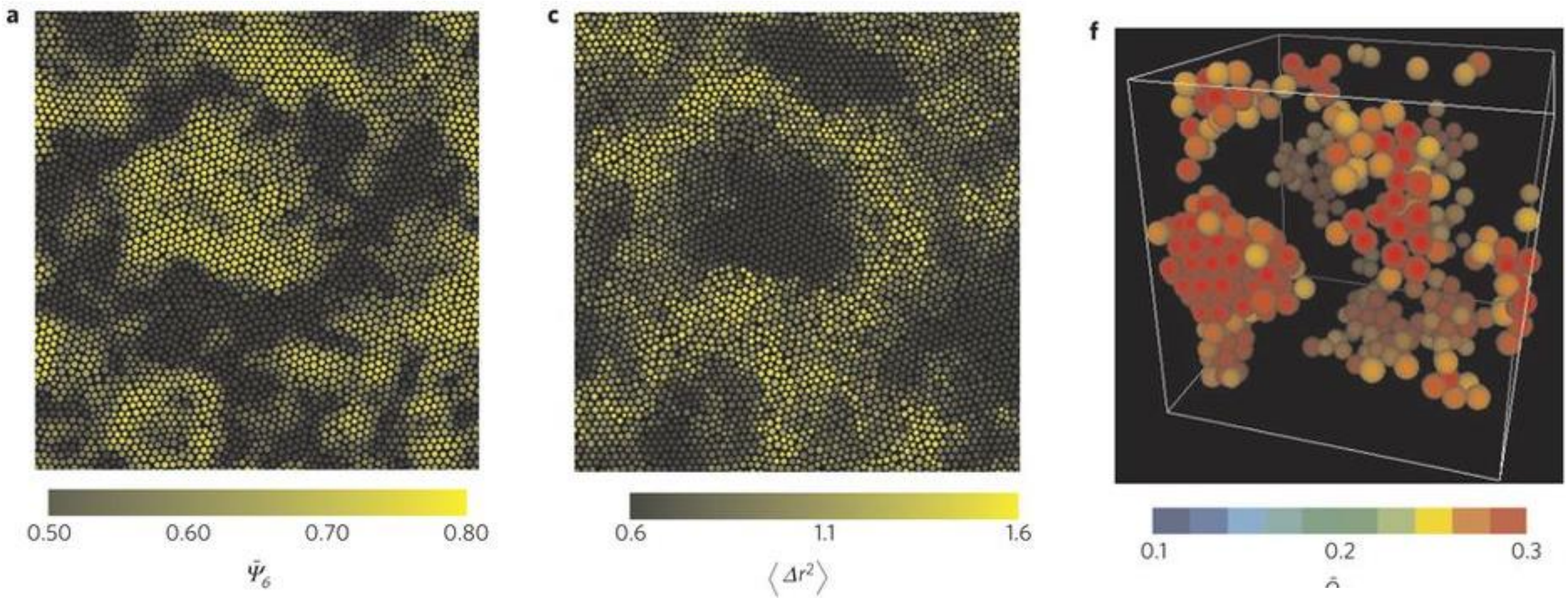


- Fingerprint for different local environments



Phys. Rev. B 28, 784 (1983)

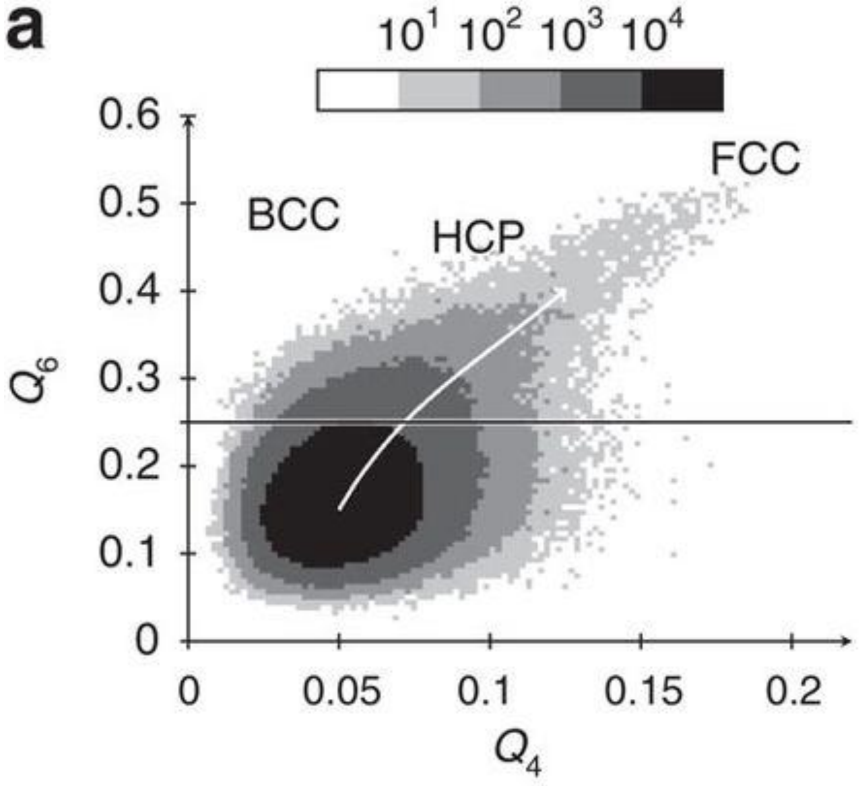
Higher-order structure in simulation and microscopy

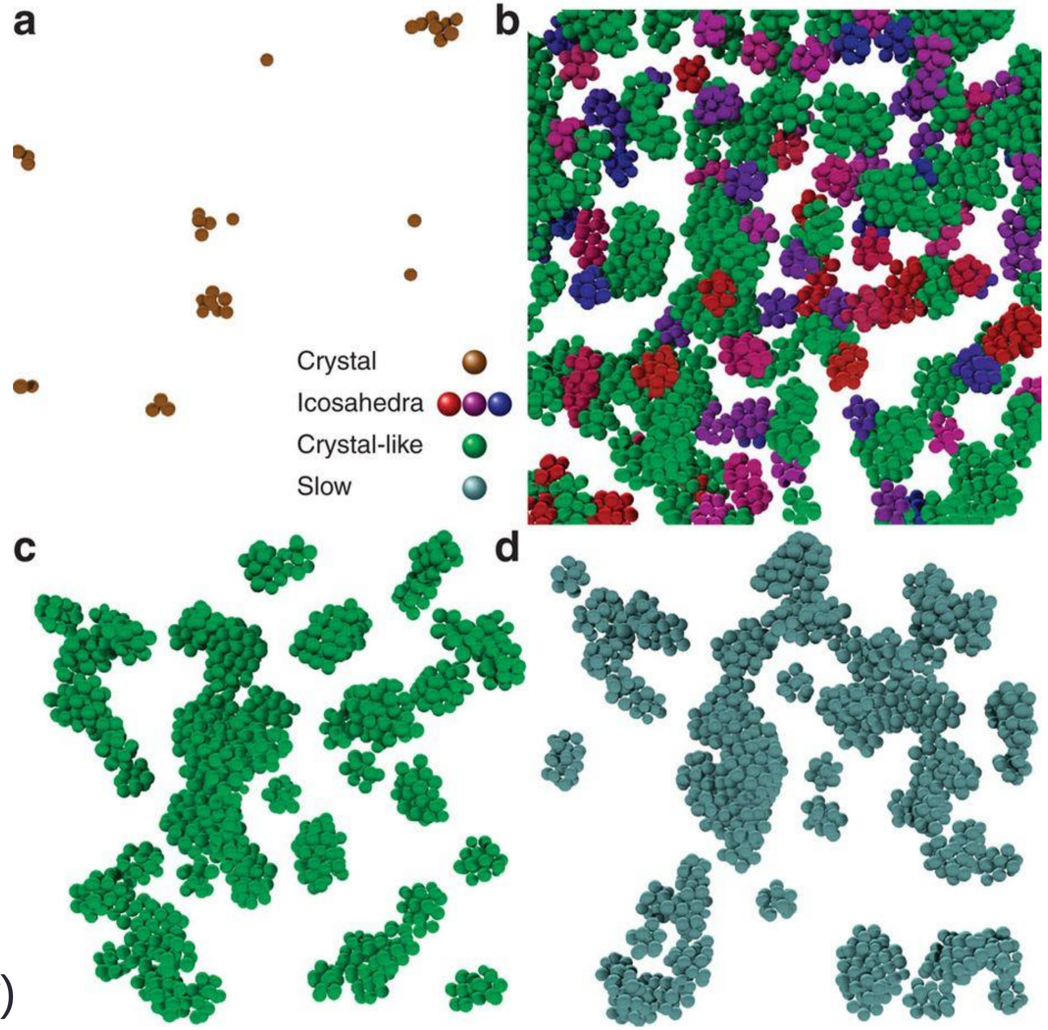


Structural and dynamical heterogeneities (simulation)

Nat. Mat. 9, 324 (2010)

Higher-order structure in simulation and microscopy



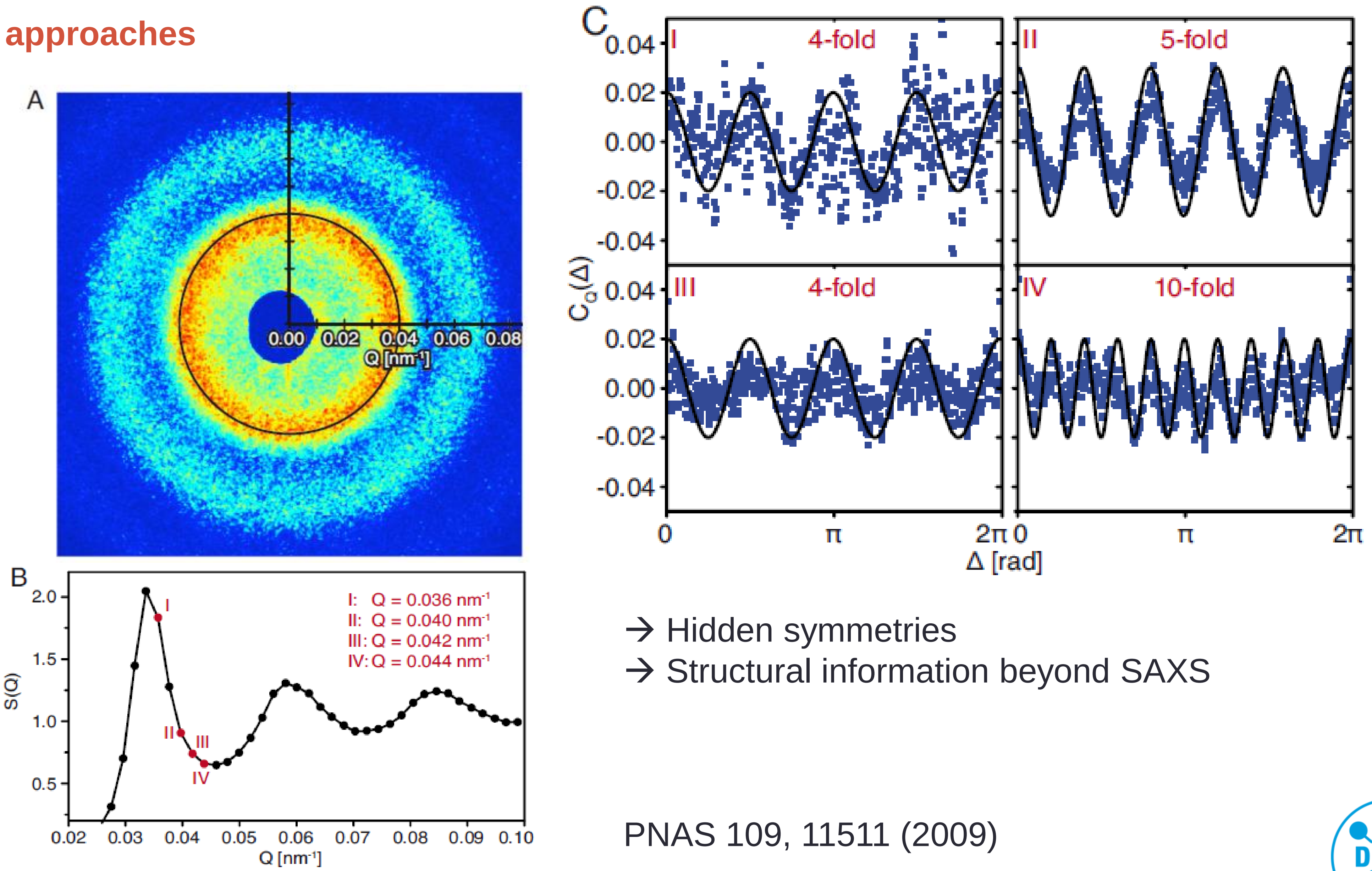


Crystal-like and icosahedral order in hard sphere fluids (microscopy)

Nat. Comm. 3, 974 (2012)

Example 3: XCCA approaches

Hard-sphere glass

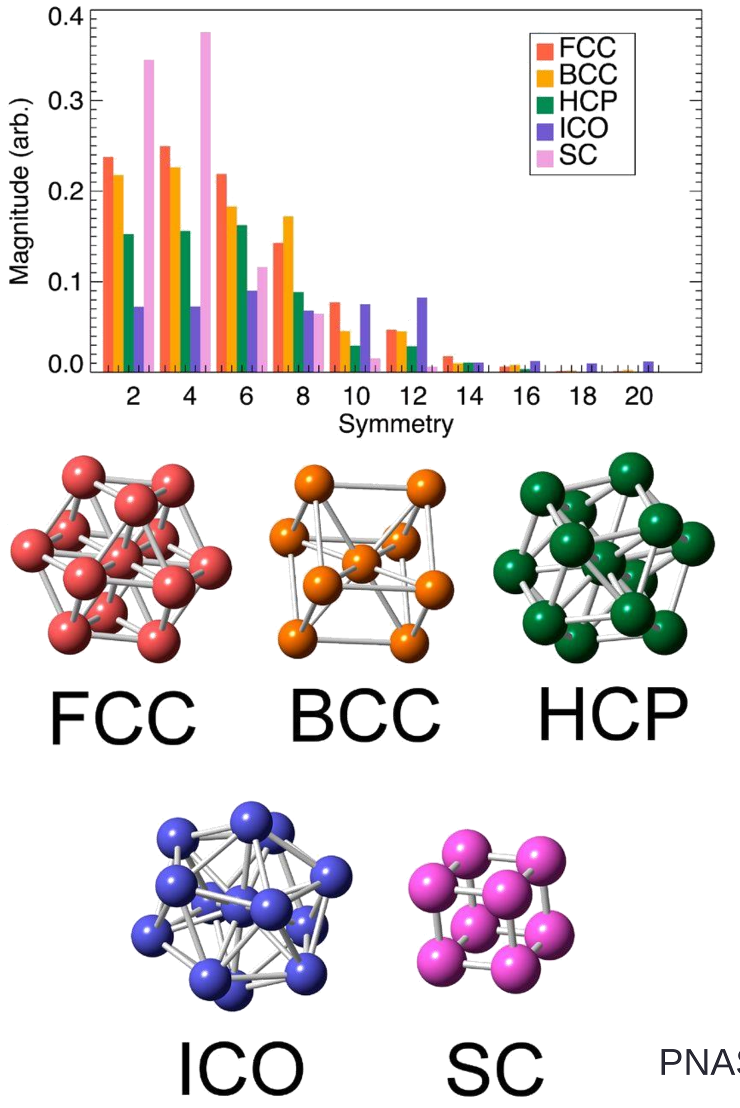


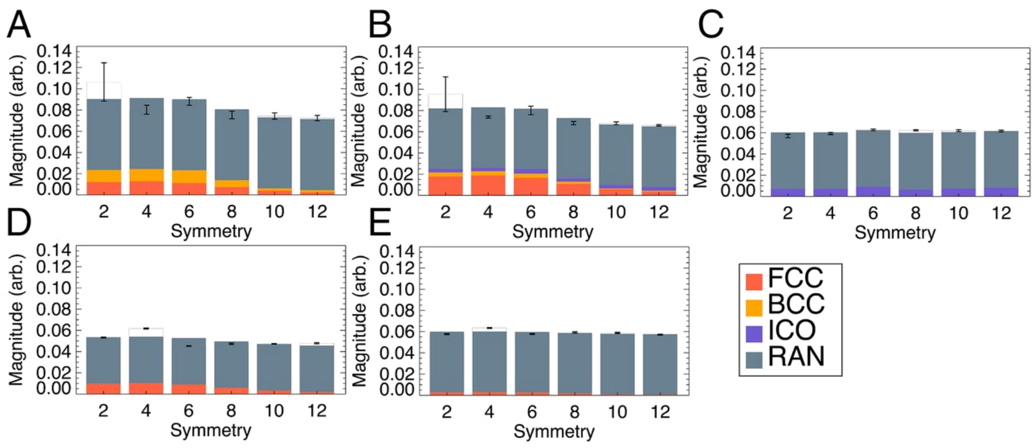
→ Hidden symmetries
→ Structural information beyond SAXS

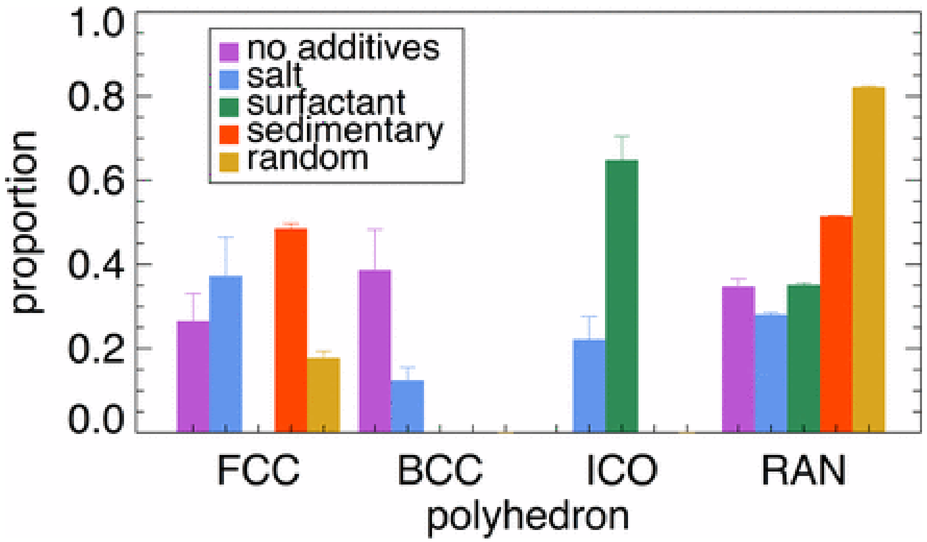
PNAS 109, 11511 (2009)

Example 3: XCCA approaches

Colloidal glasses: SiO_2 particles with additives
Salt: screening
Surfactant: short-range attractive compound

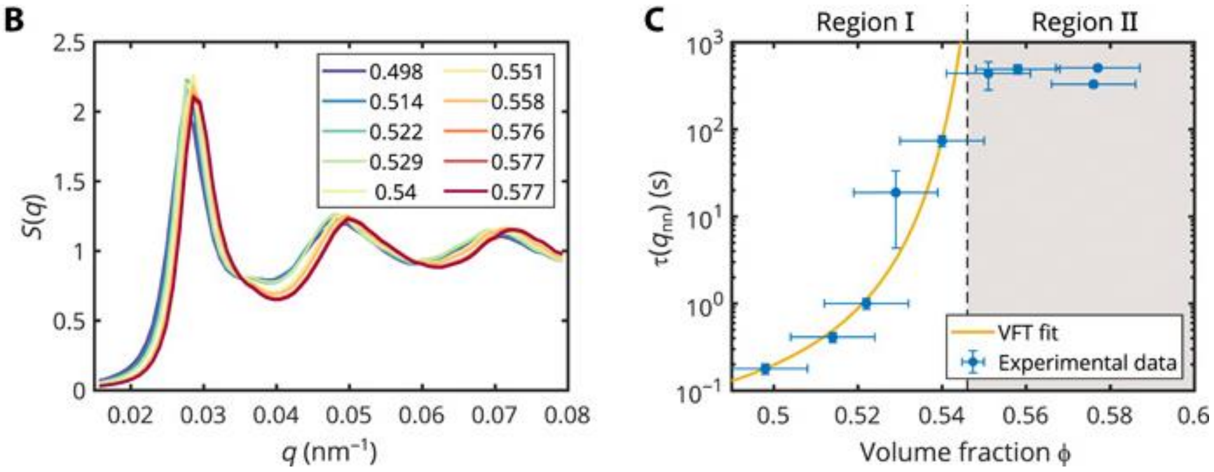


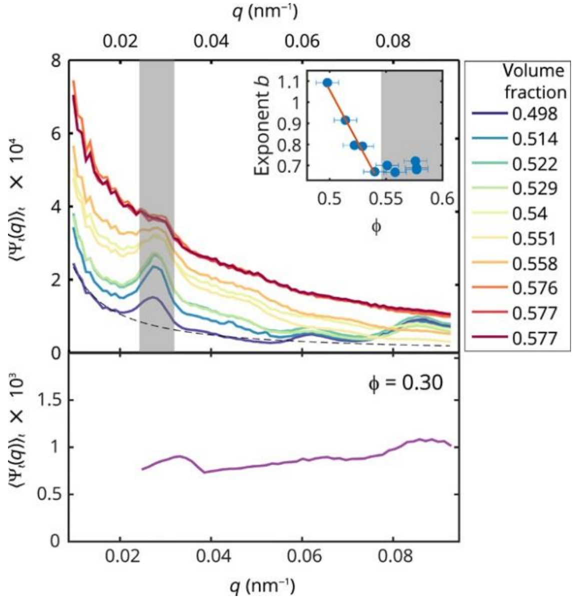


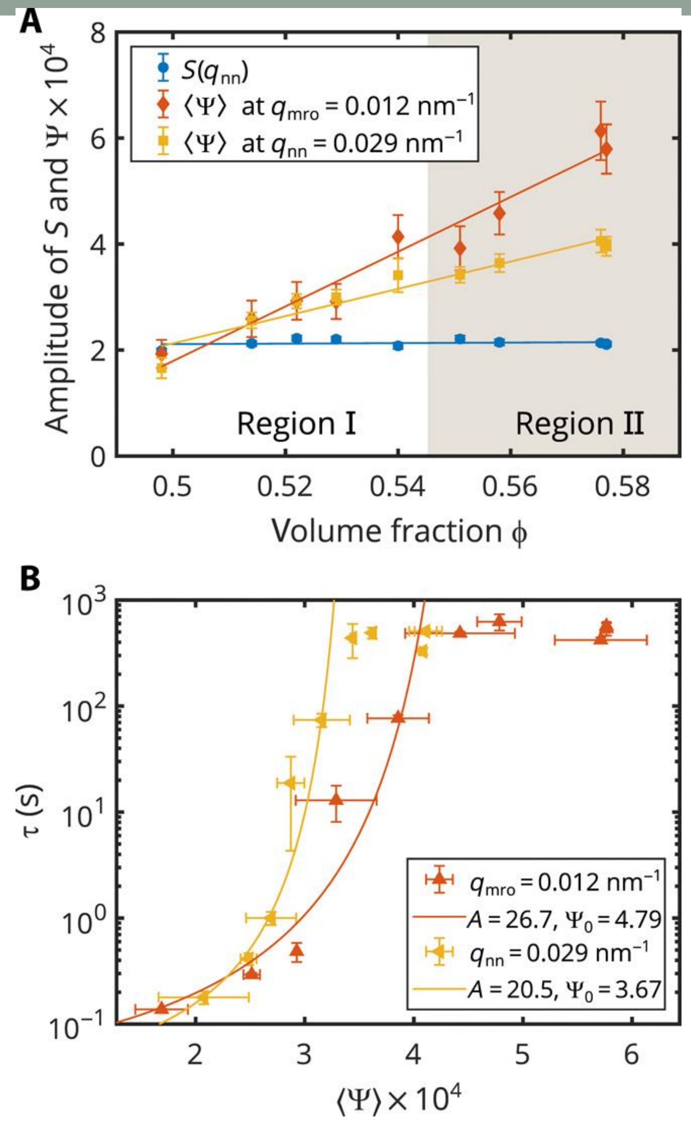


PNAS 114, 10344 (2017)

Example 3: XCCA approaches







Colloidal hard spheres

Around glass transition:

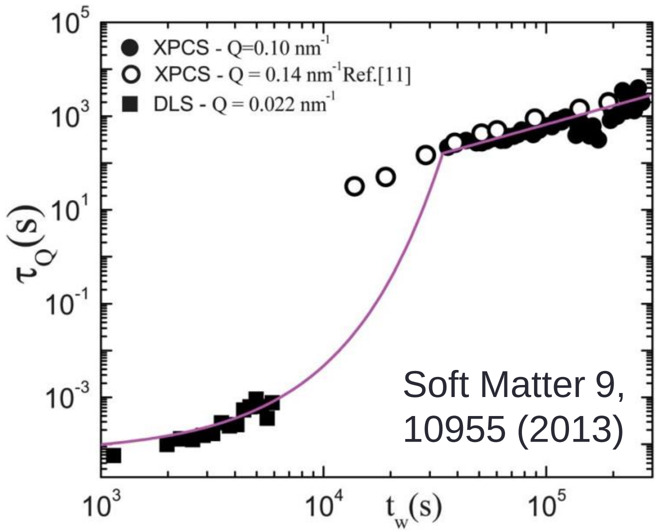
- S(q) constant
- Relaxation time increases
- $\Psi_\ell \propto C_\ell$ from XCCA as measure of local order

Correlation of dynamics and local order

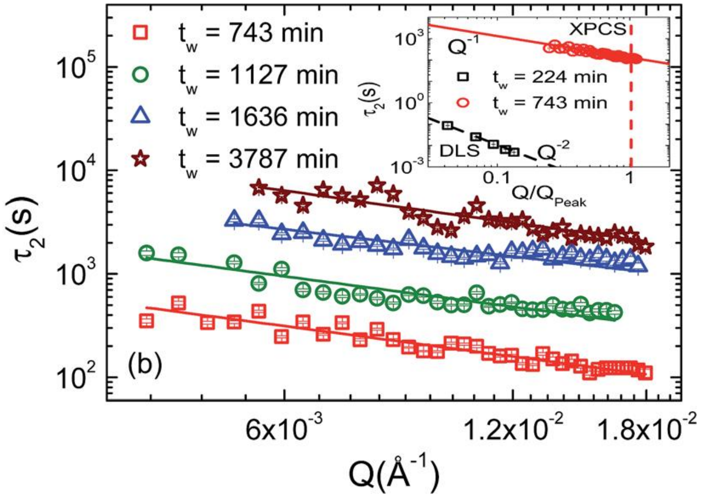
Sci. Adv. 6, eabc5916 (2020)

Example 4: Aging in colloidal glasses

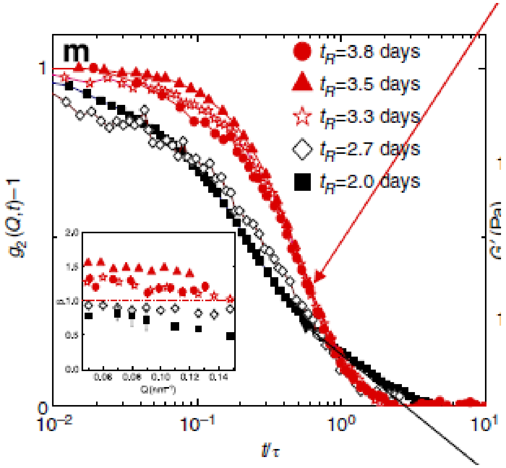
Laponite glass (clay) – dynamics change with waiting (after rejuvenation)

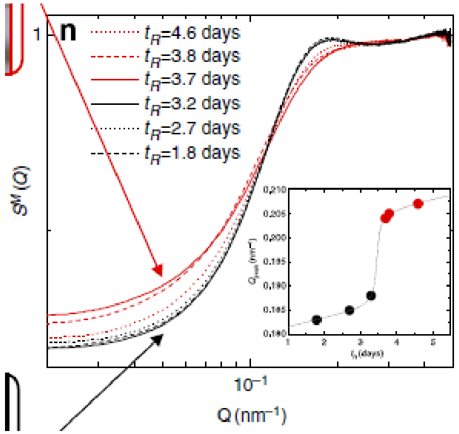


Soft Matter 9, 10955 (2013)



Soft Matter 11, 466 (2015)



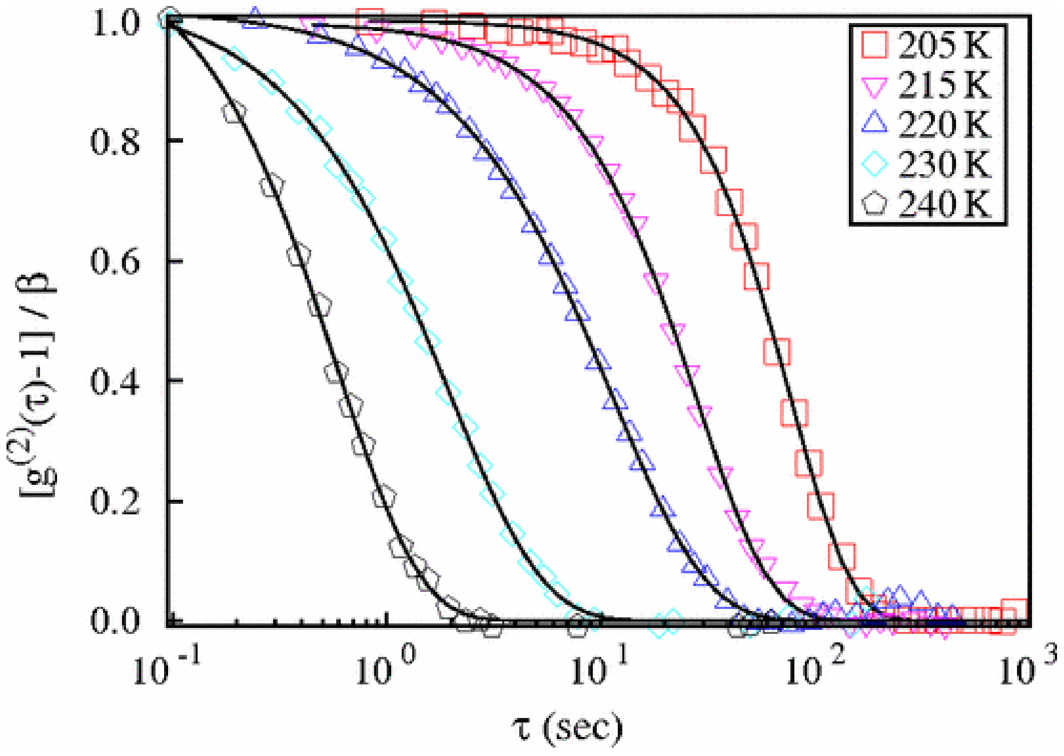


Glass-glass transition during aging

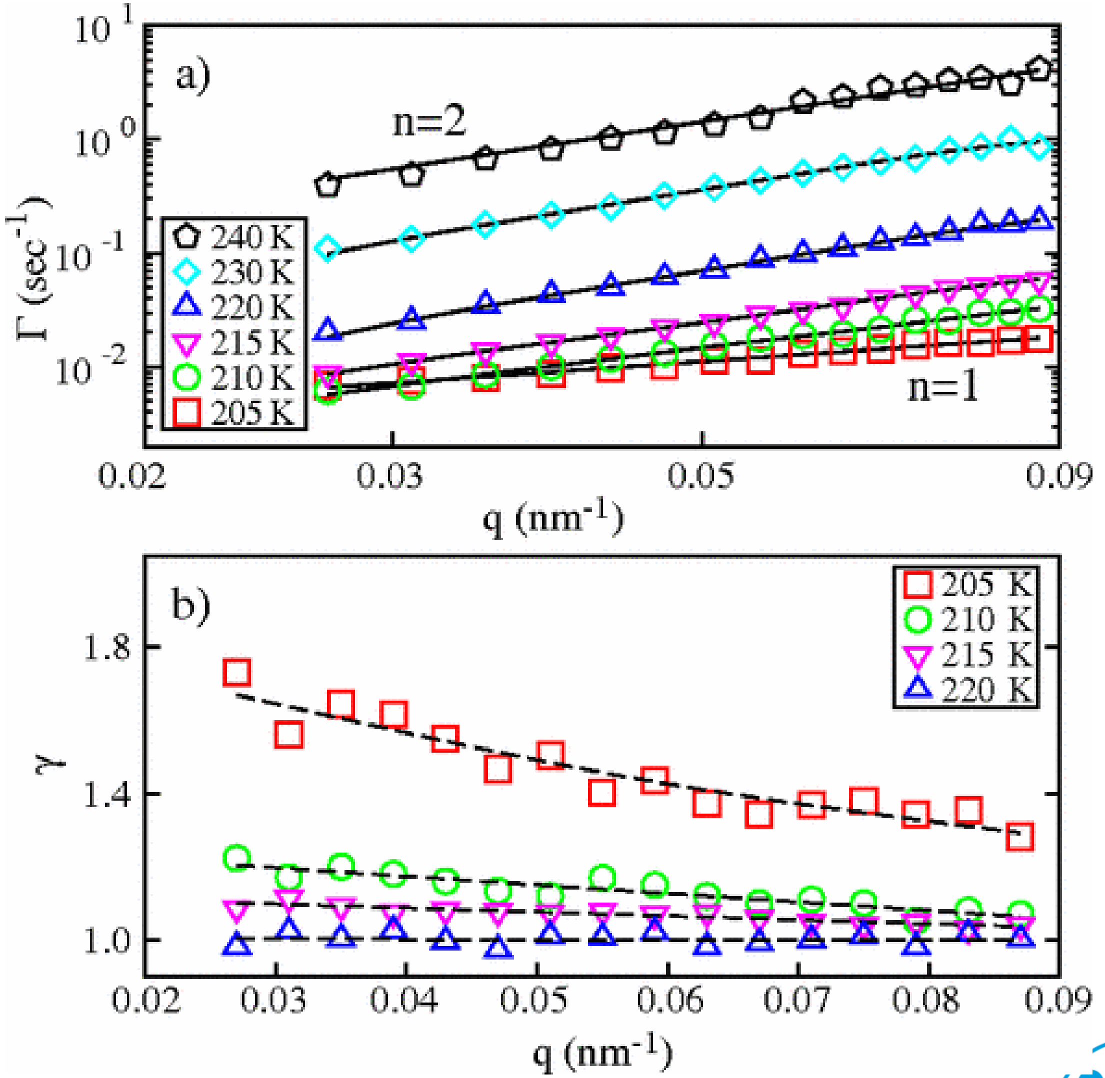
Nature Comm. 5, 4049 (2014)

Example 5: Microrheological glass transition studies on soft matter

Propanediol: $T_m \approx 245$ K, $T_g \approx 170$ K
Silica particles as tracer particles



Phys. Rev. Lett. 100, 055702 (2008)



Example 5: Microrheological glass transition studies on soft matter

KWW function $f(q,\tau) \propto \exp(-(q^n t)^\gamma)$

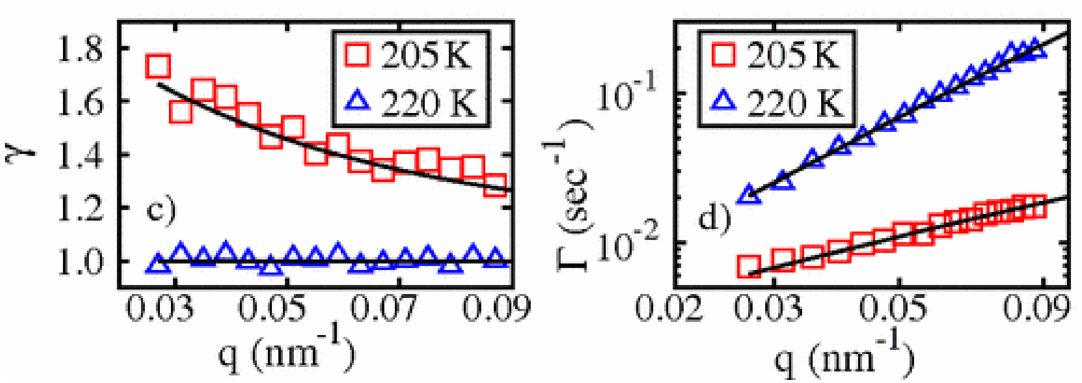
Model with continuous time random walk model: displacement of particle in time interval t consists of N discrete steps → ISF is determined by number of steps N and degree of decorrelation $h(q,N)$ between steps

$$f(q,\tau) = \sum_N P_t(N) h(q,N)$$

- $P_t(N)$ probabilty of N events ocurring during time interval t → Poisson distribution $P_t(N) = \exp(-\Gamma_0 t)(\Gamma_0 t)^N / N!$, with $1/\Gamma_0$ the mean time between events

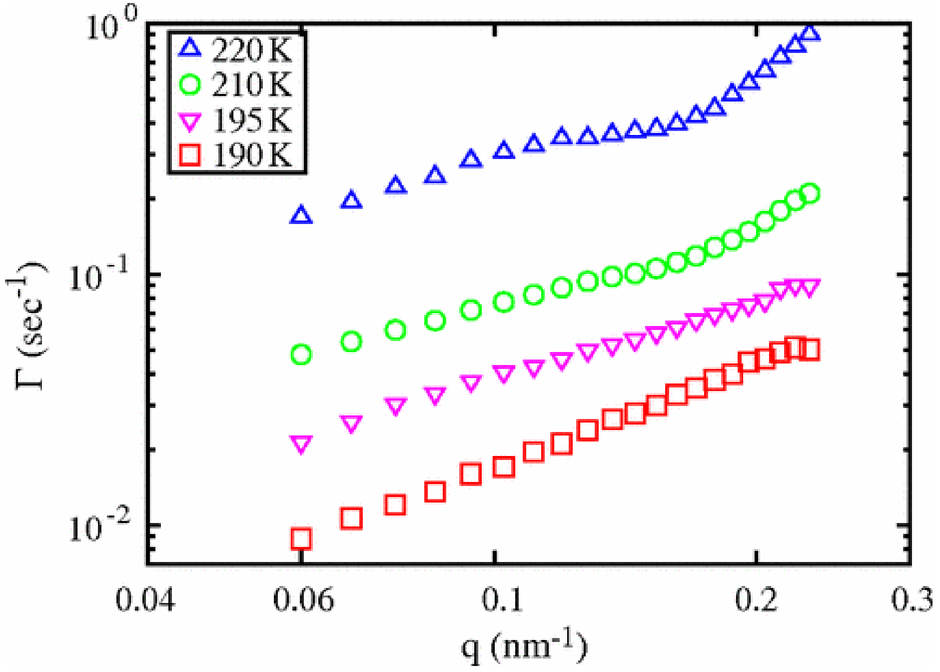
- $h(q,N) \simeq \exp[-(qN^\alpha \delta)^2]$ Gaussian distribution, with α defining (non-)diffusive motion ($\alpha = 0.5$ for diffusion) and δ average lengths of single jumps

Example 5: Microrheological glass transition studies on soft matter



$(\delta, \Gamma_0, \alpha)$=(5.4 nm,0.09 Hz,1) 205 K
(6.2 nm, 2.0 Hz, 0.5) for 220 K

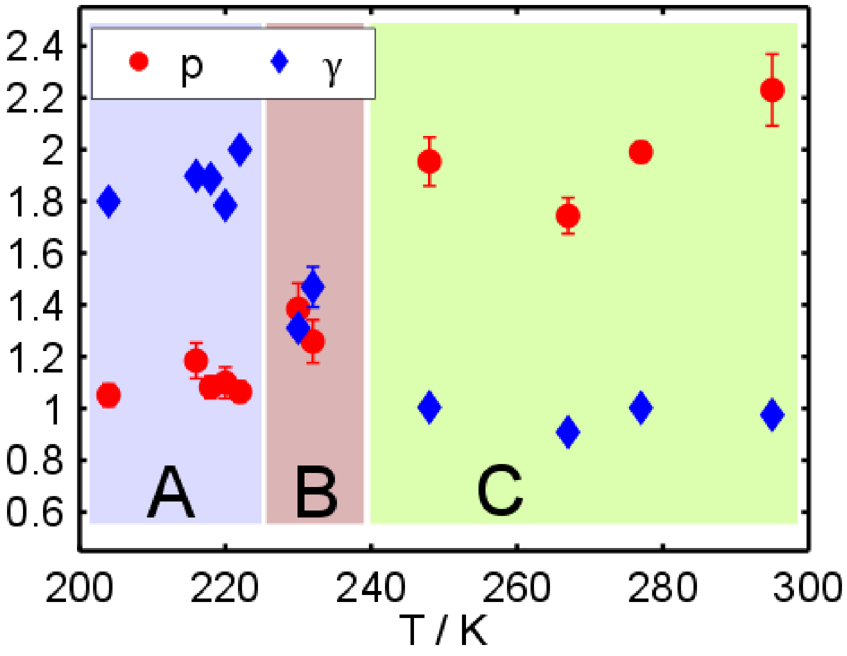
→ From diffusive to ballistic motion!



- Increasing particle concentration: deGennes narrowing
- Disappears at low temperatures: cooperative behaviour close to T_g

Phys. Rev. Lett. 100, 055702 (2008)

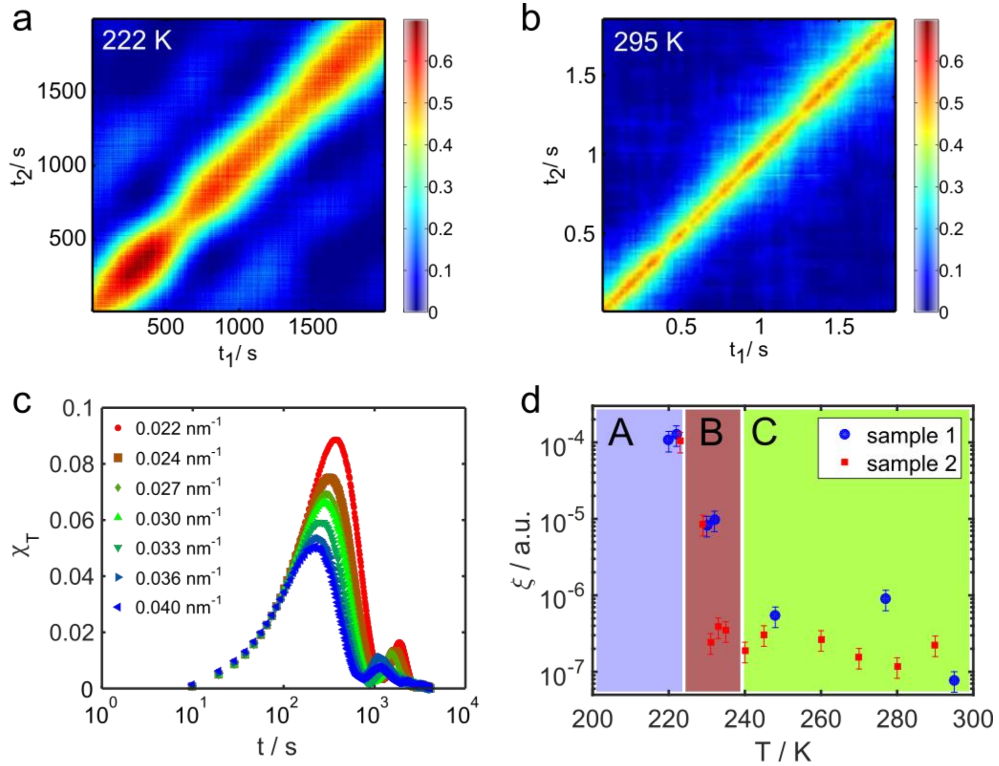
Example 5: Microrheological glass transition studies on soft matter



Silica in PPG ($T_g \approx 205$ K)

Exponents as function of temperature

- **C**: Brownian regime
- **B**: intermediate regime ($T \approx 1.12\ T_g$)
- **A**: correlated motion



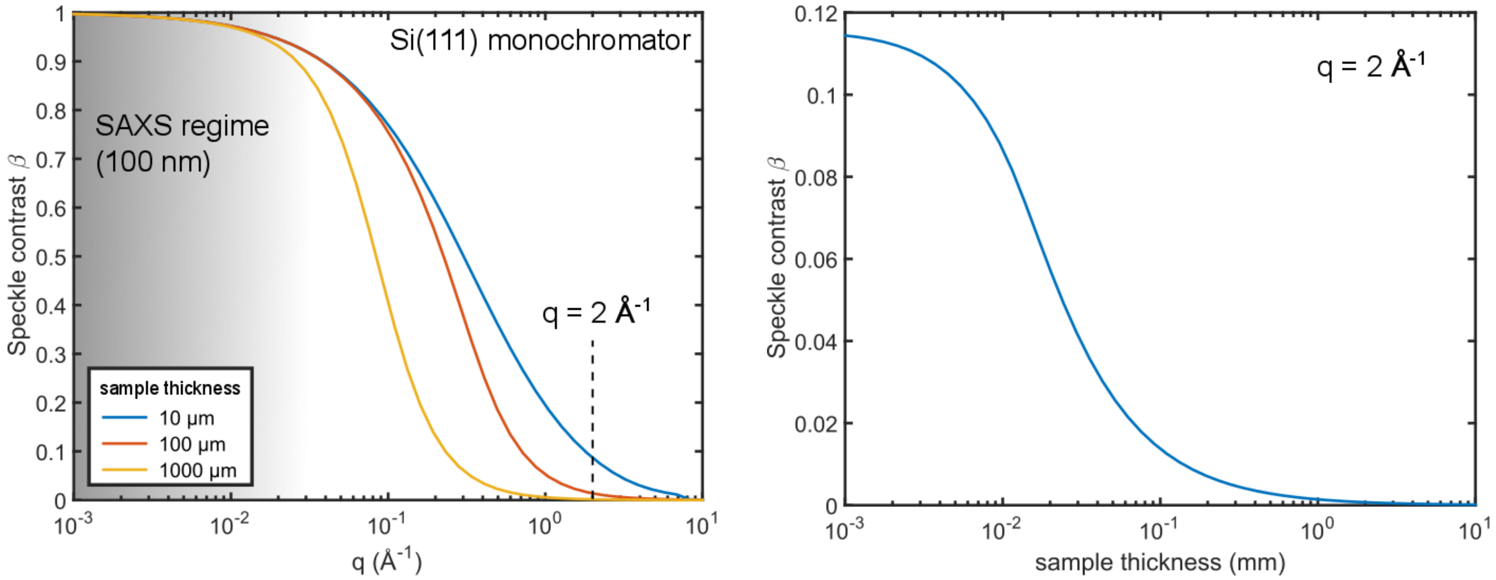
Dynamical heterogeneity

→ Correlated & heterogeneous dynamics close to T_g

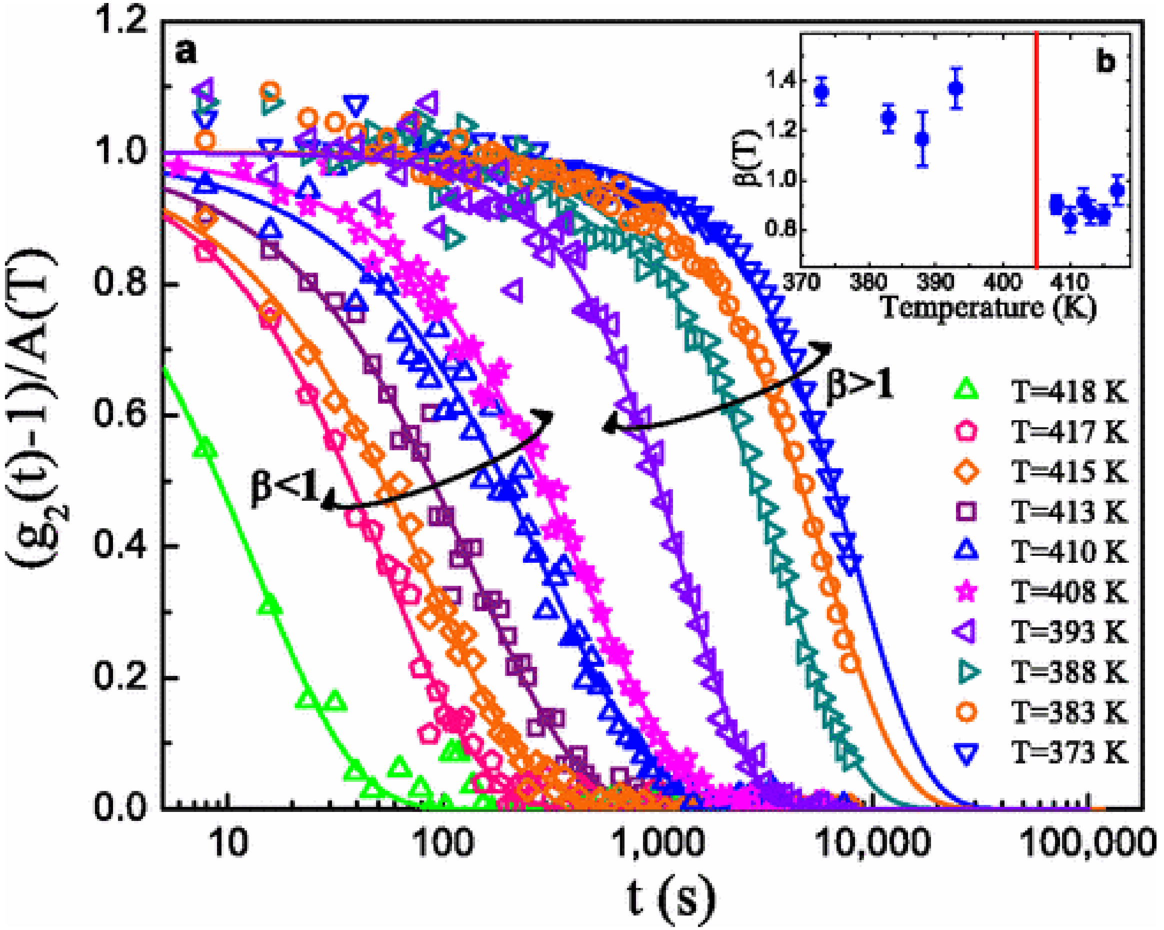
Phys. Rev. E 91, 042309 (2015)

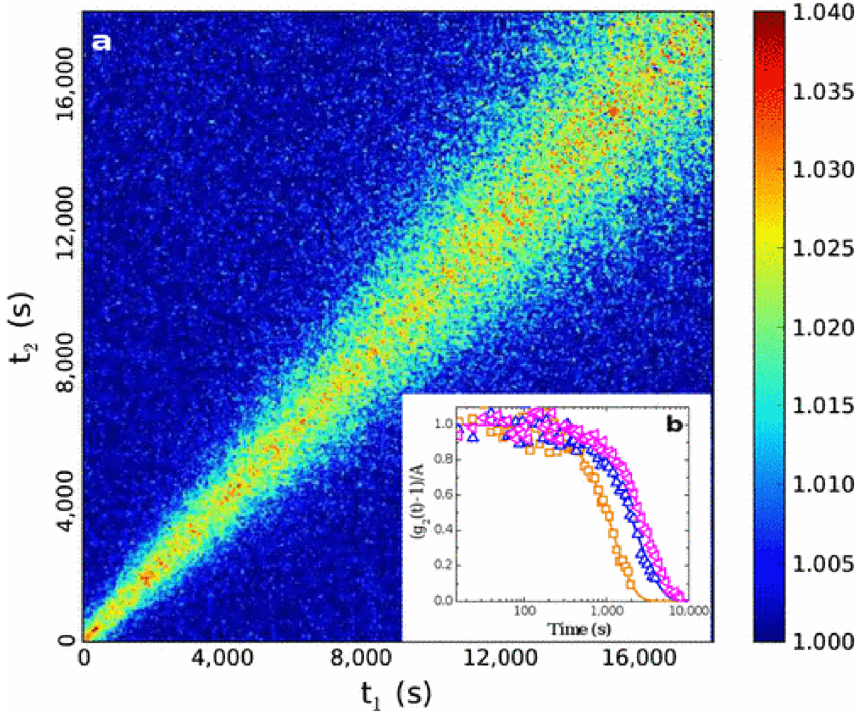
Example 6: dynamics of metallic & network glasses

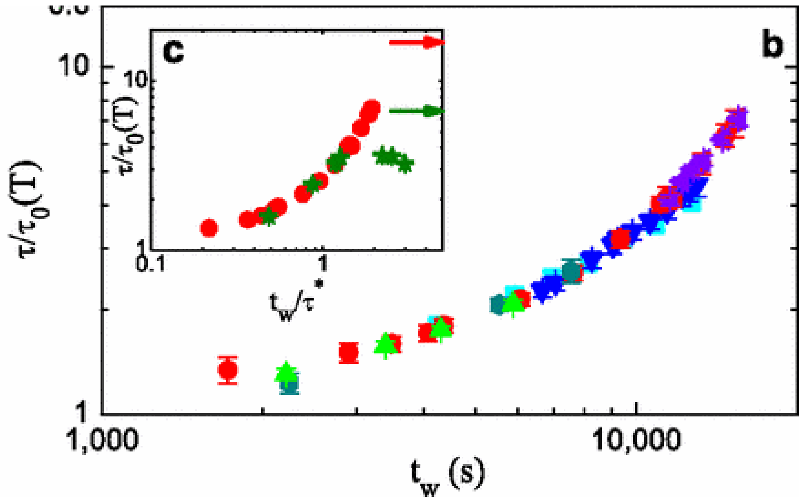
- Molecular dynamics: large q
- In general coherence factor (speckle contrast) as integral over coherence lengths → lower value in large q XPCS → Lecture 17
  - $\beta = \beta_t \beta_l$ with correction factor (for beams with a Gaussion spectrum)
  - $\beta_l = \frac{2}{b^2 d^2} \int_0^b \int_0^d (b-x)(d-y) \exp\left[-\frac{x^2}{\xi_h^2}\right] [\exp(-2|Ax+By|) + \exp(-2|Ax-By|)]$, with $A = \frac{\Delta\lambda}{\lambda} q \sqrt{1 - \frac{q^2}{4k_0^2}}$, $B = -\frac{\Delta\lambda}{2\lambda} \cdot \frac{q^2}{k_0}$, $k_0 = \frac{2\pi}{\lambda}$, width b, depth d



Example 6: dynamics of metallic glasses



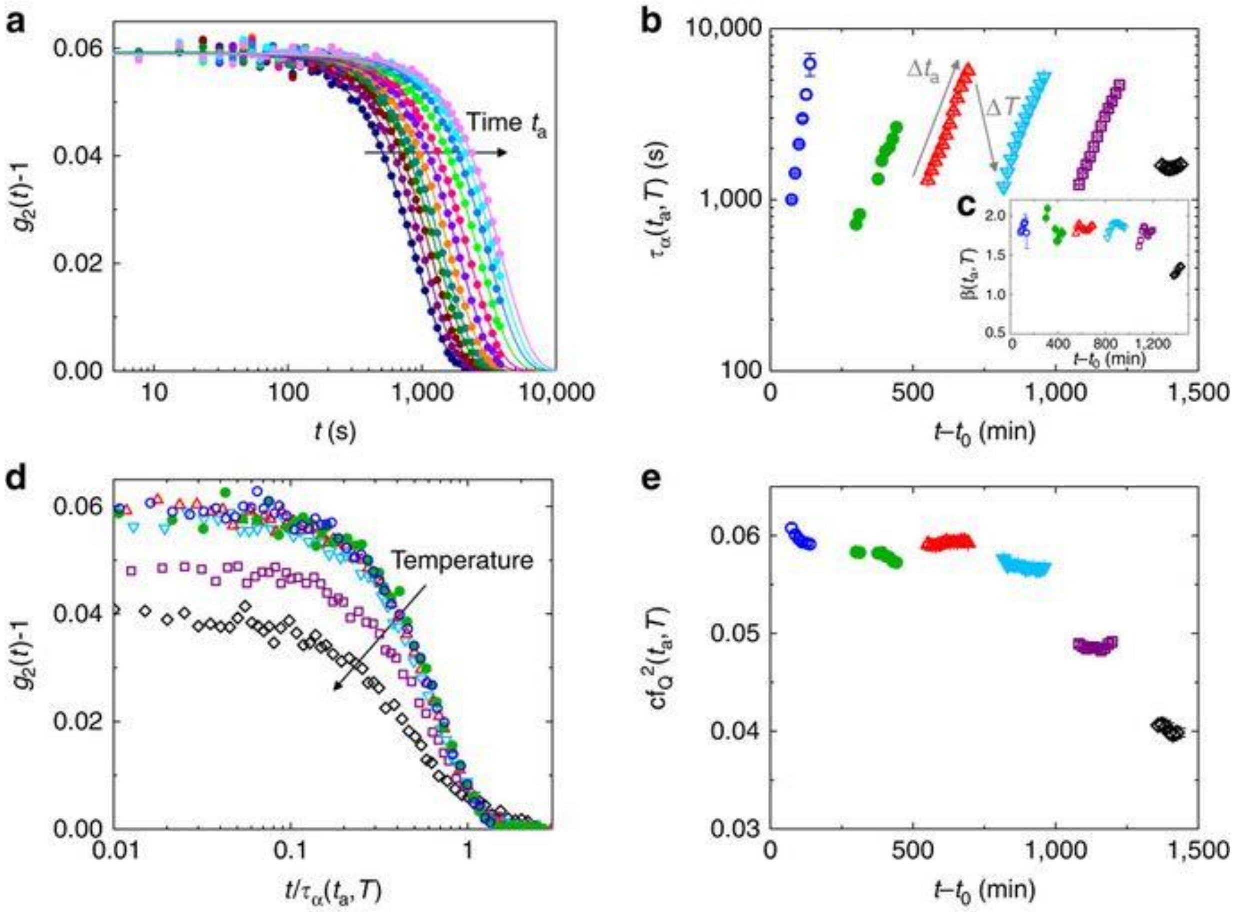


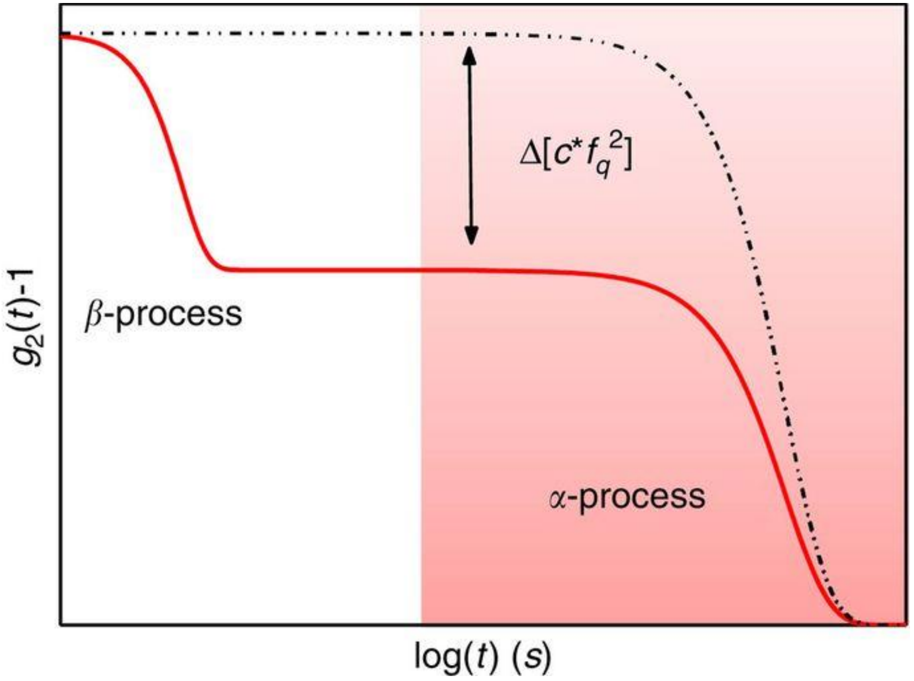


- Dynamics transition: stress relaxation below T_g
- Aging

PRL 109, 165701 (2012)

Example 6: dynamics of metallic glasses

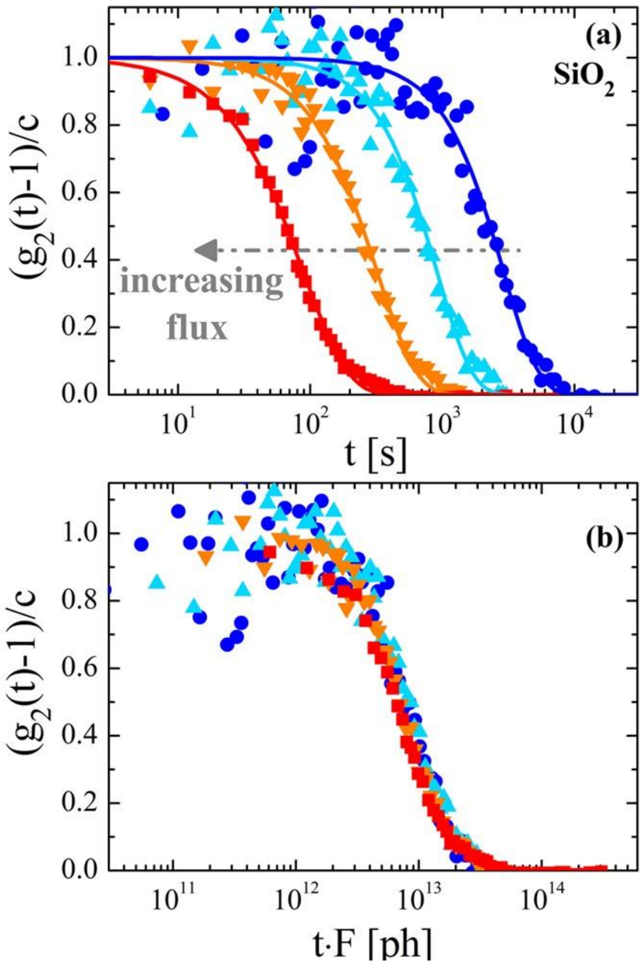




- Missing contrast: faster, non-accessible dynamics
- Aging

Nat. Commun. 7, 10344 (2016)

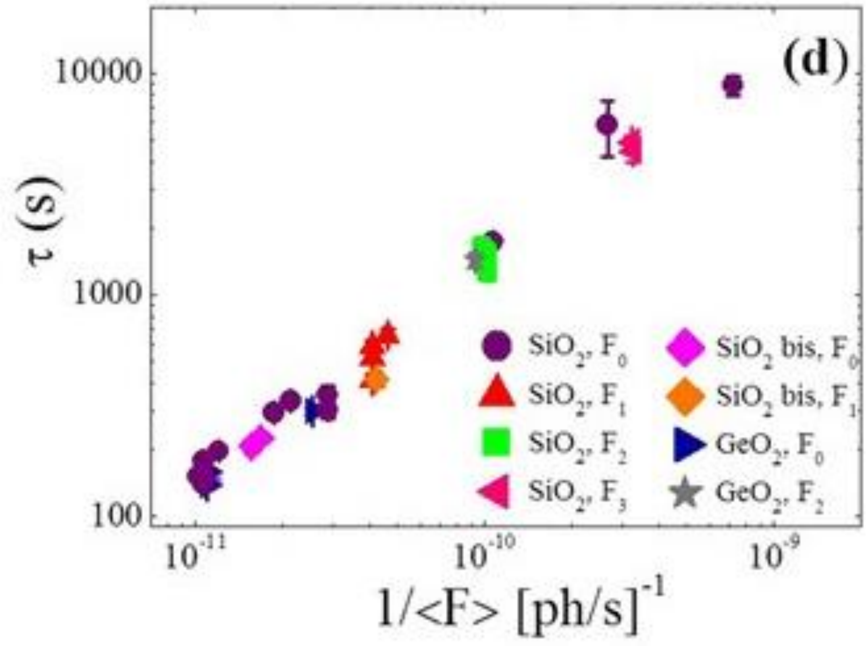
Example 7: oxide glasses

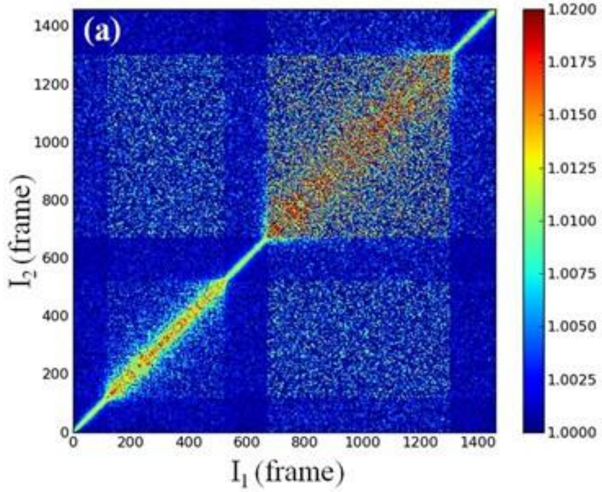


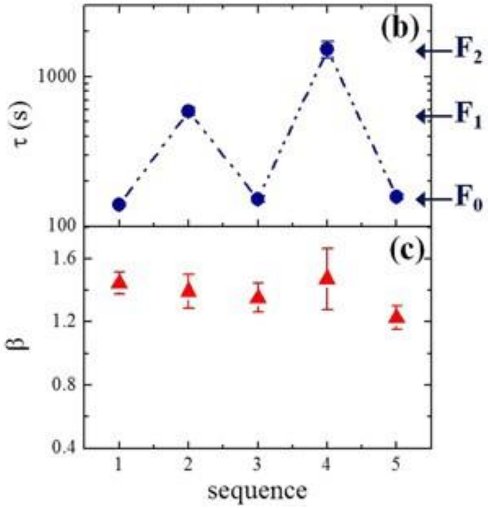
Silica glass: dynamics scale with x-ray flux

Fully reversible

Underlying process unclear

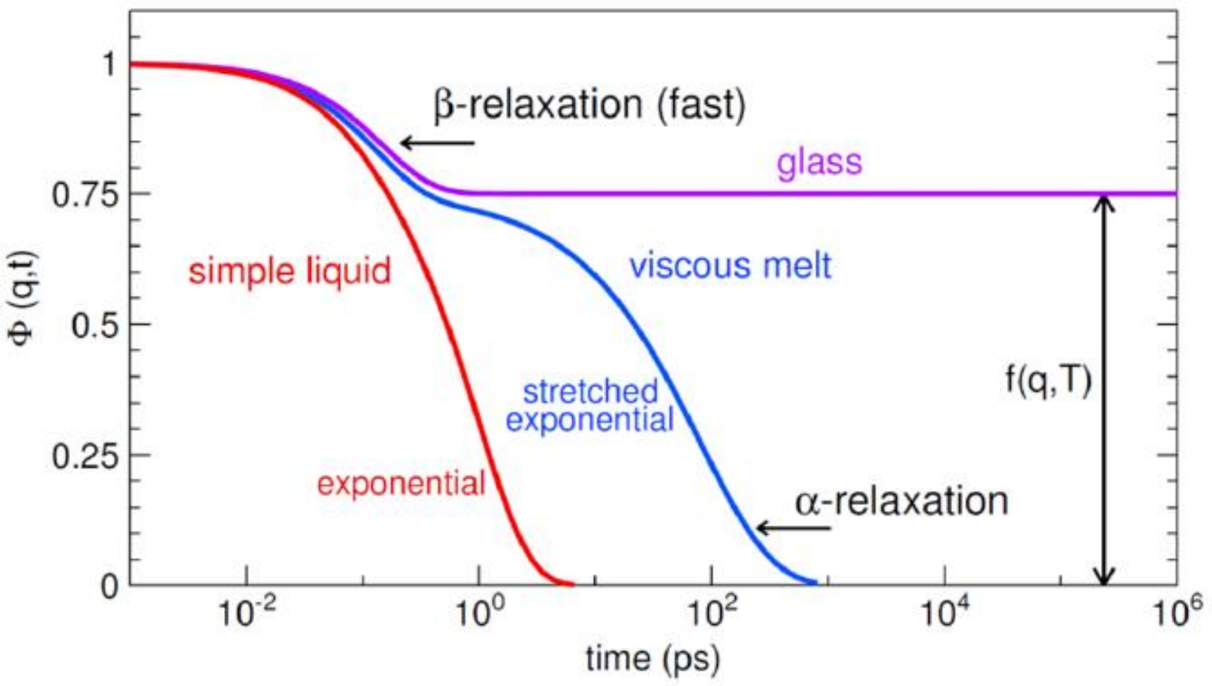


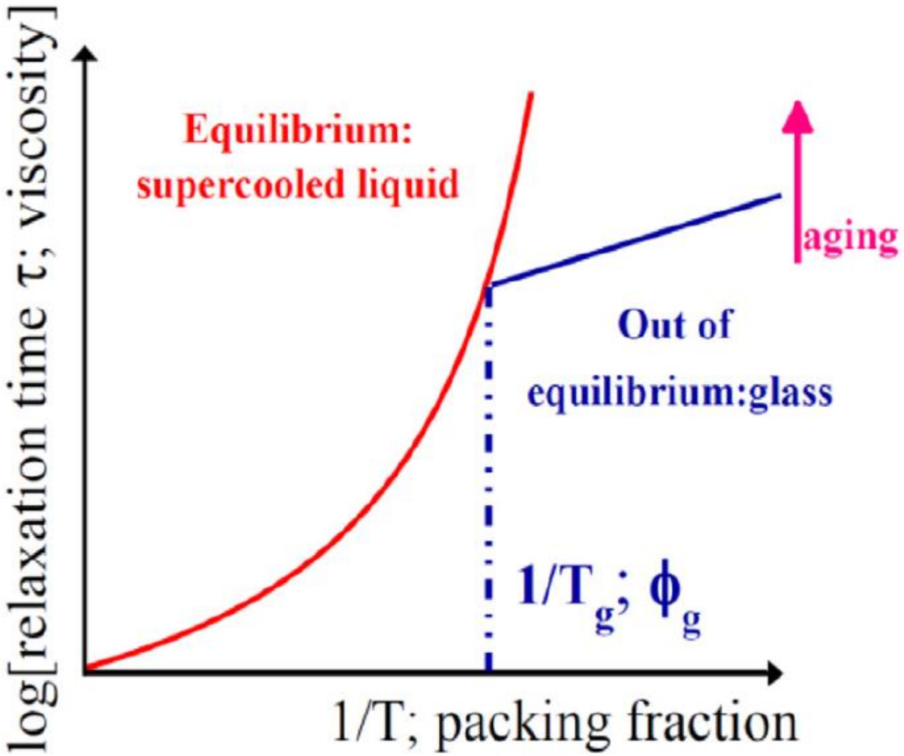




B. Ruta et al. Sci. Rep. 7, 3962 (2017)

Dynamics towards glass transition





JPCD 29, 503002 (2017)