

# Methoden moderner Röntgenphysik: Streuung und Abbildung

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Lecture 15	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2019 G. Grübel, <u>F. Lehmkuhler</u> , L. Müller, O. Seeck, L. Frenzel, M. Martins, W. Wurth		
Location	Lecture hall AP, Physics, Jungiusstraße		
Date	Tuesday	12:30 - 14:00	(starting 2.4.)
	Thursday	8:30 - 10:00	(until 11.7.)



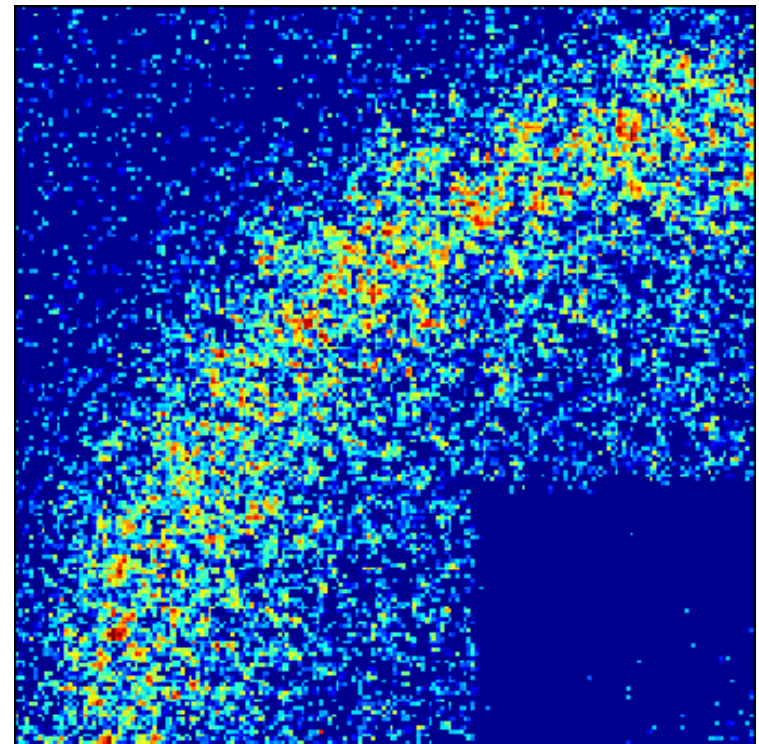
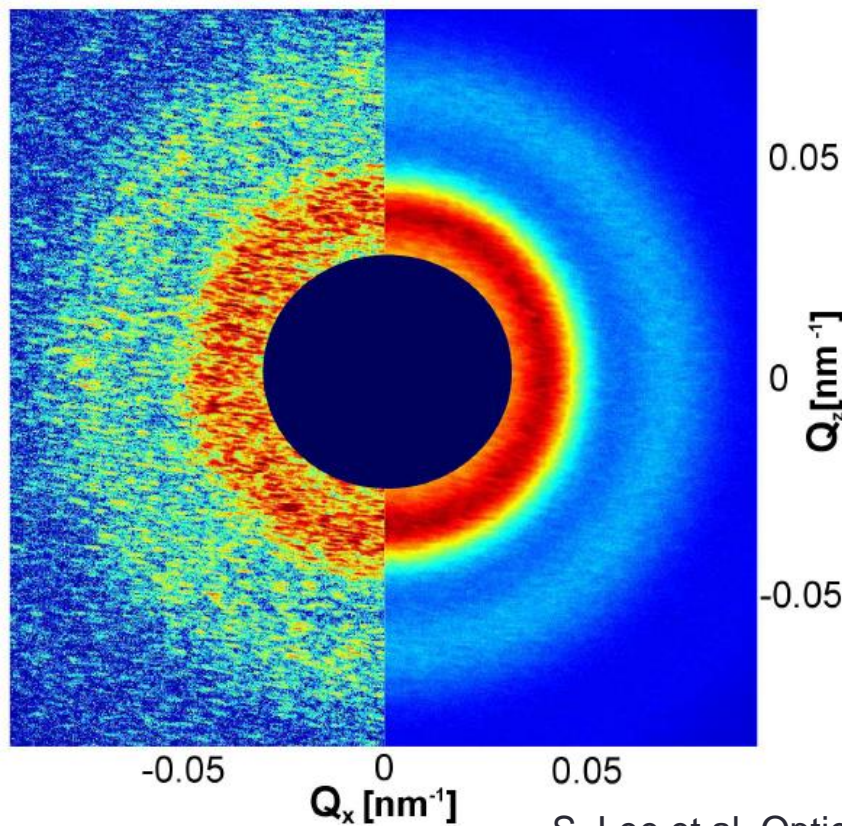
# Soft Matter – Timeline

- Di 07.05.2019 Soft Matter studies I: Methods & experiments  
*Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, ...*
- Do 09.05.2019 Soft Matter studies II: Structure  
*SAXS & WAXS applications, X-ray cross correlations, ...*
- Di 14.05.2019 Soft Matter studies III: Dynamics  
*XPCS applications, diffusion, dynamical heterogeneities, ...*
- Do 16.05.2019 XPCS and XCCA simulation and modelling
- Di 21.05.2019 **Case study I: Glass transition**  
*Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, ...*
- Do 23.05.2019 **Case study II: Water**  
*Phase diagram, anomalies, crystalline and glassy forms, FEL studies, ...*



## 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 ( $\text{SiO}_2$ )
  - Network glasses (phosphate glasses, borate glasses, ...)
  - Obsidian
  - Glass fibres
  - Metallic glasses
  - Polymer glasses (plastics)
  - Colloidal glasses
  - Glassy water (→ lecture 17)

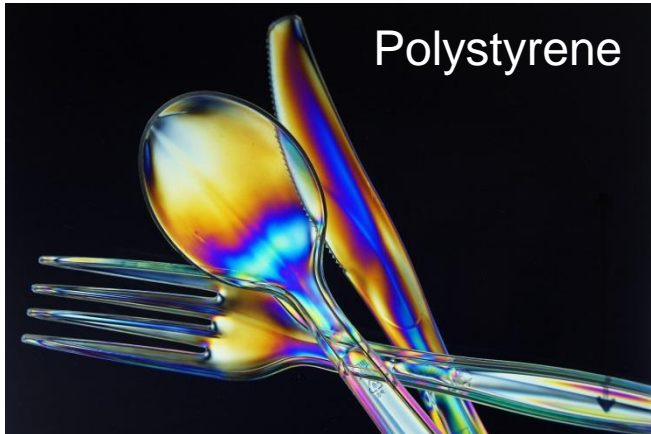
Metallic glass



Obsidian



Polystyrene



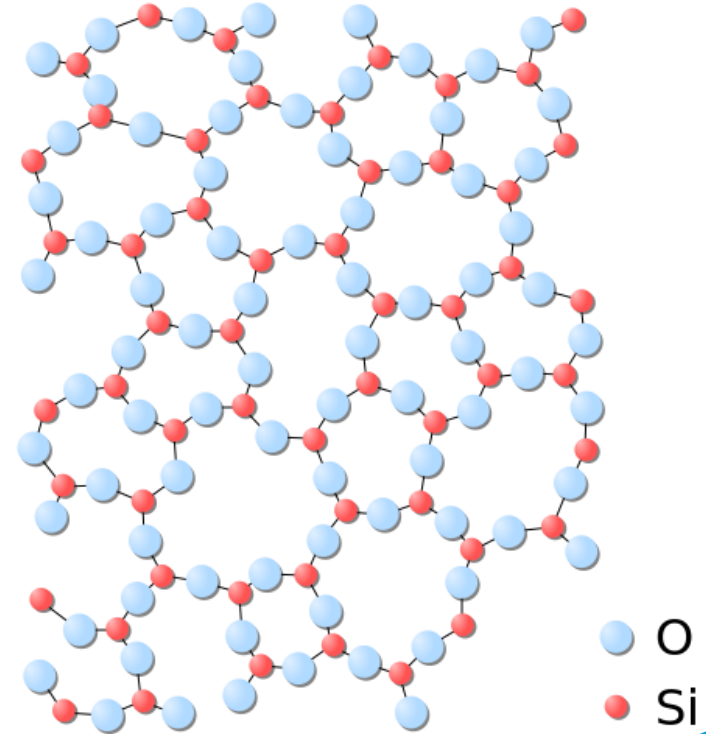
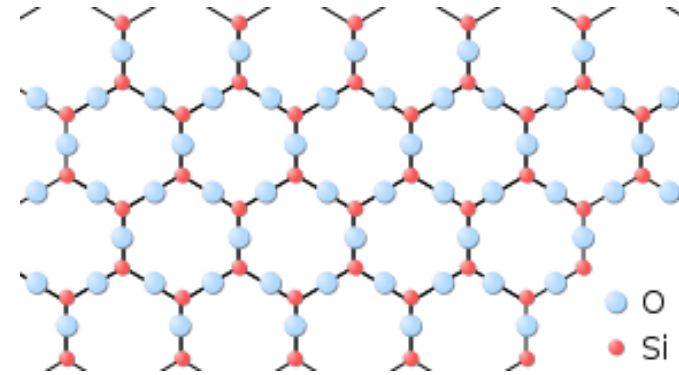
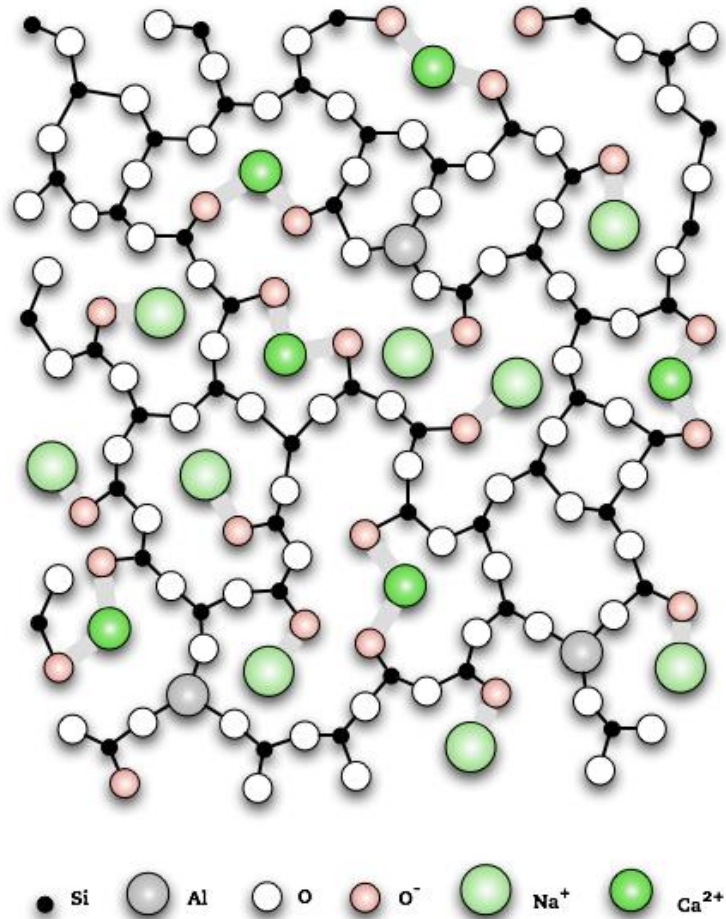
Roman glasses

Pictures: wikipedia

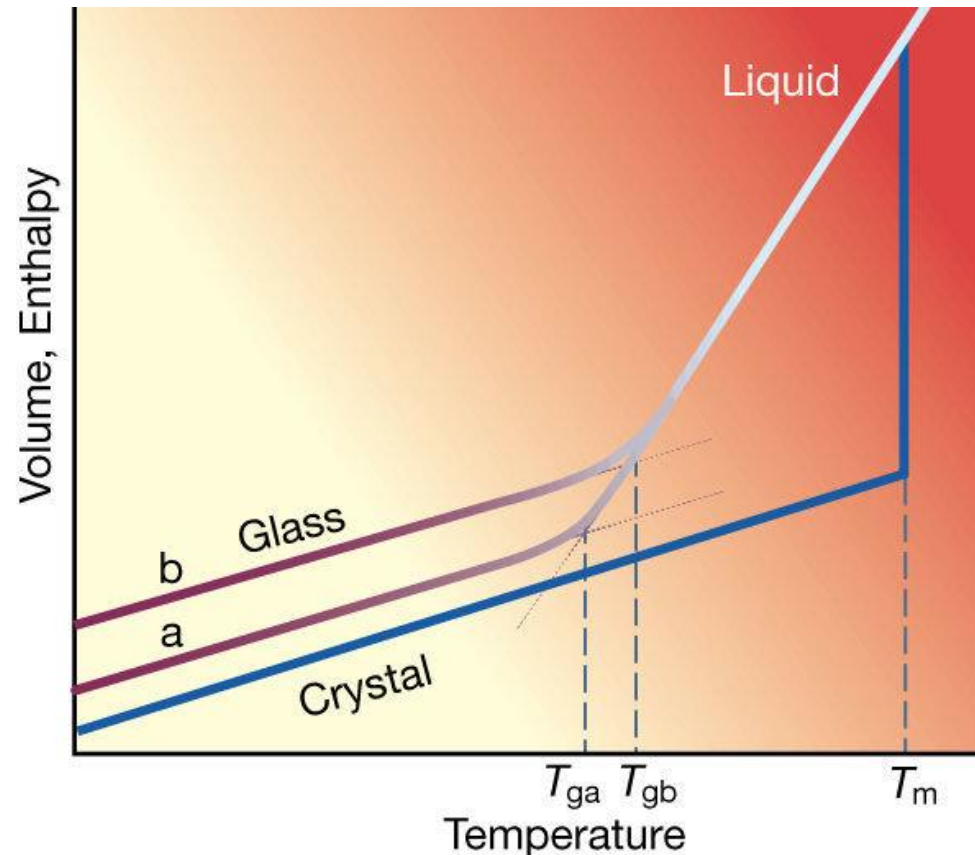




## What is a glass?



## 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  $\sim 100$  s
- Viscosity of  $10^{12}$  Pa s
- Change of heat capacity, thermal expansion, ...

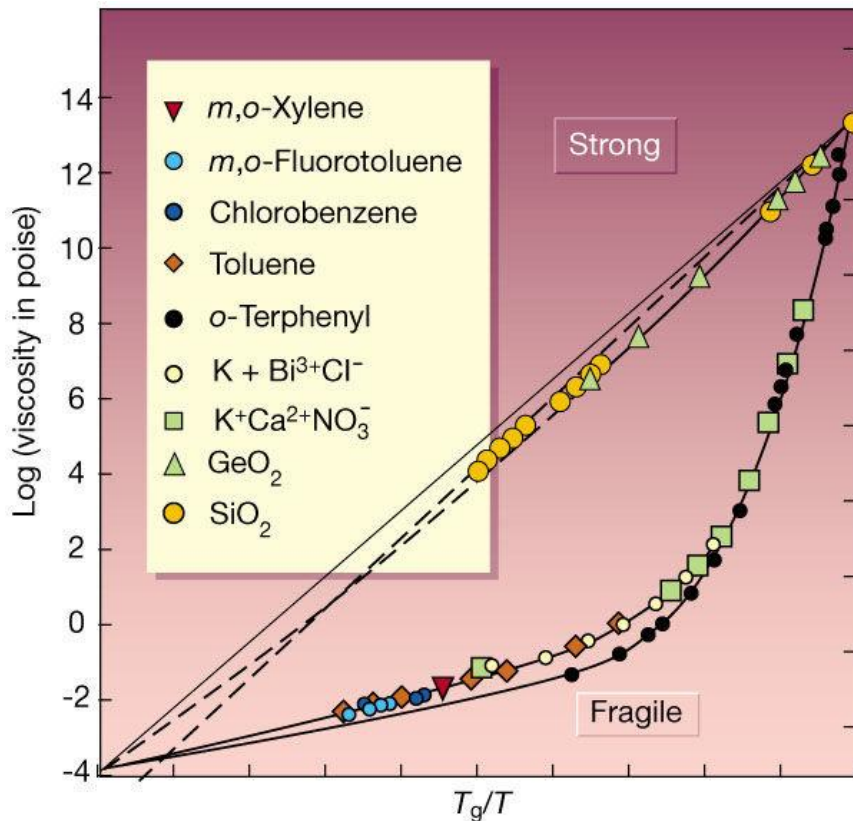


## Glass transition temperatures

Material	$T_g$ (°C)	$T_m$ (°C)
Silica SiO <sub>2</sub>	~1200	1713
Borosilicate glass	~500	
GeO <sub>2</sub>	~700	~1000
Polystyrene	95	~240-270
Teflon	115	327
PMMA (Plexiglas)	105	
Glycerol	~ -70	18
Zr <sub>65</sub> Al <sub>7.5</sub> Ni <sub>10</sub> Cu <sub>17.5</sub>	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  $\eta = A \exp\left(\frac{B}{T-T_0}\right)$

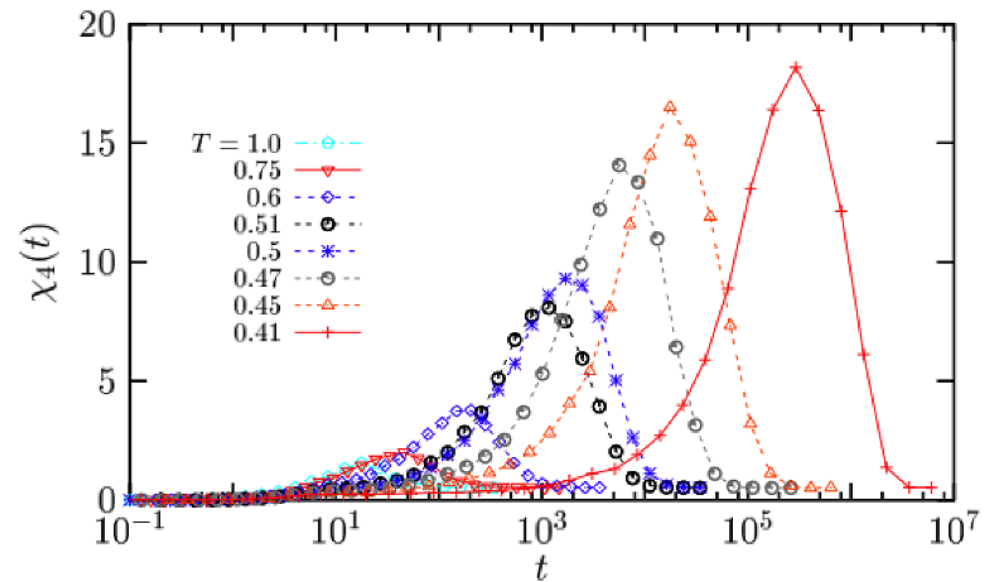
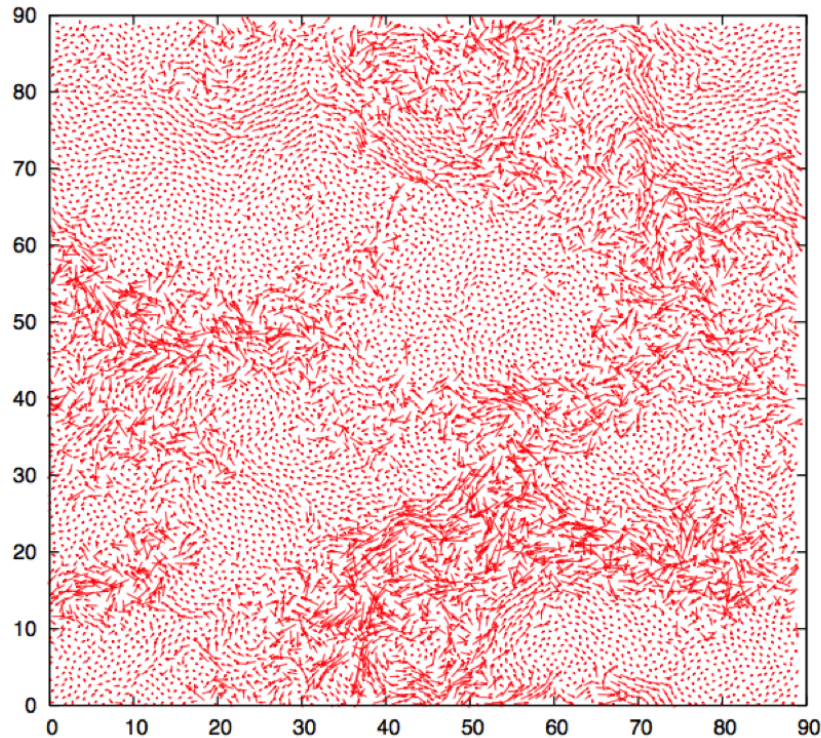
→ Fragility index:  $m := \left(\frac{\partial \log_{10} \eta}{\partial \left(\frac{T_g}{T}\right)}\right)_{T=T_g}$

## 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  $F(t) = \exp\left(-\left(\frac{t}{\tau}\right)^\gamma\right)$  with  $\gamma < 1$  (cf. Lecture 13)  $\rightarrow$  XPCS experiments
- Contrasts to liquids  $\rightarrow$  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  $\chi_4(t) \sim$  volume of correlated clusters
- Need higher-order correlations to be determined

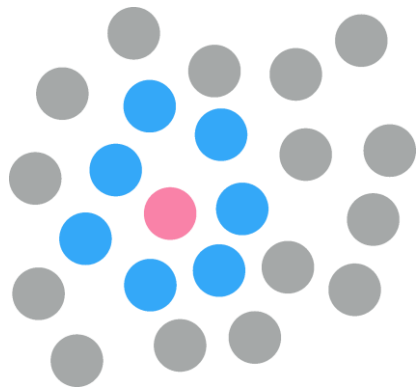


Physics 4, 42 (2011)

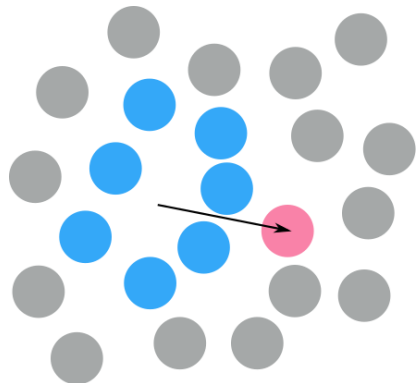


## Alpha- & beta-relaxation

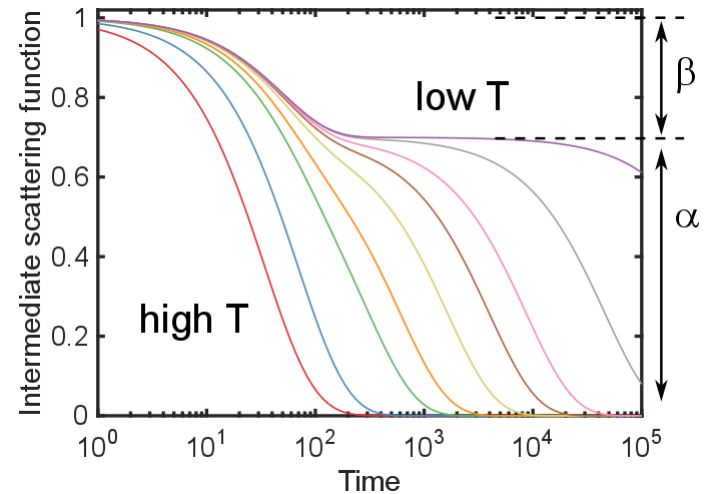
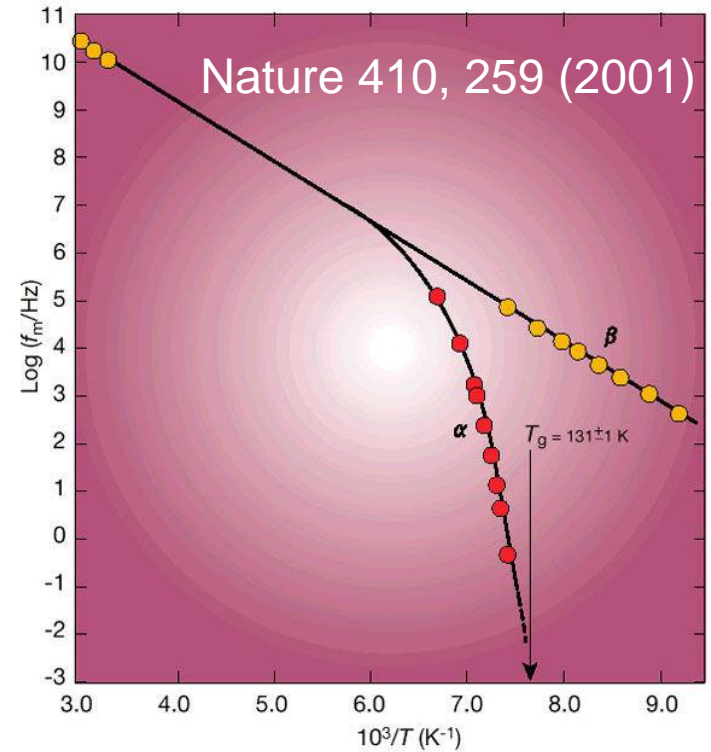
- Decoupling of dynamics near  $T_g$ :  $\alpha$ - and  $\beta$ -relaxations



$\beta$ -relaxation

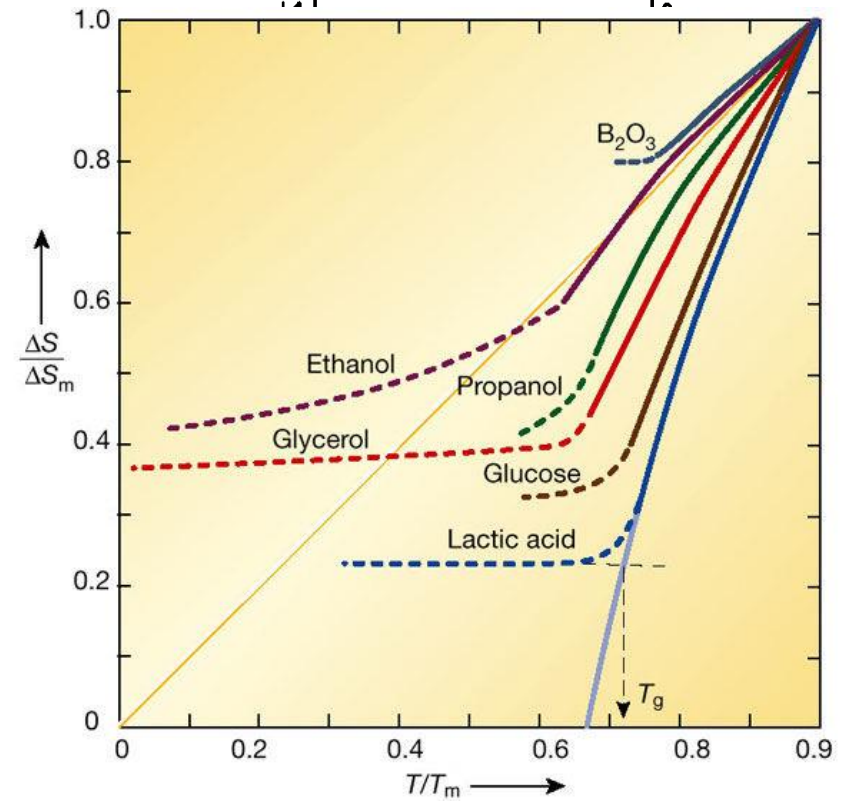
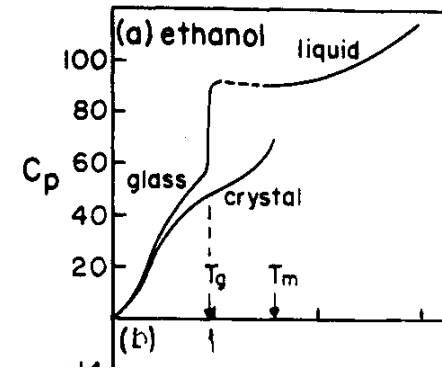


$\alpha$ -relaxation



## Thermodynamics: Adam-Gibbs model

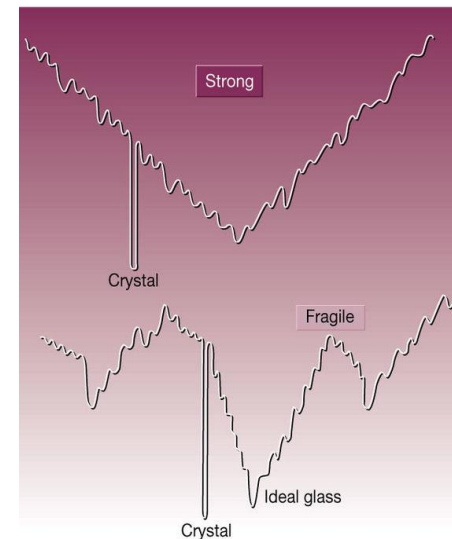
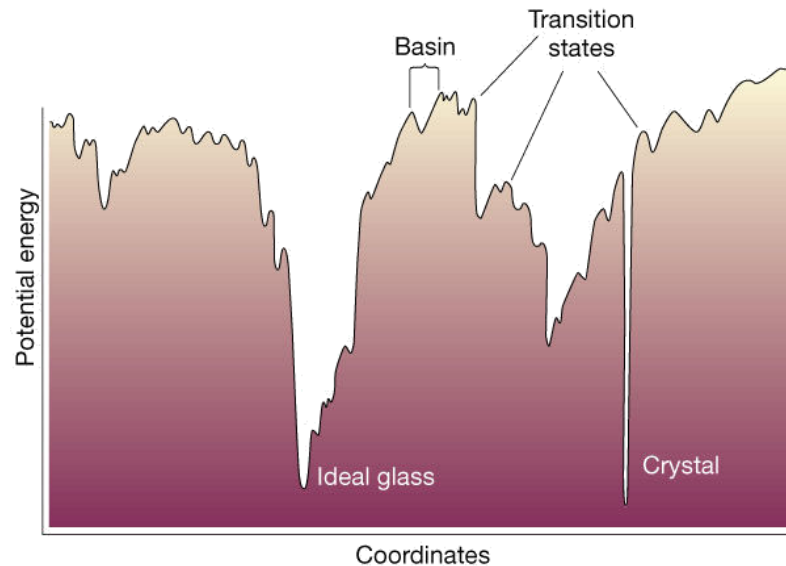
- Entropy difference liquid and crystal: glass transition before  $\Delta S = 0$
- Entropy crisis:  $S_{cryst}(T \rightarrow 0) \rightarrow 0 \rightarrow$  third law of thermodynamics
- Kauzmann temperature  $T_K$ :  $S_{liquid} = S_{crystal} \rightarrow$  ideal glass
- Glass transition: Kinetics vs.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





## Energy landscapes

- Configurational entropy  $s_C \sim$  number of minima in potential energy surface



- At Kauzmann temperature: non-crystalline state of lowest energy (ideal glass)
- Strong vs. Fragile – heterogeneous landscapes of fragile glass-formers  $\rightarrow$  broad range of relaxation times  $\rightarrow$  dynamical heterogeneity
- $\alpha$ -relaxations correspond to configurational sampling of neighbouring "megabasins", whereas  $\beta$ -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

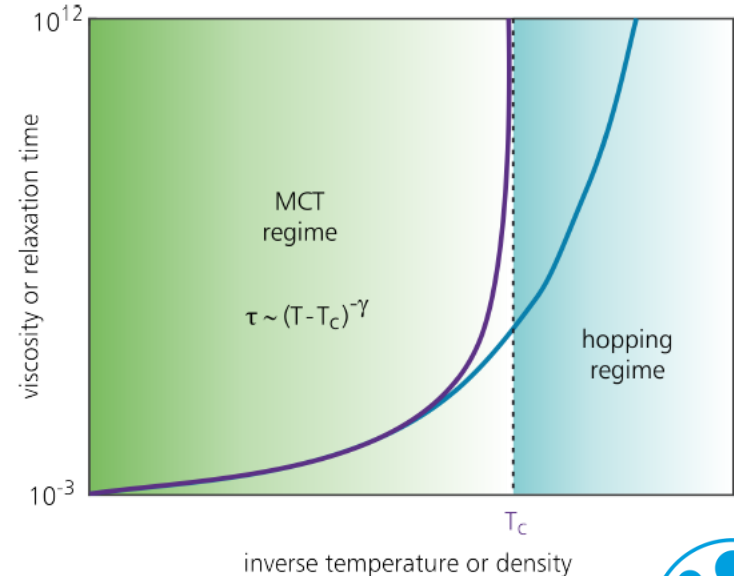
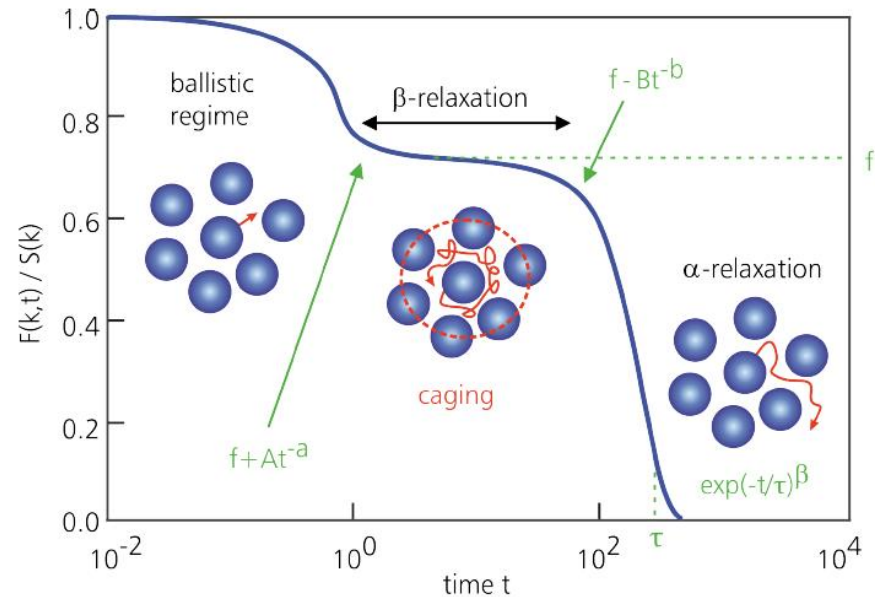


## Predictions from MCT

- 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  $\alpha, \beta$ -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



arXiv:1806.01369 (2018)

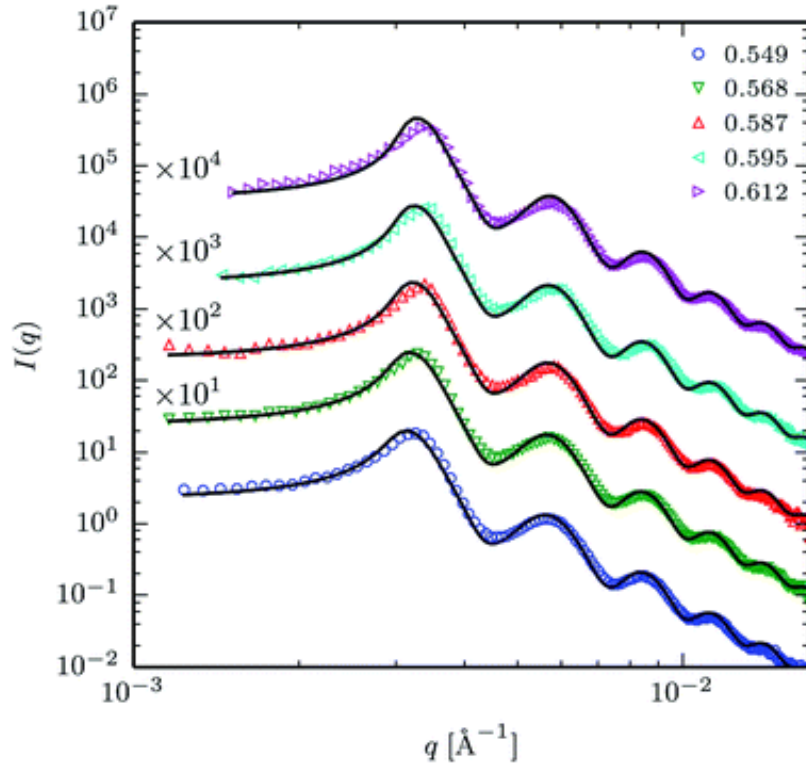
## X-ray scattering studies of glass transition

- 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

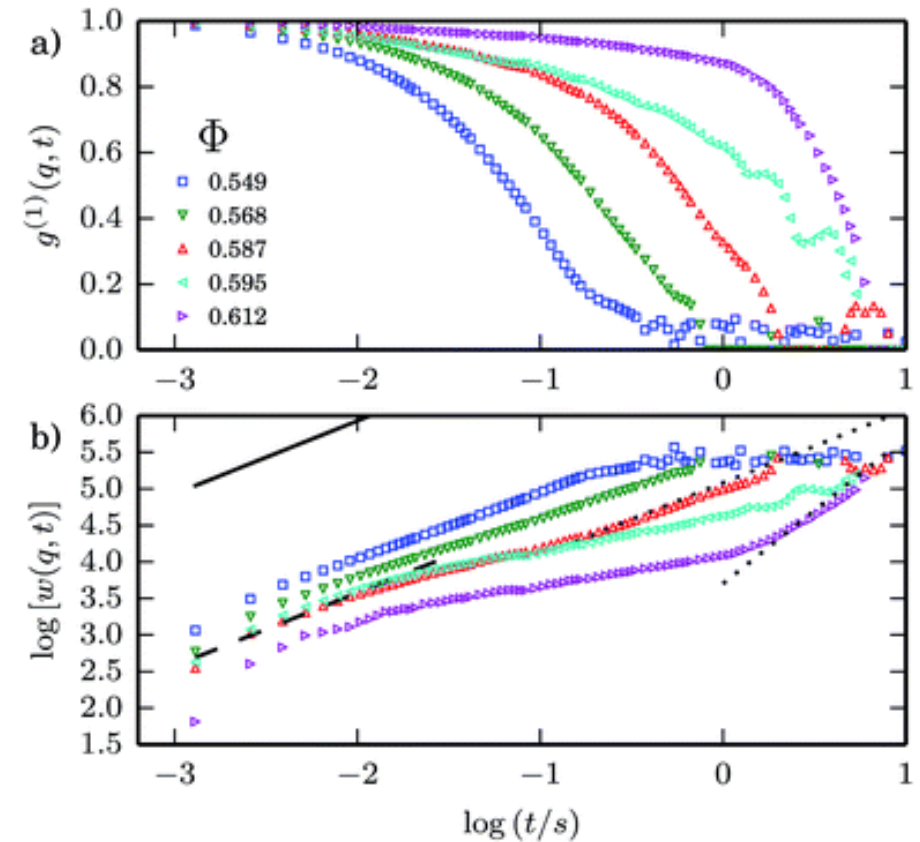


## Example 1: Colloidal hard sphere glasses

### Hard sphere colloidal glasses



Soft Matter 10, 8698 (2014)

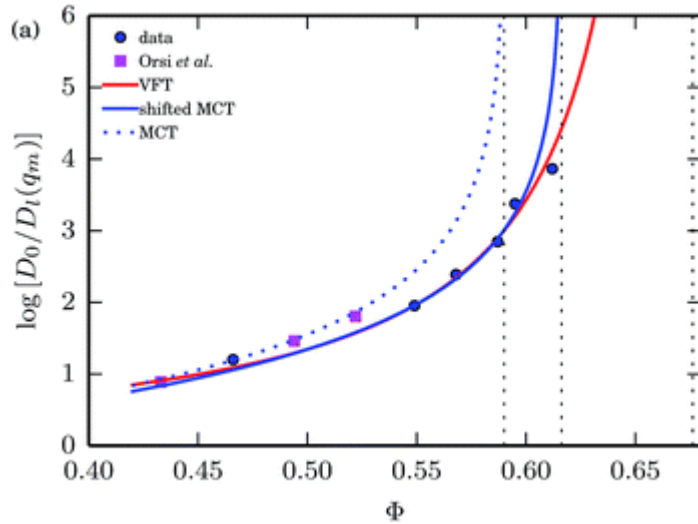


ISF  $g^{(1)}(q, t)$

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

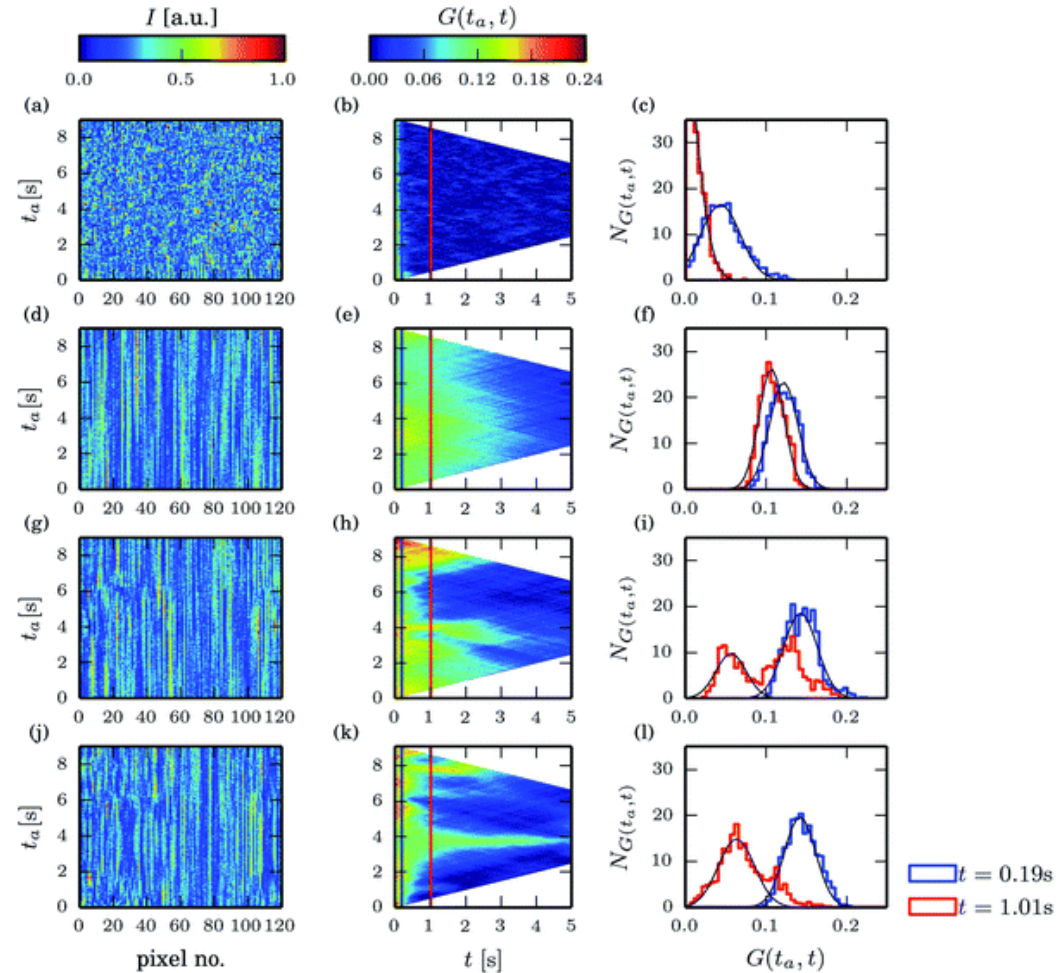


## Example 1: Colloidal hard sphere glasses



Long time diffusion  $\rightarrow$  structural relaxation

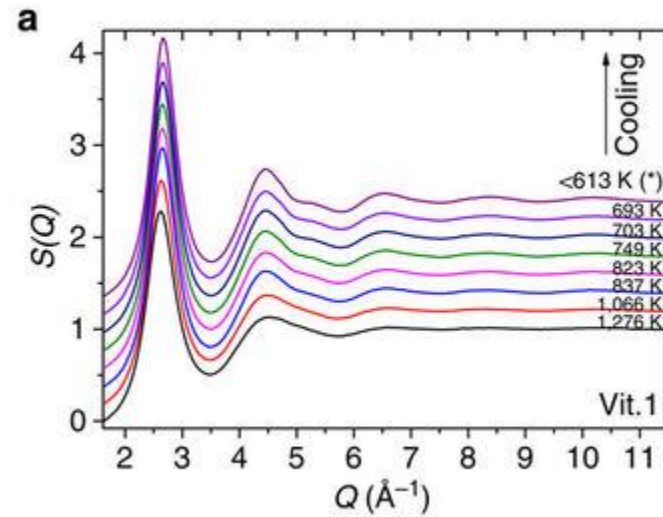
MCT & VFT modelling  $\rightarrow$  3% shift necessary



Soft Matter 10, 8698 (2014)

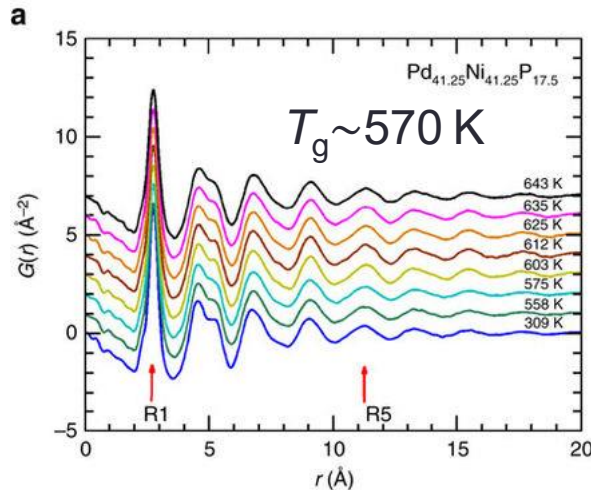
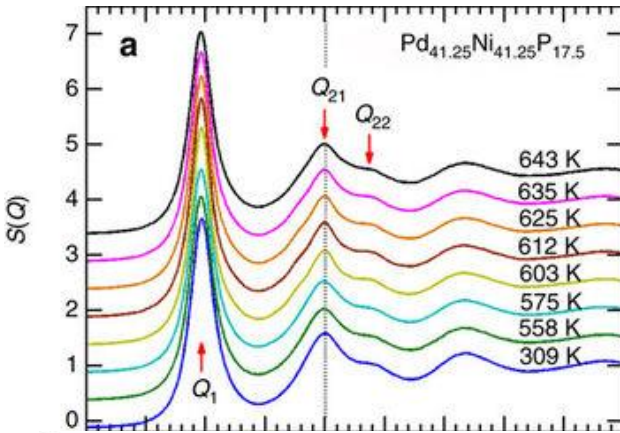
## Example 2: Structure factors

### Metallic glasses



$\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$   
 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?



Nat. Commun. 8, 14679 (2017)

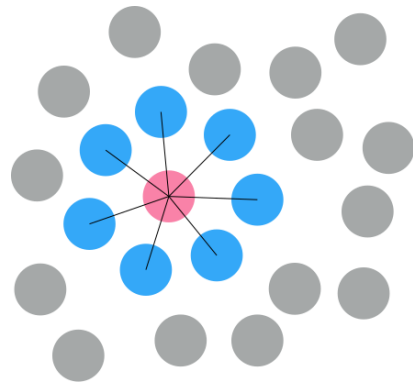
## Higher-order structure in simulation and microscopy

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

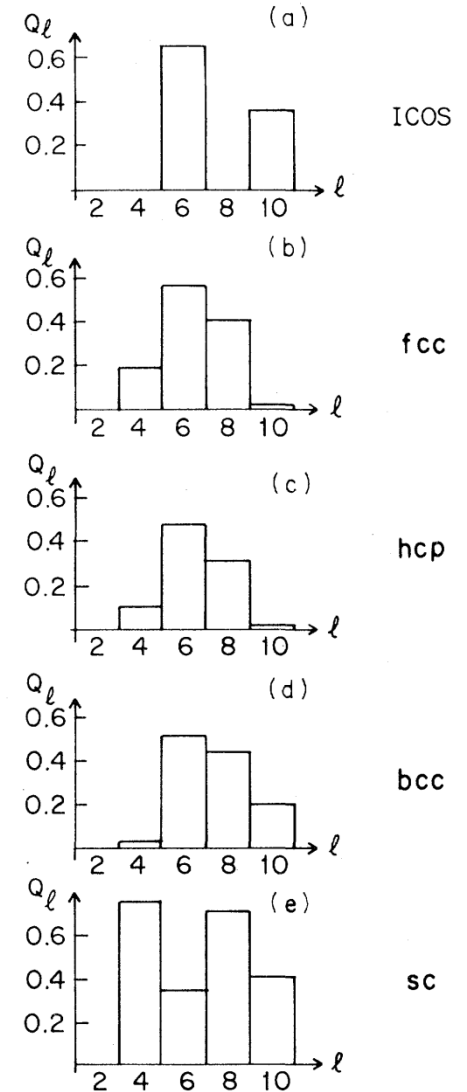
$$Q_{lm} = \frac{1}{N} \sum_0^N Y_{lm}(\theta(\mathbf{r}), \phi(\mathbf{r}))$$

- Rotationally invariant coordinate system

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



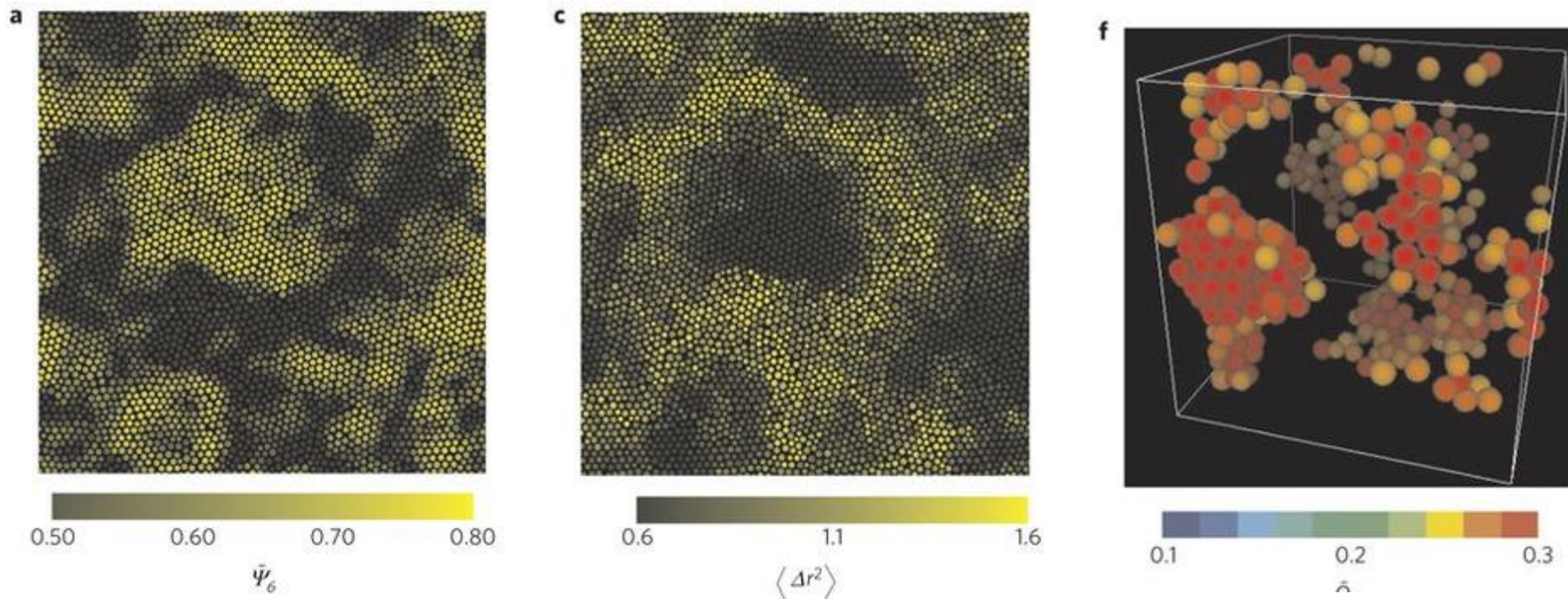
- Fingerprint for different local environments



Phys. Rev. B 28, 784 (1983)



## Higher-order structure in simulation and microscopy

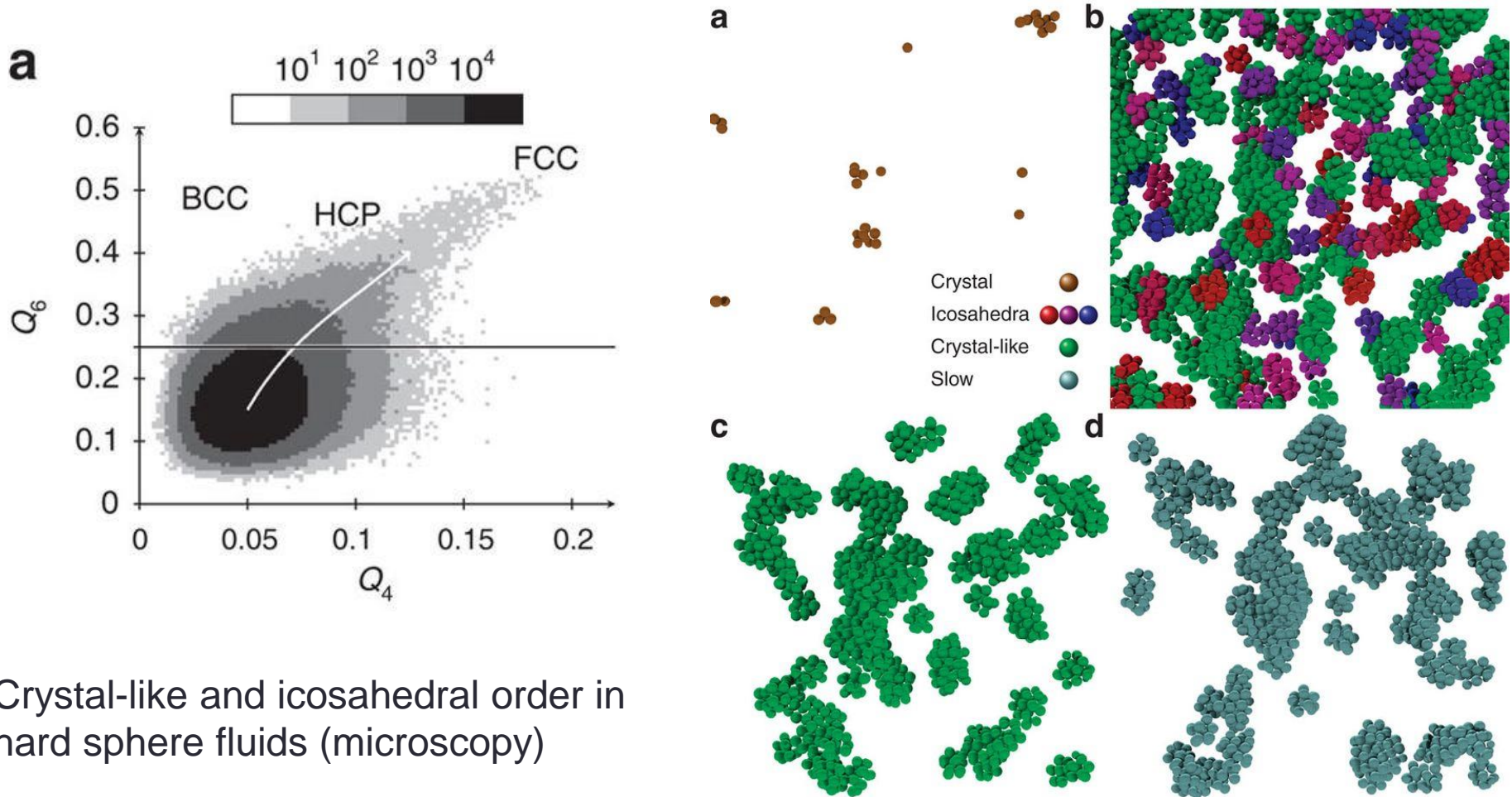


Structural and dynamical heterogeneities (simulation)

Nat. Mat. 9, 324 (2010)



## Higher-order structure in simulation and microscopy



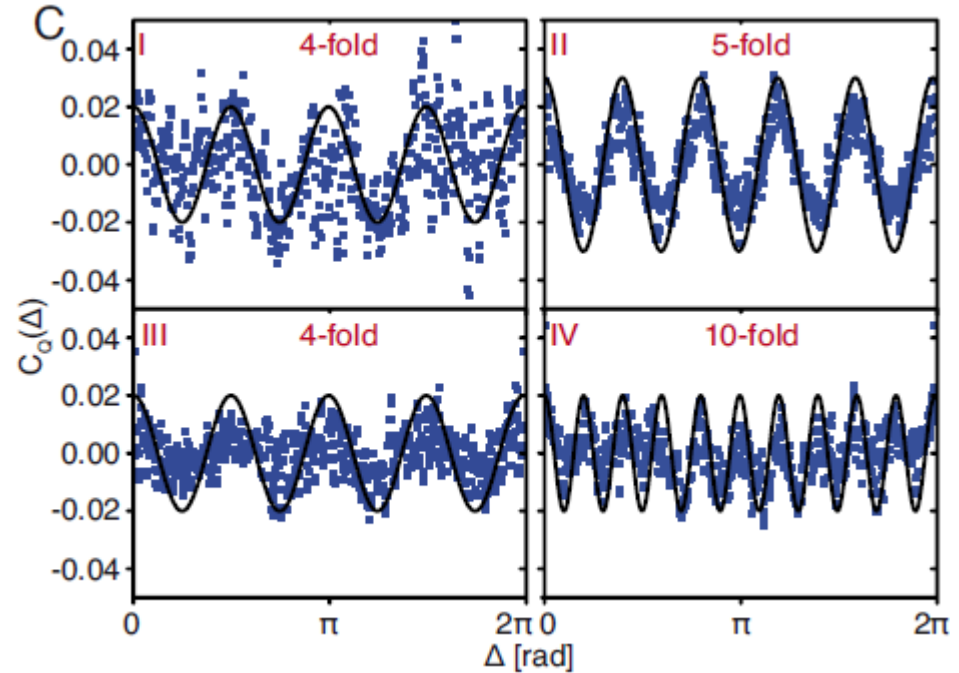
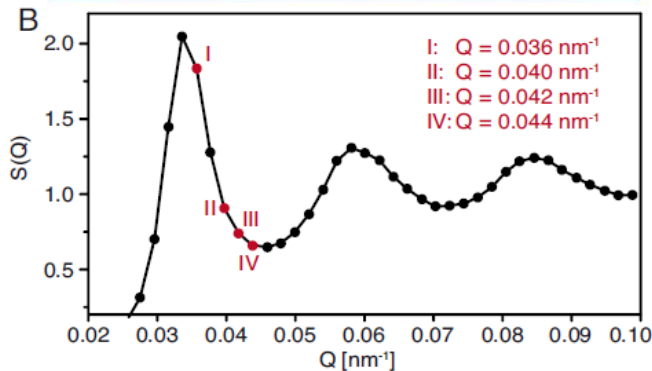
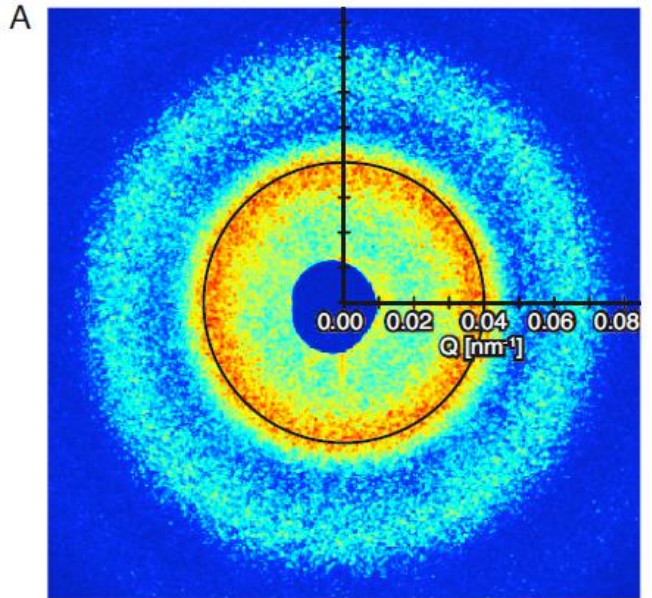
Crystal-like and icosahedral order in hard sphere fluids (microscopy)

Nat. Comm. 3, 974 (2012)



## Example 3: XCCA approaches

Hard-sphere glass

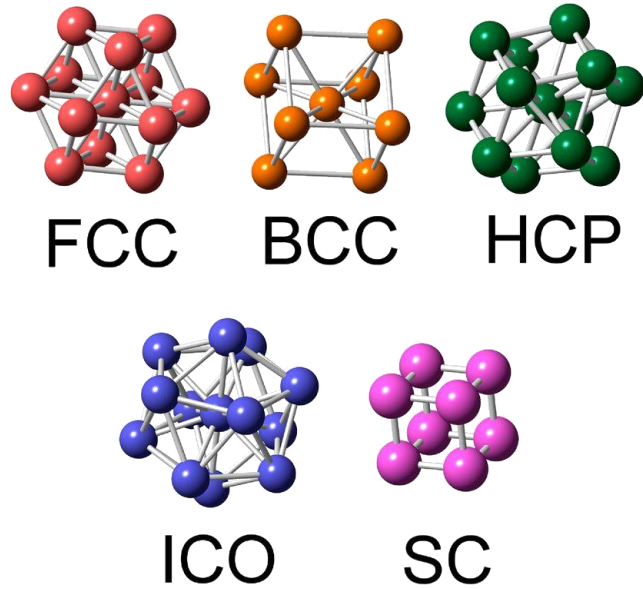
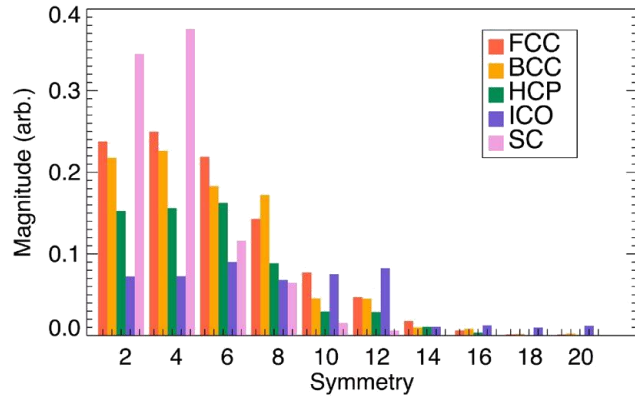


- Hidden symmetries
- Structural information beyond SAXS

PNAS 109, 11511 (2009)

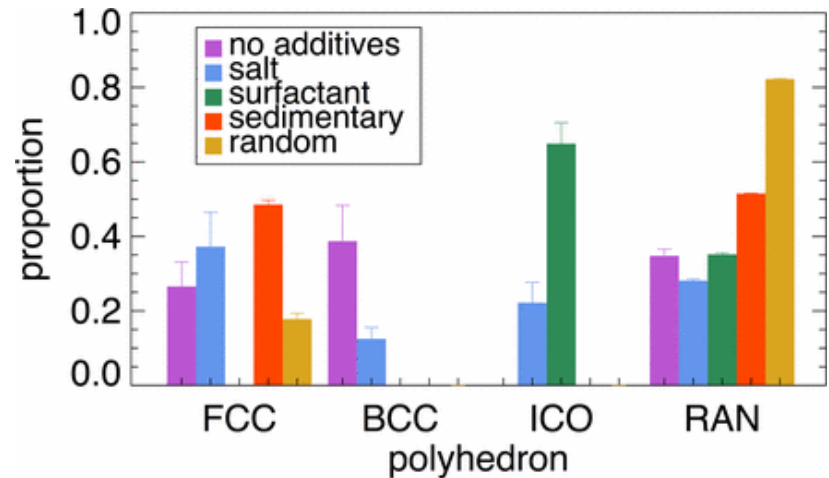
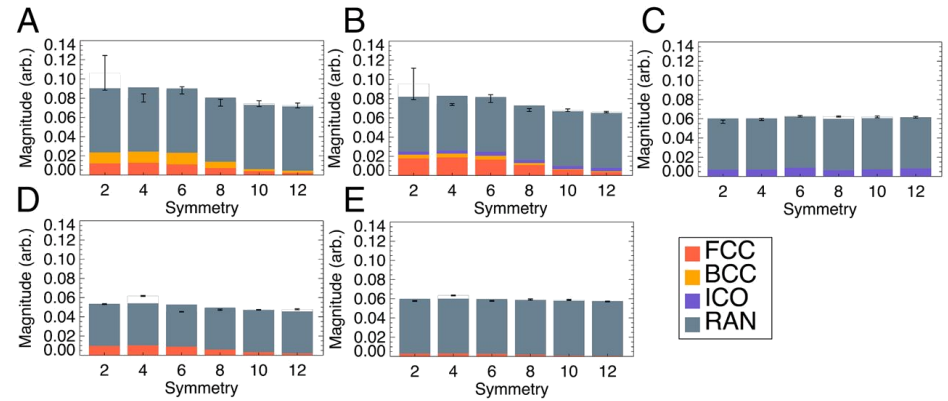


## Example 3: XCCA approaches



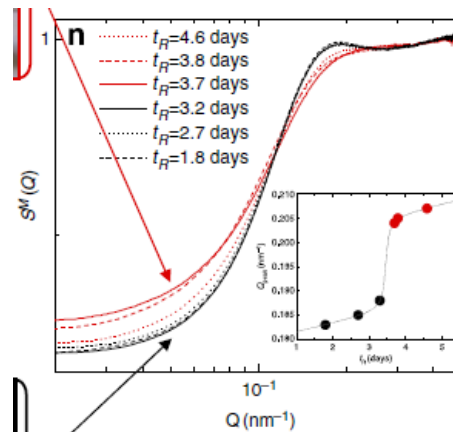
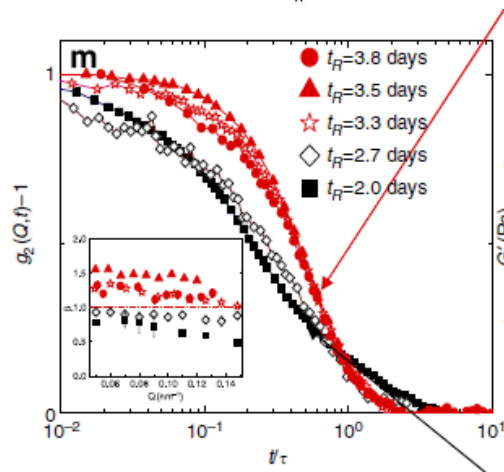
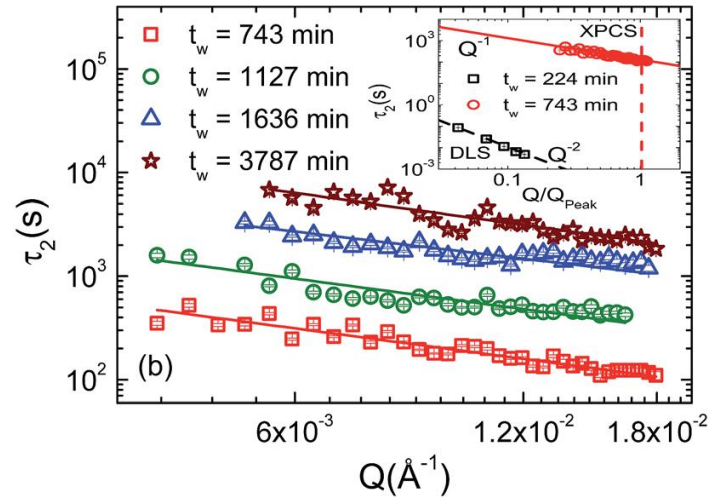
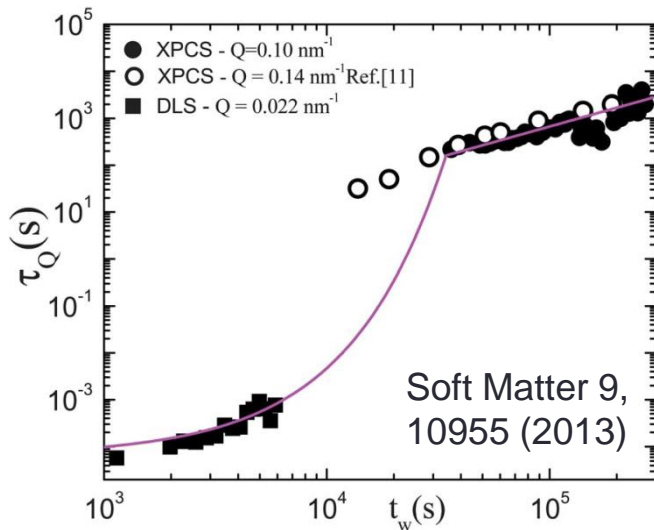
PNAS 114, 10344 (2017)

Colloidal glasses: SiO<sub>2</sub> with additives  
Salt: screening  
Surfactant: short-range attractive compound



## Example 4: Aging in colloidal glasses

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



Glass-glass transition during aging

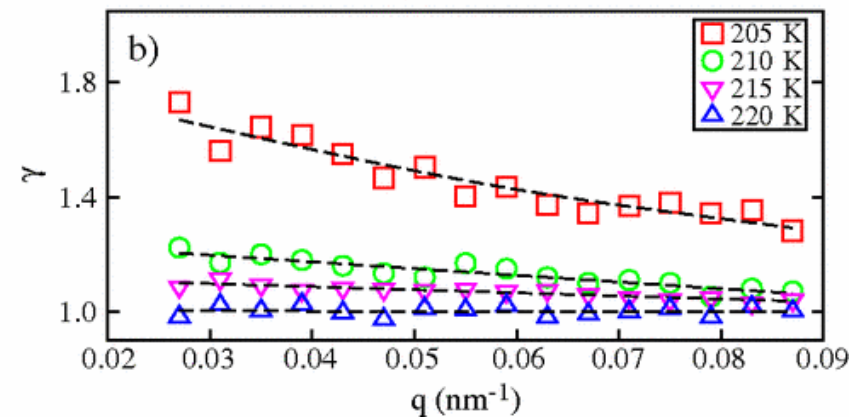
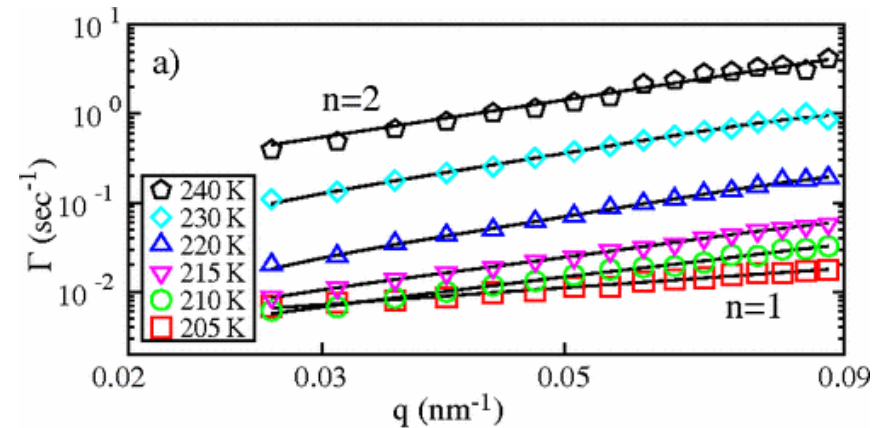
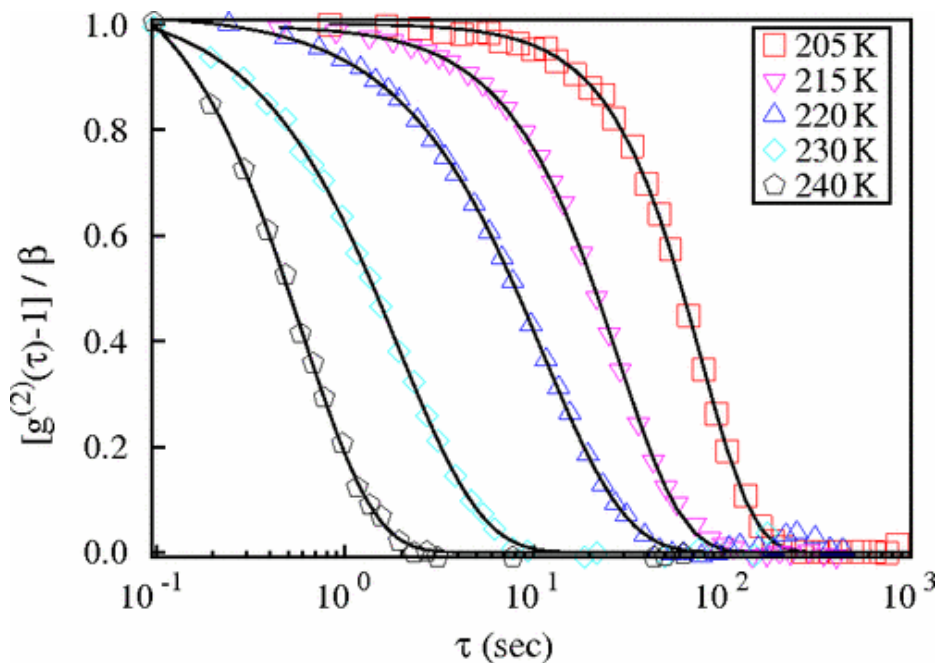
Nature Comm. 5, 4049 (2014)



## 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  $f(q, \tau) \propto \exp(-(q^n t)^\nu)$

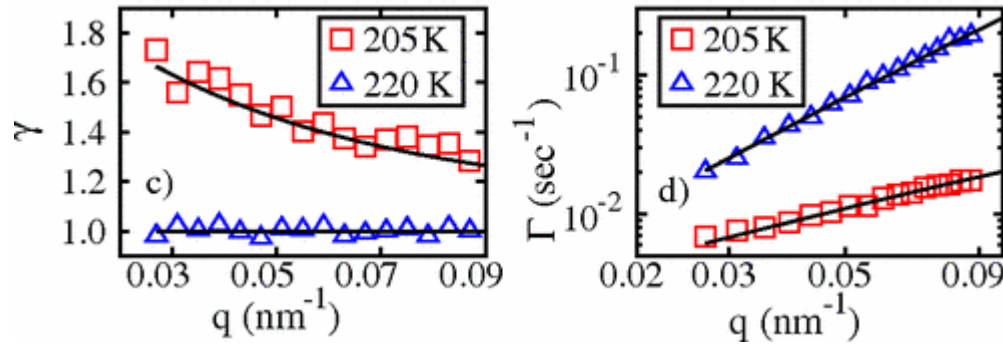
Model with continuous time random walk model: displacement of particle in time interval  $t$  consists of  $N$  discrete steps  $\rightarrow$  ISF is determined by number of steps  $N$  and degree of decorrelation  $h(q, N)$  between steps

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

- $P_t(N)$  probability of  $N$  events occurring during time interval  $t \rightarrow$  Poisson distribution  $P_t(N) = \exp(-\Gamma_0 t) (\Gamma_0 t)^N / N!$ , with  $1/\Gamma_0$  the mean time between events
- $h(q, N) \simeq \exp[-(q N^\alpha \delta)^2]$  Gaussian distribution, with  $\alpha$  defining (non-)diffusive motion ( $\alpha = 0.5$  for diffusion) and  $\delta$  average lengths of single jumps

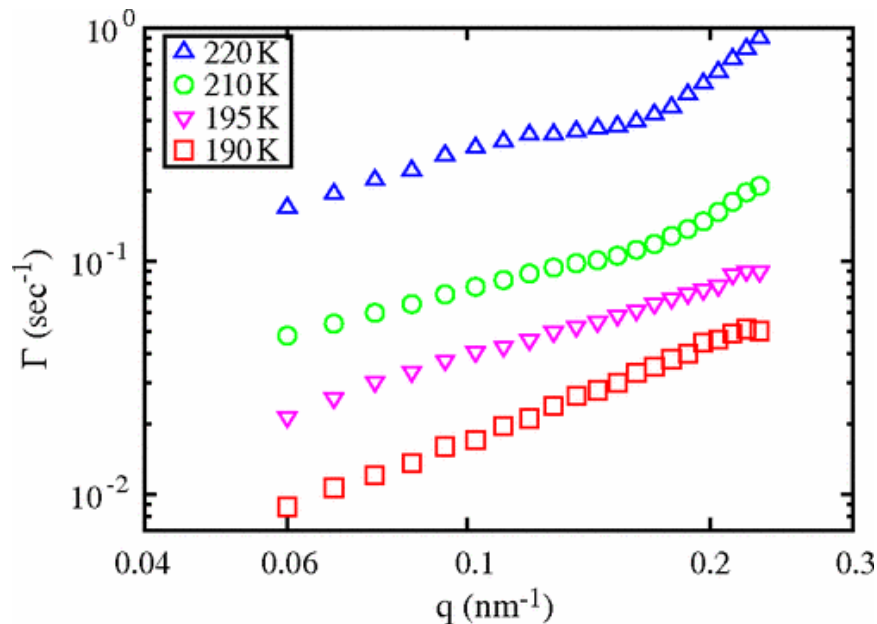


## Example 5: Microrheological glass transition studies on soft matter



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

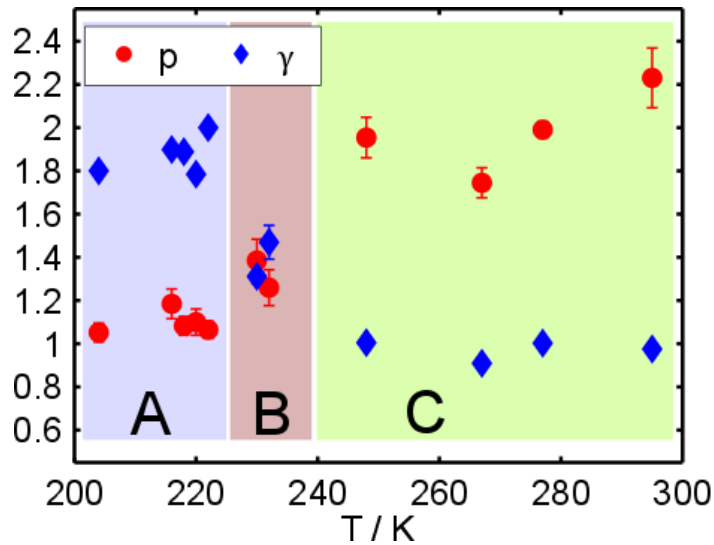
→ From diffusive to ballistic motion!



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

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

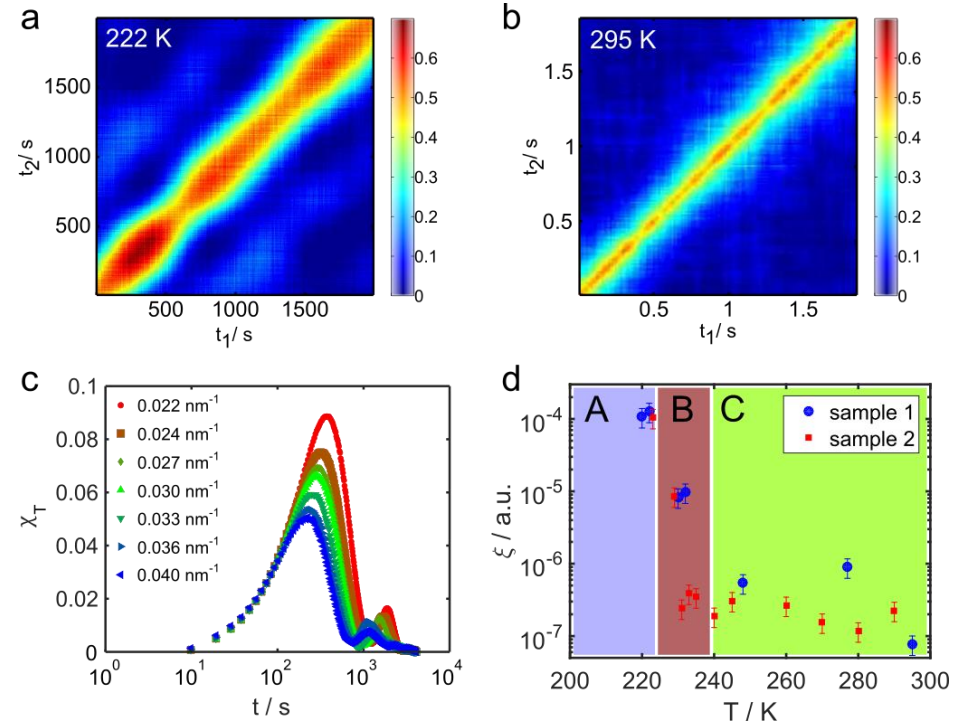
## Example 5: Microrheological glass transition studies on soft matter



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

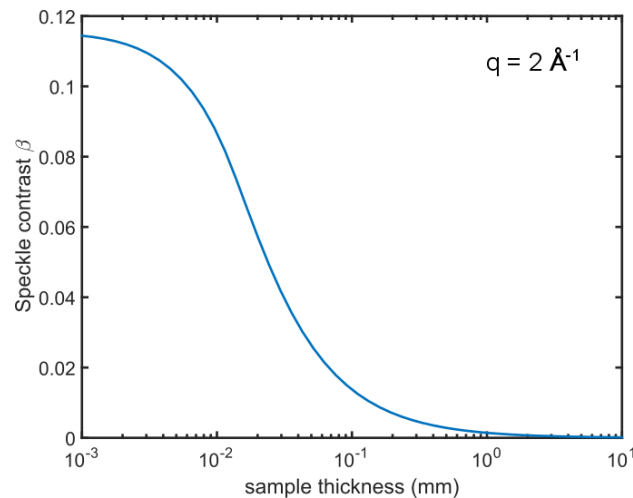
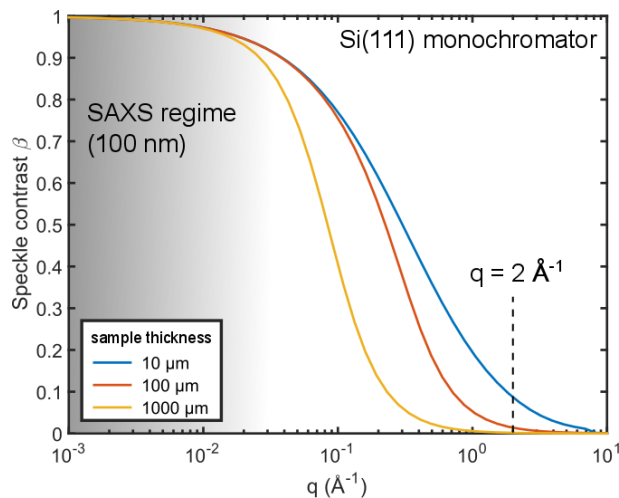
- Molecular dynamics: large  $q$
- In general coherence factor (= speckle contrast) as integral over coherence lengths  $\rightarrow$  lower value in large  $q$  XPCS

- $\beta = \beta_t \beta_l$  with correction factor (for beams with a Gaussian spectrum)

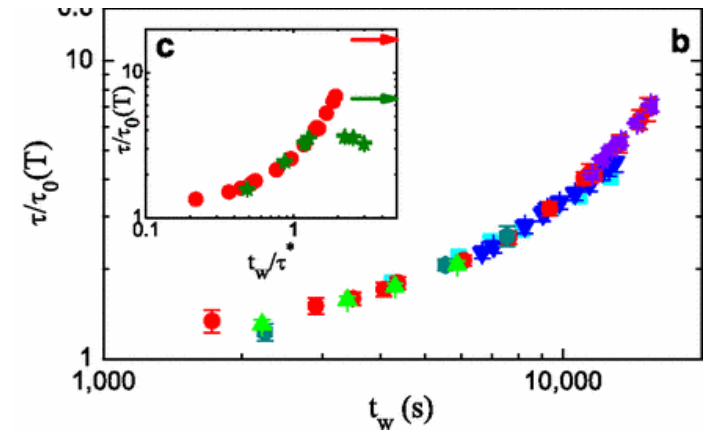
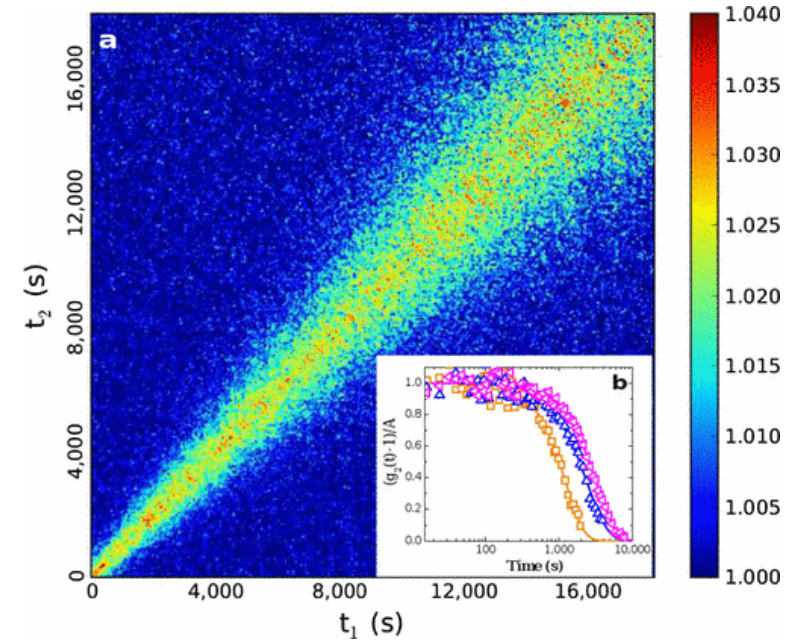
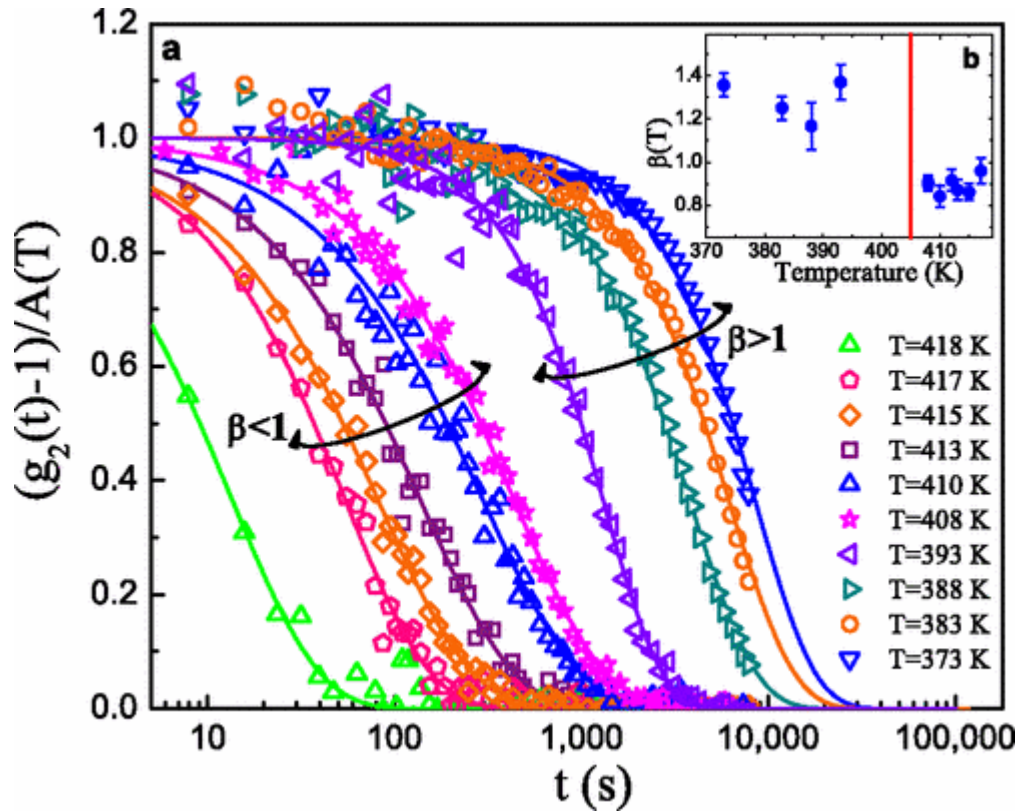
$$\beta_l =$$

$$\frac{2}{b^2 d^2} \int_0^b \int_0^d (b-x)(d-y) \exp\left[-\frac{x^2}{\xi_h^2}\right] [\exp(-2|Ax+By|) + \exp(-2|Ax-By|)]$$

- 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  $d$



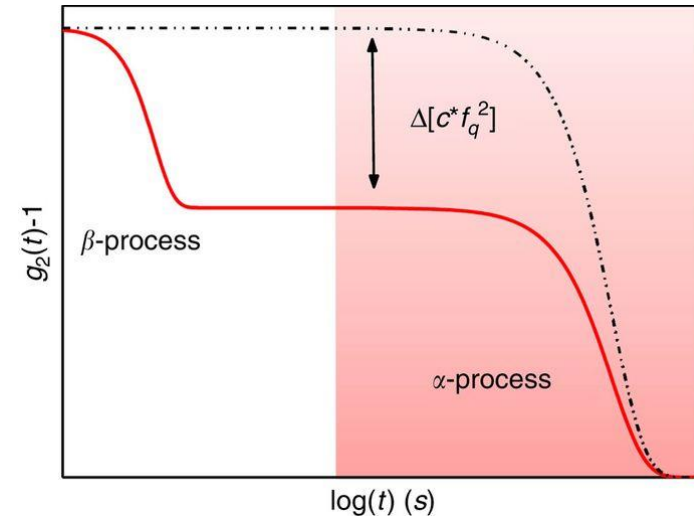
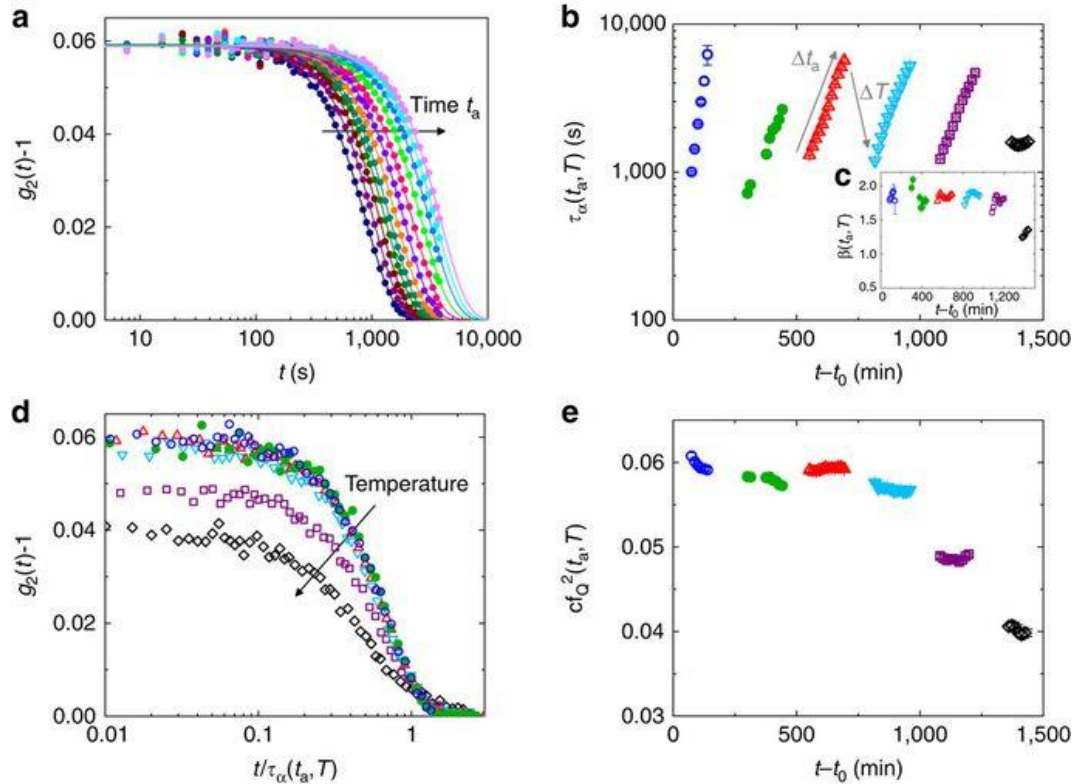
## Example 6: dynamics of metallic glasses



- Dynamics transition: stress relaxation below  $T_g$
- Aging

PRL 109, 165701 (2012)

## Example 6: dynamics of metallic glasses

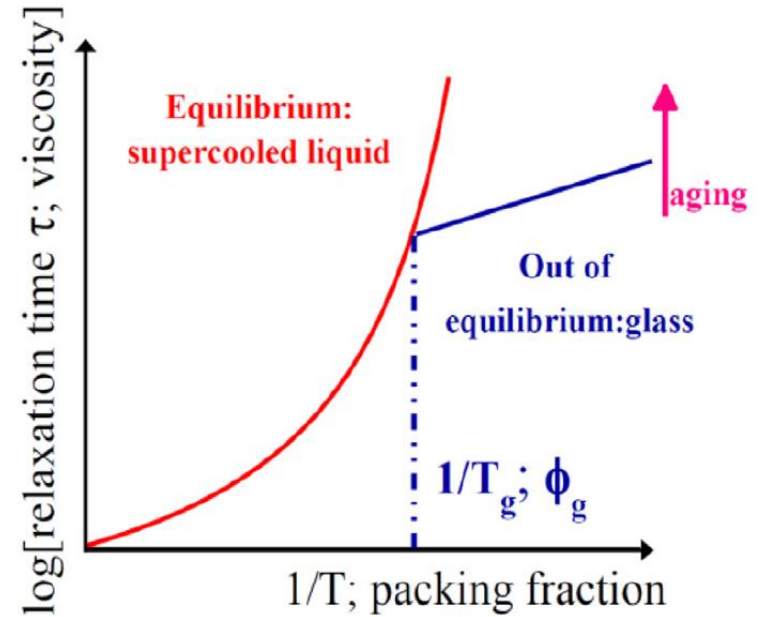
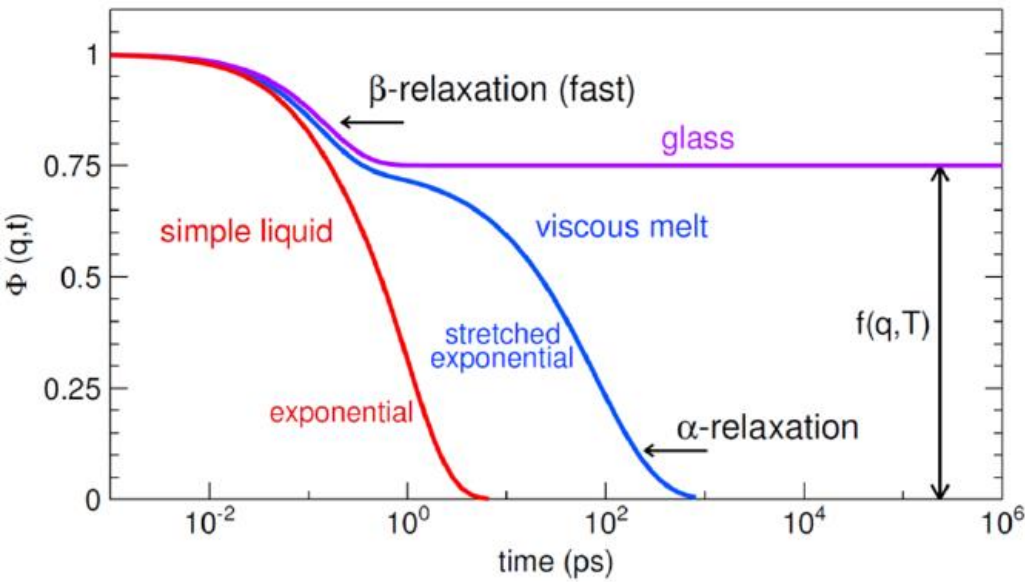


- Missing contrast: faster, non-accessible dynamics
- Aging

Nat. Commun. 7, 10344 (2016)



# Dynamics towards glass transition



JPCD 29, 503002 (2017)