Structure, Dynamics and Response of Liquids:

Time correlation functions and transport quantities

Walter Kob
Laboratoire des Colloïdes, Verres et Nanomatériaux
Université Montpellier 2

http://www.lcvn.univ-montp2.fr/kob

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Outline of the talk

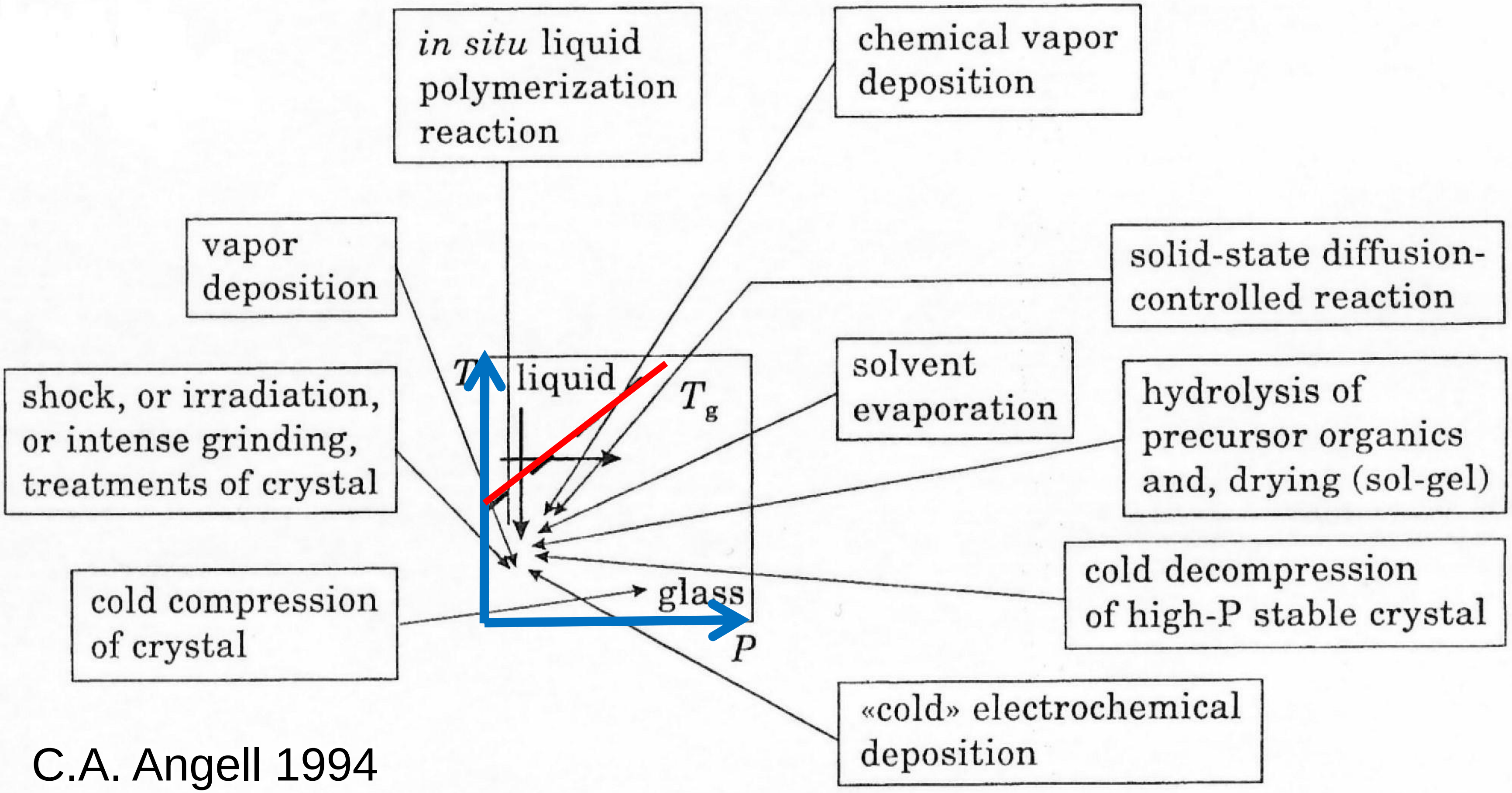
- Why discuss liquids?

- Characterizing the structure of liquids
    - radial distribution function
    - static structure factor
    - ...

- Characterizing the dynamics of liquids
    - mean squared displacement
    - diffusion constant
    - van Hove function
    - intermediate scattering function
    - susceptibilities
    - viscosity
    - Stokes-Einstein relation
    - rotational correlation functions

Why discuss liquids in this School?

- Recall: Glasses can be produced in many ways!



C.A. Angell 1994

However, in practice the most common route is to start with a liquid and to lower temperature (slowly) in order to stay in quasi-equilibrium

⇒ **One needs to understand the properties of the liquid**

Structure: Radial distribution function

- Consider a system of *N* identical classical particles; let ***r**$_j$(t)* be the position of particle *j* at time *t*

- Define the radial distribution function g(**r**) via

$$g(\boldsymbol{r}) = \frac{1}{N\rho}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\langle\delta(\boldsymbol{r}+\boldsymbol{r}_j-\boldsymbol{r}_i)\rangle$$

⇒ g(**r**) is the (non-normalized) probability that two particles are separated by a vector **r**

- For isotropic systems g(**r**) depends only on r = |**r**| ⇒ make a spherical integration of g(**r**) and define the pair correlation function g(r)

$$g(r) = \frac{1}{4\pi r^2}\frac{1}{N\rho}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\langle\delta(\boldsymbol{r} - |\boldsymbol{r}_j-\boldsymbol{r}_i|)\rangle$$

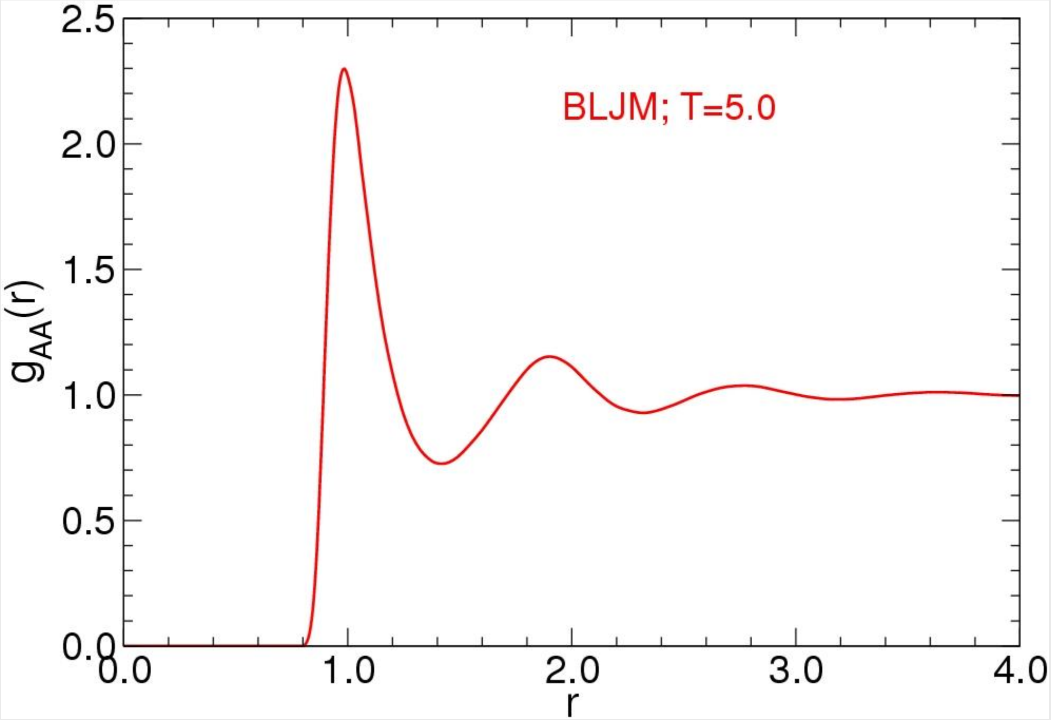
- g(r) can be measured in experiments on colloidal systems with confocal microscopy (if the particles are not too small)

- g(r) can be calculated within integral theories: Percus-Yevick approximation, hypernetted chain equation, ...

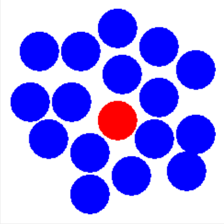
Structure: Radial distribution function: 2

- pair correlation function g(r)

$$g(r) = \frac{1}{4\pi r^2}\frac{1}{N\rho}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\langle\delta(\boldsymbol{r} - |\boldsymbol{r}_j - \boldsymbol{r}_i|)\rangle$$



- g(r) for a simple liquid (binary Lennard-Jones mixture)



Structure: Static structure factor

- g(r) is useful to characterize the local structure of the system; for intermediate and large scales the function is not very useful ⇒ define the static structure factor

$$S(\boldsymbol{q}) = \frac{1}{N}\langle \rho_{\boldsymbol{q}}\, \rho_{-\boldsymbol{q}} \rangle = \frac{1}{N}\sum_{j=1}^{N}\sum_{l=1}^{N}\langle \exp[-i\boldsymbol{q}\cdot(\boldsymbol{r}_j - \boldsymbol{r}_l)]\rangle$$

- Using the definition of g(**r**), $g(\boldsymbol{r}) = \frac{1}{N\rho}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\langle \delta(\boldsymbol{r} + \boldsymbol{r}_j - \boldsymbol{r}_i)\rangle$, one obtains

$$S(\boldsymbol{q}) = 1 + \rho \int \exp[-i\boldsymbol{q}\cdot\boldsymbol{R}]\, g(\boldsymbol{R})\, d\boldsymbol{R}$$

- For isotropic systems S(**q**) depends only on the module q=|**q**| :

$$S(q) = 1 + \rho \int_0^\infty g(R)\frac{\sin(qR)}{qR}\, 4\pi R^2 dR$$

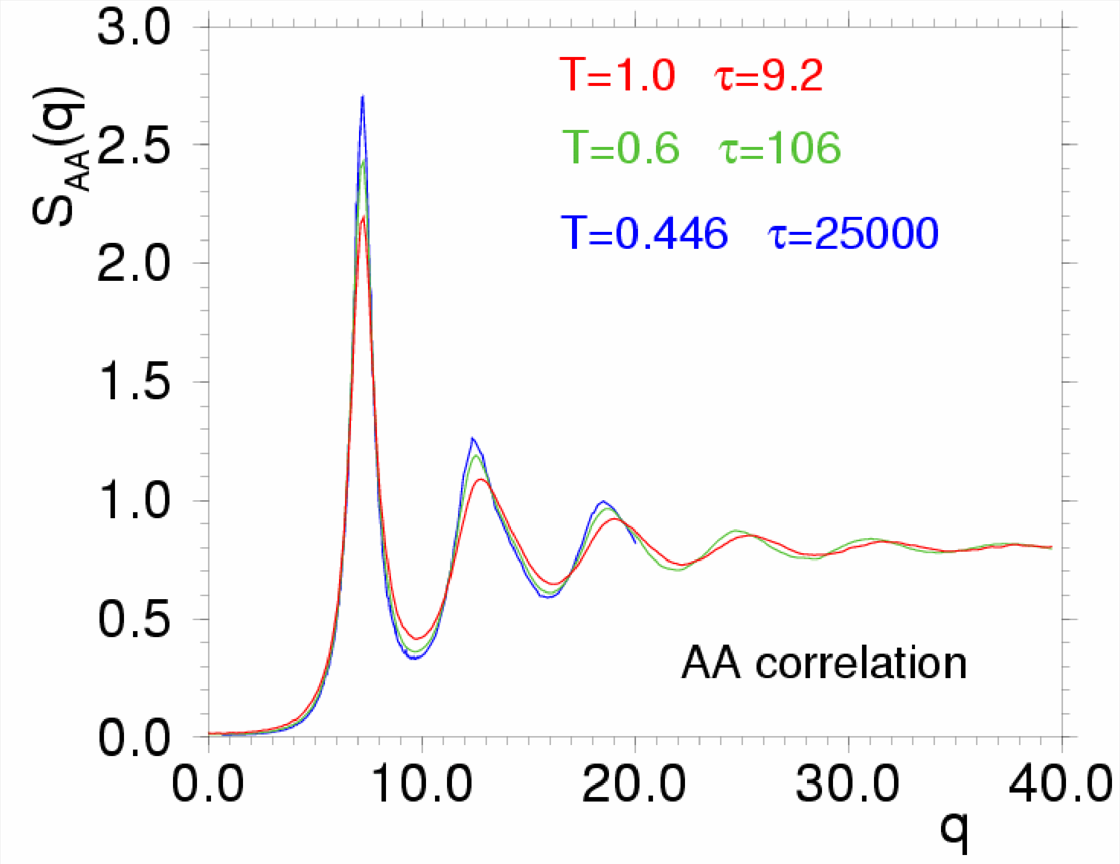
- Since S(q) is related to the Fourier transform of g(r) one has the relation that g(r) is the FT of S(q) :

$$g(R) = 1 + \frac{1}{2\pi^2\rho}\int_0^\infty [S(q) - 1]\frac{\sin qR}{qR} q^2 dk$$

BUT beware of g(r) obtained from FT of S(q)!

Structure: Static structure factor: 2

- S(**q**) can be measured in neutron and X-ray scattering experiments since S(**q**) is proportional to the scattering intensity of the "particles" that have been scattered by a wave-vector $\mathbf{q}=\mathbf{q}_{\text{inital}}-\mathbf{q}_{\text{final}}$



- S(q) of a simple liquid (binary Lennard-Jones mixture)
- NB: The limit S(q→0) is related to the isothermal compressibility:

$$S(q \to 0) = \rho k_B T \kappa_T$$

with

$$\kappa_T \equiv -(1/V)\,(\partial V/\partial p)_T$$

Structure: Multi-component systems

- Consider a system with ν components; number of particles is N_1, N_2,... N_ν
- The generalization of the radial distribution function is

$$g_{\alpha\alpha}(\vec{r}) = \frac{N}{\rho N_\alpha^2} \sum_{i}^{N_\alpha} \sum_{j(\neq i)}^{N_\alpha} \langle \delta(\vec{r} + \vec{r}_i - \vec{r}_j) \rangle$$

$\alpha \in \{1,\dots\nu\}$

$$g_{\alpha\beta}(\vec{r}) = \frac{N}{\rho N_\alpha N_\beta} \sum_{i}^{N_\alpha} \sum_{j}^{N_\beta} \langle \delta(\vec{r} + \vec{r}_i - \vec{r}_j) \rangle \quad \text{for} \quad \alpha \neq \beta$$

- Similarly one defines the “partial structure factors” $S_{\alpha\beta}(\boldsymbol{q})$:

$$S_{\alpha\beta}(\boldsymbol{q}) = \frac{f_{\alpha\beta}}{N} \sum_{j=1}^{N_\alpha} \sum_{l=1}^{N_\beta} \langle \exp[-i\boldsymbol{q} \cdot (\vec{r}_j - \vec{r}_l)] \rangle$$

$f_{\alpha\alpha}=1$; $f_{\alpha\beta}=1/2$ for $\alpha \neq \beta$

Structure: Multi-component systems: 2

- Experiments do usually not allow to measure the partial structure factors directly; within a neutron scattering experiments one measures

$$S^{\mathrm{neu}}(\boldsymbol{q}) = \frac{N}{\sum_{\alpha} N_\alpha b_\alpha^2} \sum_{\alpha\beta} b_\alpha b_\beta S_{\alpha\beta}(\boldsymbol{q})$$

where the constant b_α is the "neutron scattering cross section" for an element of type α (see www for values); N.B. b_α depends on the isotope

Similarly one measures in a X-ray diffraction experiments the quantity

$$S^{\mathrm{xr}}(\boldsymbol{q}) = \frac{N}{\sum_{\alpha} N_\alpha x_\alpha^2(q)} \sum_{\alpha\beta} x_\alpha(q) x_\beta(q) S_{\alpha\beta}(\boldsymbol{q})$$

where $x_\alpha(q)$ is a function that can be found on the www

NB: For one component systems we have $S^{neu}(q)=S^{xr}(q)=S(q)$

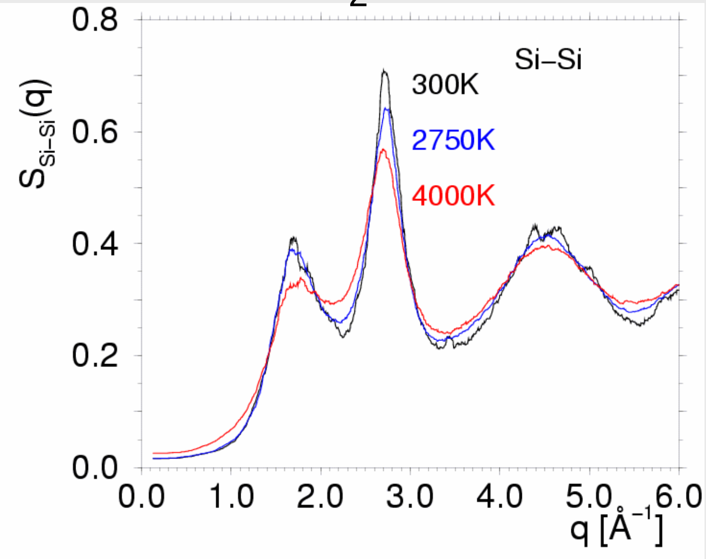
Structure: Multi-component systems: 3

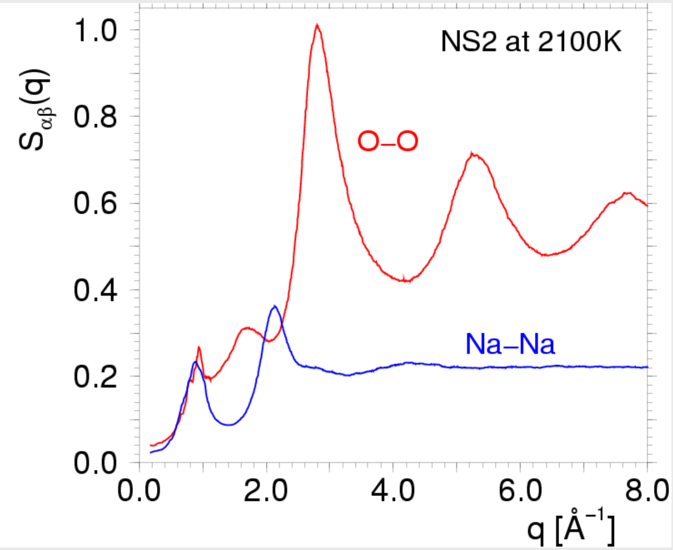
- Compare $S^{neu}(q)$ with $S(q)$ for different glass-formers

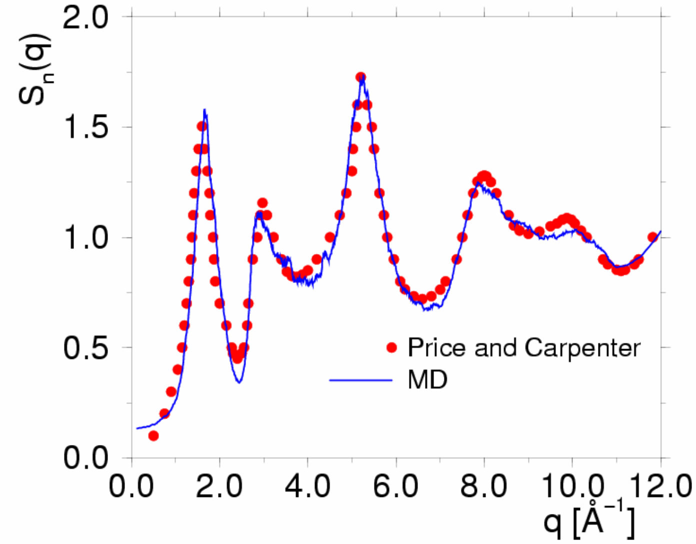
$$S^{\mathrm{neu}}(\boldsymbol{q}) = \frac{N}{\sum_{\alpha} N_\alpha b_\alpha^2} \sum_{\alpha\beta} b_\alpha b_\beta S_{\alpha\beta}(\boldsymbol{q})$$

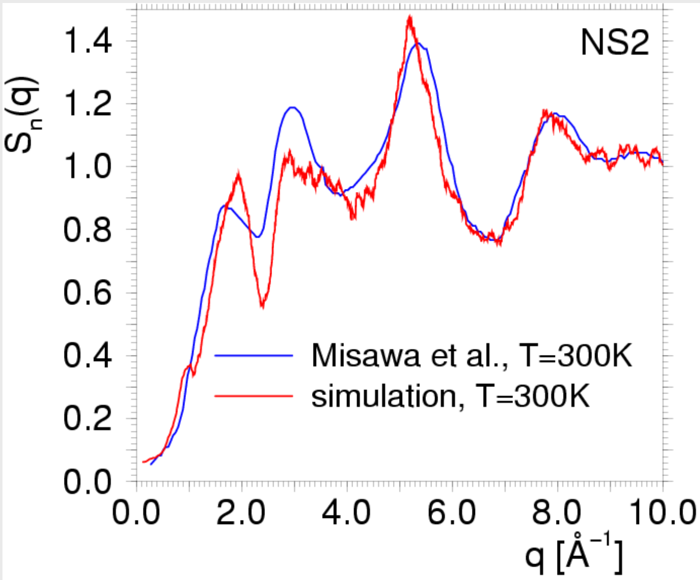
SiO_2

$Na_2O\text{-}2(SiO_2)$



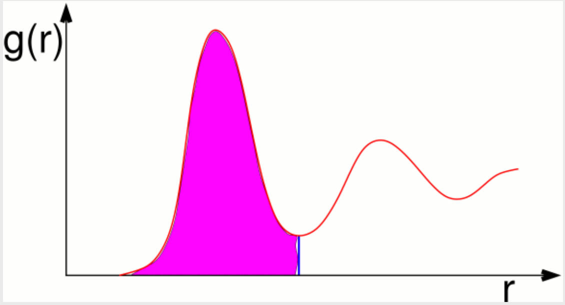






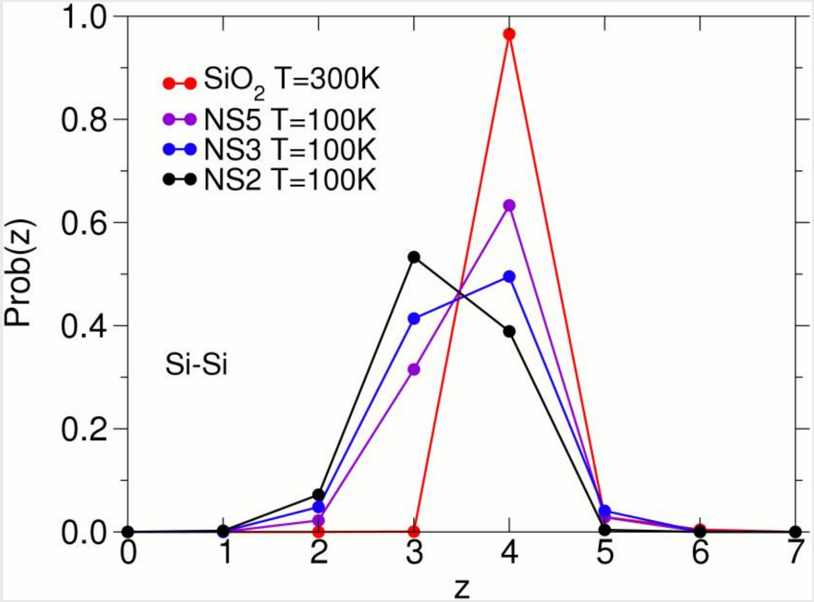
Structure: Coordination number

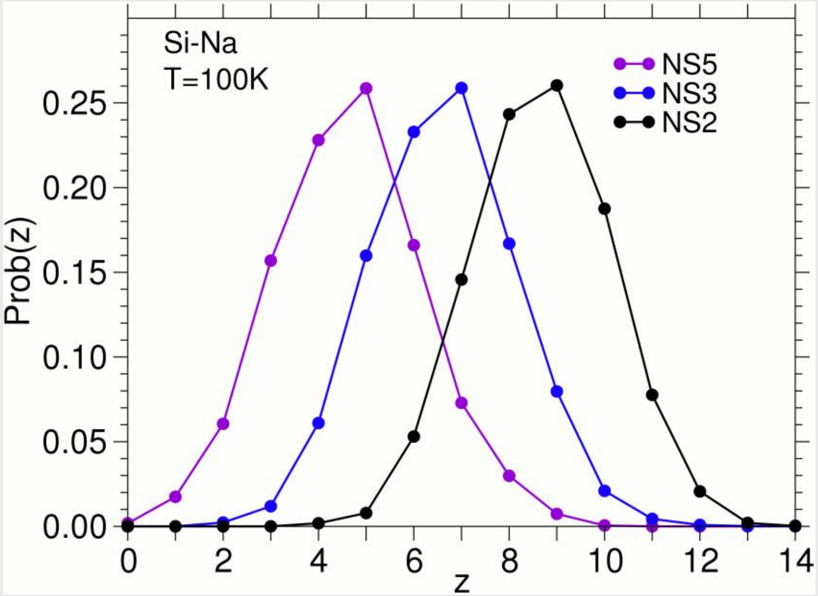
- The integral $\int_0^R 4\pi r^2 g(r)\,dr$ gives the number of atoms up to distance *R*



- First minimum in $g_{\alpha\beta}(r) \Rightarrow$ can be used to defined nearest neighbor $\Rightarrow$ coordination number (NB: can be measured by NMR)

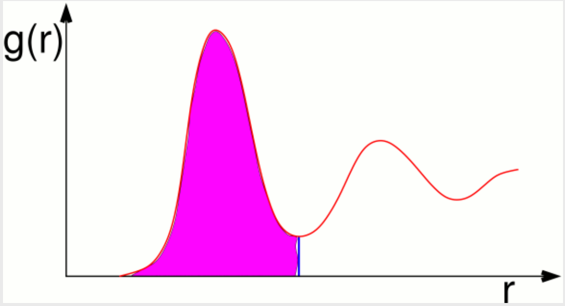
Coordination numbers in Na_2O-x(SiO_2) = NSx



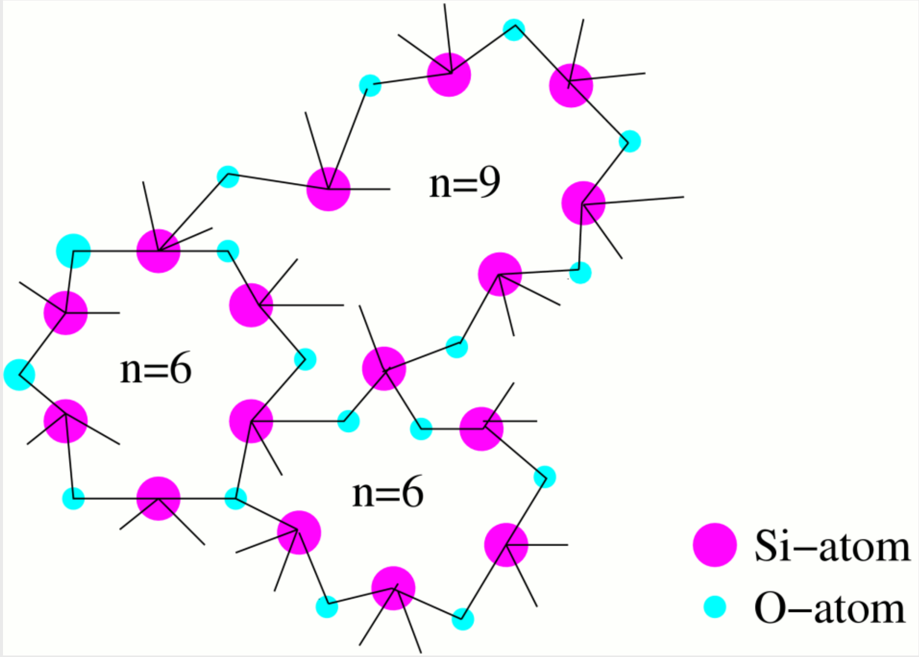


Structure: Rings

- In covalently bonded atoms the $g_{\alpha\beta}(r)$ has often a very deep first minimum $\Rightarrow$ definition of nearest neighbors is very clear



$\Rightarrow$ It makes sense to look at the second, third nearest neighbors $\Rightarrow$ ring statistics



- What is the probability that an atom is member of a ring of size n?

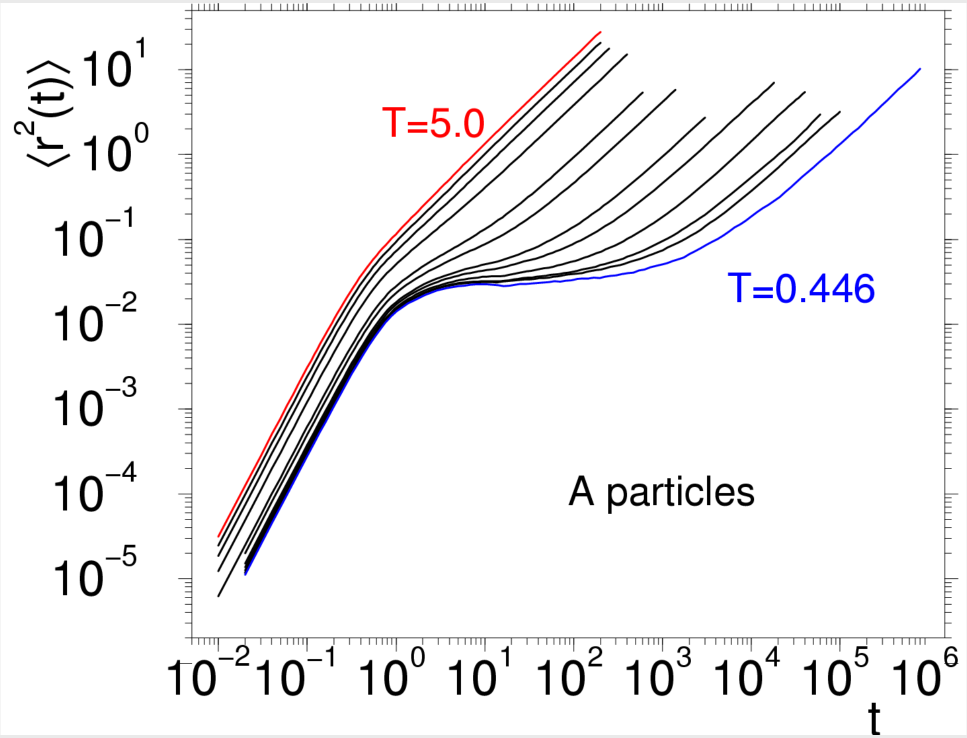
$\Rightarrow$ information on the structure on intermediate length scale

Dynamics: The mean squared displacement

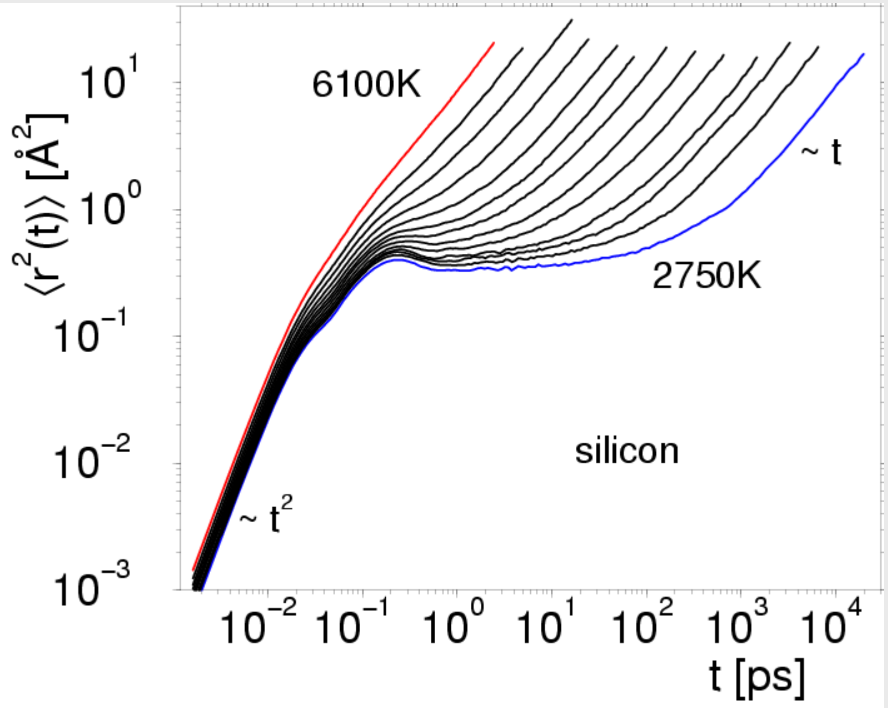
- Mean squared displacement is defined as

$$\langle r^2(t)\rangle = \langle|\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2\rangle$$

T-dependence of MSD for a simple liquid



T-dependence of MSD for a network-forming liquid: SiO_2

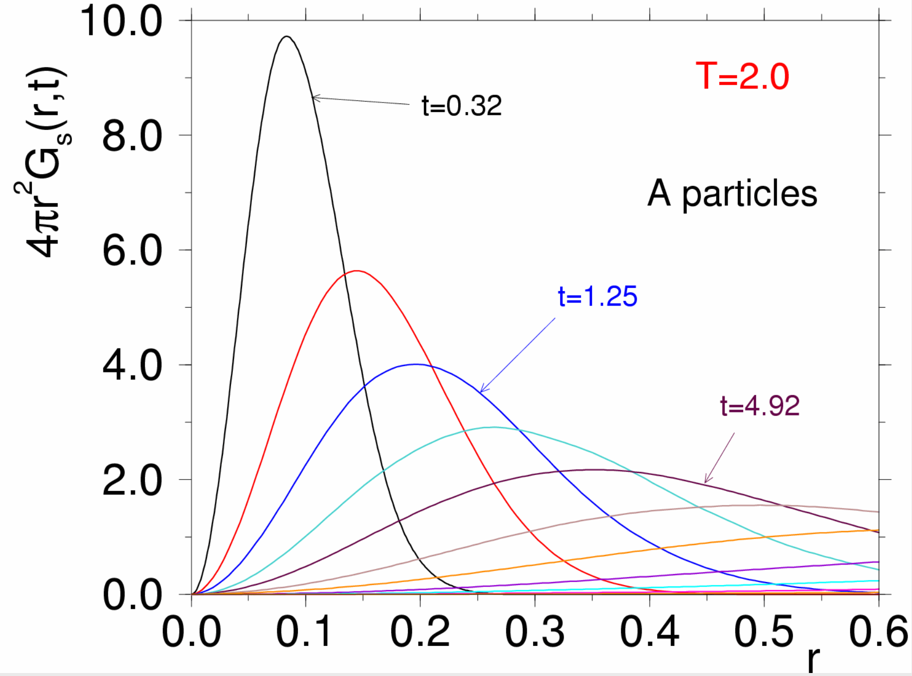


The van Hove correlation function (self part)

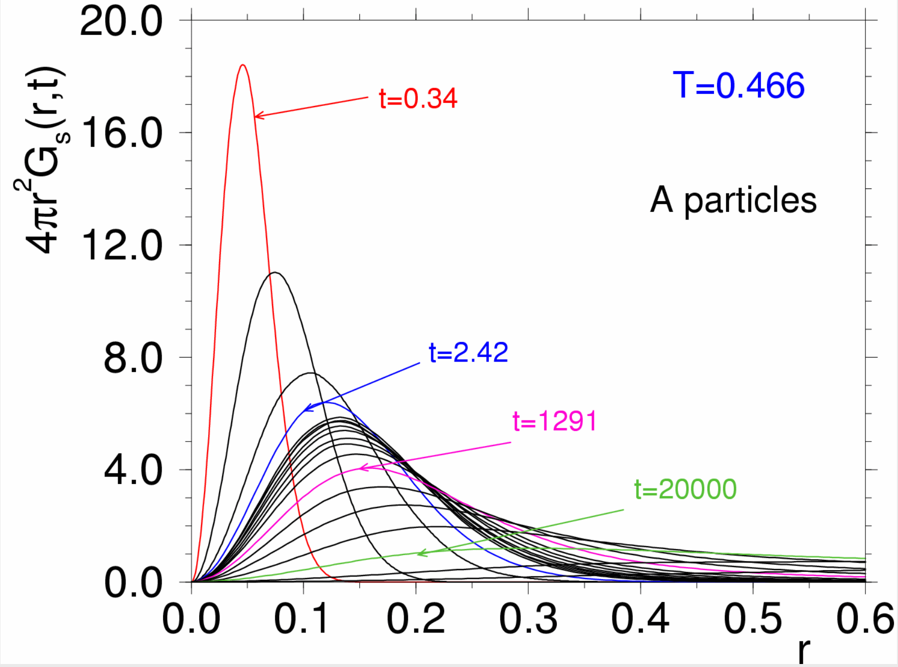
- Self part of van Hove correlation function $G_s(r,t)$ = probability that a particle has moved a distance r in time t:

$$G_s(r,t) = N^{-1} \sum_i \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_i(0)|) \rangle$$

Self part of van Hove correlation function for a simple liquid



high T: no cage effect



low T: cage effect

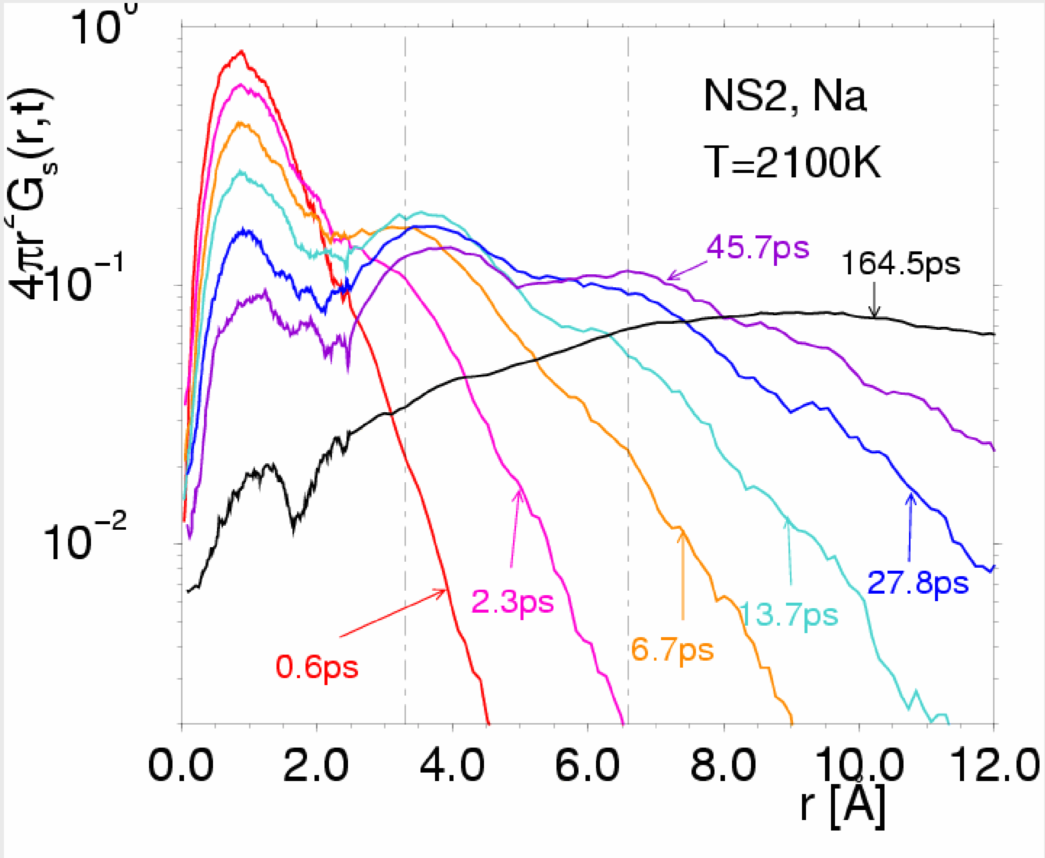
N.B. cage is quite small!

The van Hove correlation function (self part): 2

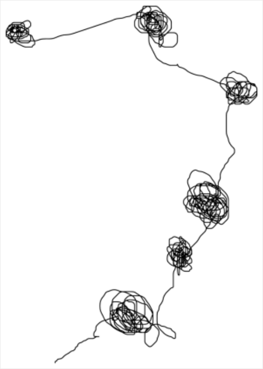
- Self part of van Hove correlation function $G_s(r,t)$ = probability that a particle has moved a distance r in time t:

$$G_s(r,t) = N^{-1} \sum_i \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_i(0)|) \rangle$$

$G_s(r,t)$ for a ion-conducting liquid: Na_2O-x(SiO_2)



- low T: rattling and hopping motion on the length scale of nearest neighbors



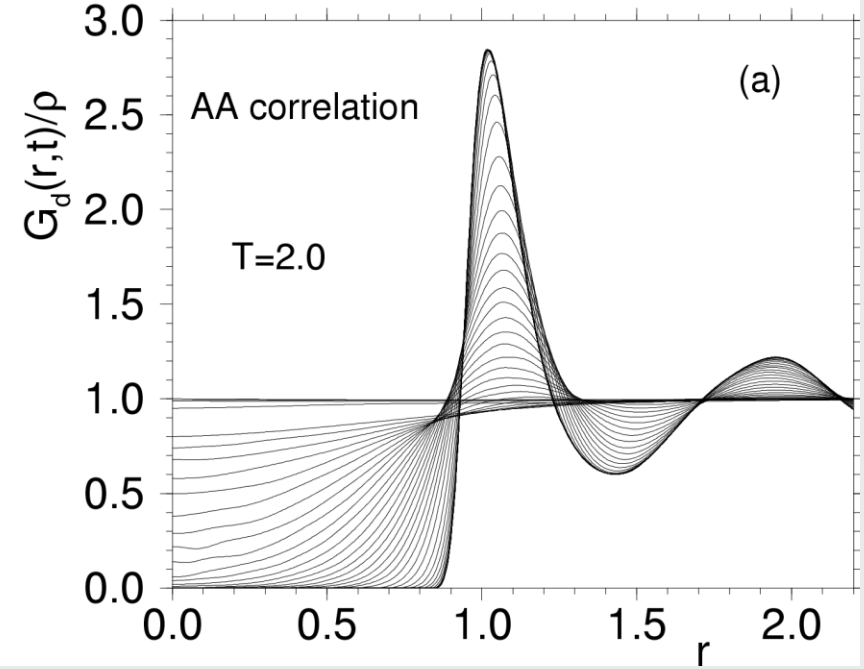
- dynamics of Si and O show only a very weak signature of hopping

The van Hove correlation function (distinct part)

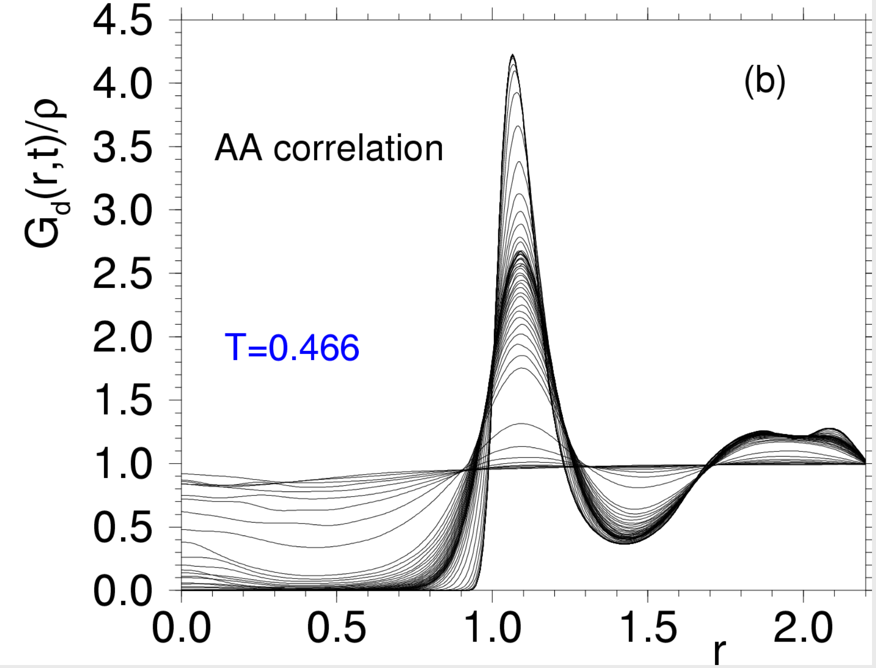
- Distinct part of van Hove correlation function $G_d(r,t) \propto$ probability to find at time t a different particle at a distance r from a place at which at time t=0 there was a particle:

$$G_d(r,t) = N^{-1} \sum_i \sum_{j\neq i} \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_j(0)|) \rangle \quad \text{N.B.} \quad G_d(r,0) = g(r)$$

Distinct van Hove correlation function for a simple liquid



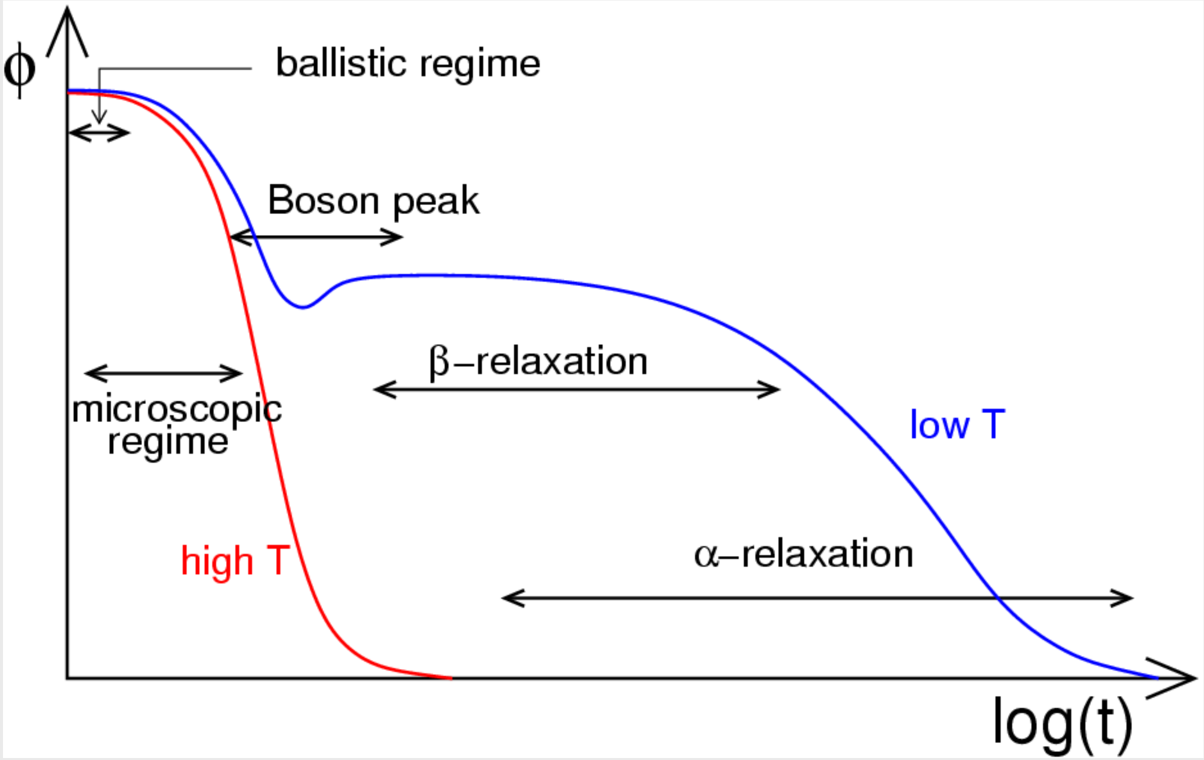
high T: correlation hole at r=0 is quickly filled up

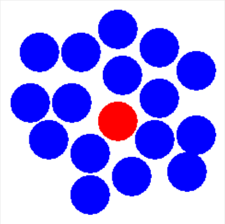


low T: correlation hole at r = 0 survives for a long time (note small peak at r=0!)

Time correlation functions

- Form of a typical time correlation function $\phi(t)$ of a glass-forming system (e.g., intermediate scattering function $F_s(q,t) = \langle N^{-1} \sum_j \exp(i\, q \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)))\rangle$,...)





- Short times: Microscopic dynamics
- Intermediate times: Motion in the cage (=β-relaxation)
- Long times: Particles are leaving their cage; correlator is stretched and can be fitted well by Kohlrausch-Williams-Watts law: $\exp(-(t/\tau)^{\beta})$ with $\beta < 1.0$

$\Rightarrow$ **Dynamical heterogeneities, i.e. complex relaxation in space/time**

(see talks of Miyazaki and Berthier)

Time correlation functions: 2

- At every time there are equilibrium fluctuations in the local density distribution; how do these fluctuations relax?
- Consider the incoherent intermediate scattering function $F_s(q,t)$

$$F_s(q,t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp\left(i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))\right)\right\rangle$$

N.B.

1) $F_s(q,t)$ is the space FT of the self part of the van Hove function $G_s(r,t) = N^{-1} \sum_i \langle\, \delta(r - |\mathbf{r}_i(t)-\mathbf{r}_i(0)|)\, \rangle$

2) $F_s(q,t)$ can be measured in incoherent *inelastic* neutron- or x-ray scattering experiments: $\mathbf{q}=\mathbf{q}_{\text{inital}} - \mathbf{q}_{\text{final}}$; t from the time Fourier transform of the energy transfer

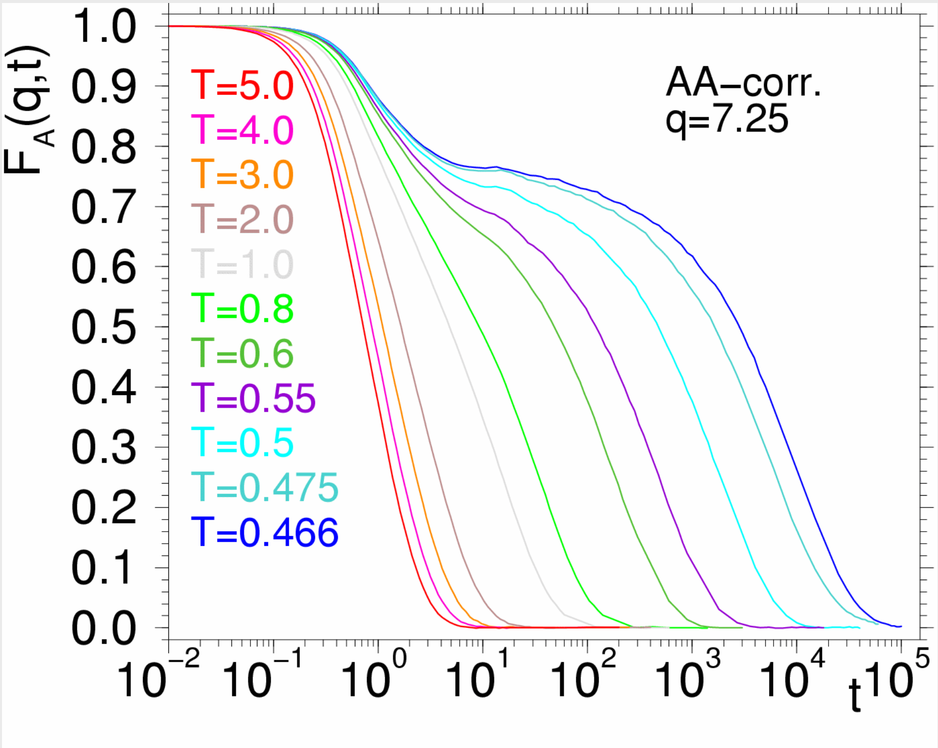
3) Area under $F_s(q,t)$ can be used to define a relaxation time τ

4) $F_s(q,t)$ characterizes the *mean* (space and time) relaxation of the system; if one looks at fluctuations of this quantity in space one has access to spacial dynamical heterogeneities ⇒ talk Berthier

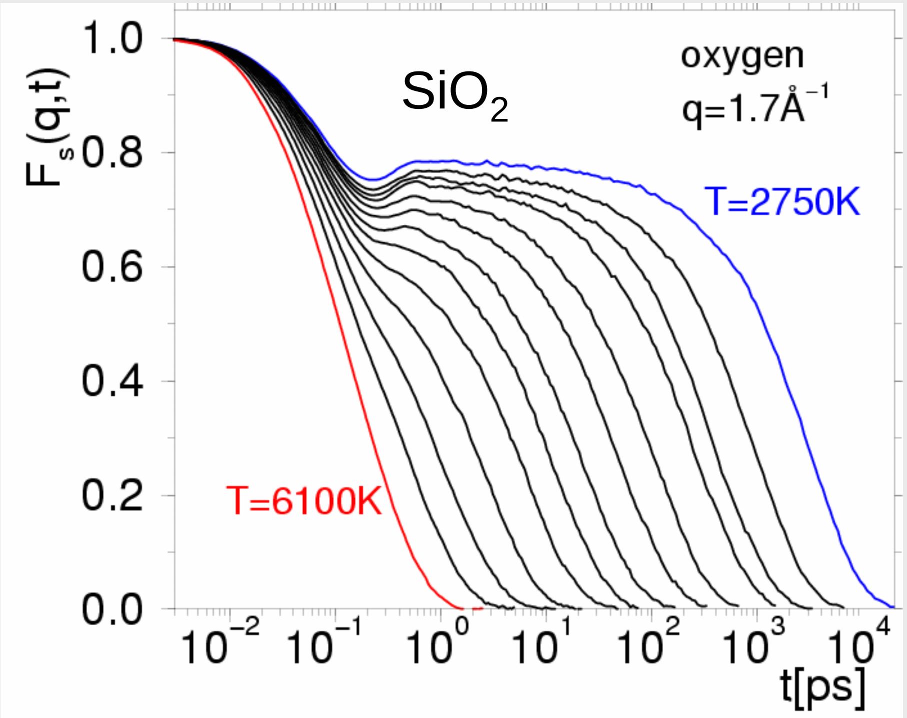
Time correlation functions: 3

$$F_s(q,t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp\left(i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))\right)\right\rangle$$

$F_s(q,t)$ for a simple liquid



$F_s(q,t)$ for a network forming liquid



- Intermediate times: viscoelastic effects, Boson peak

NB: we are above the melting temperature T_m = 2000K !

⇒ slow dynamics has nothing to do with supercooling

Time correlation functions: 4

- $F_s(q,t)$ characterizes how a density fluctuation of a tagged particle relaxes. Similarly one can study the relaxation of a density fluctuation relative to a given particle, i.e. a collective quantity

$\Rightarrow$ define the coherent intermediate scattering function F(q,t):

$$F(q,t) = \frac{1}{N} \sum_{k=1}^{N} \sum_{j=1}^{N} \langle \exp\left(i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_k(0))\right) \rangle$$

N.B.

1) F(q,t) is the space FT of the (distinct) van Hove function $G_d(r,t) = N^{-1} \sum_i \sum_{j\neq i} \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_j(0)|) \rangle$

2) F(q,t) can be measured in coherent *inelastic* neutron- or x-ray scattering experiments: $\mathbf{q} = \mathbf{q}_{\mathrm{inital}} - \mathbf{q}_{\mathrm{final}}$; t from the time Fourier transform of the energy transfer

3) Fluctuations of F(q,t) $\Rightarrow$ dynamical heterogeneities

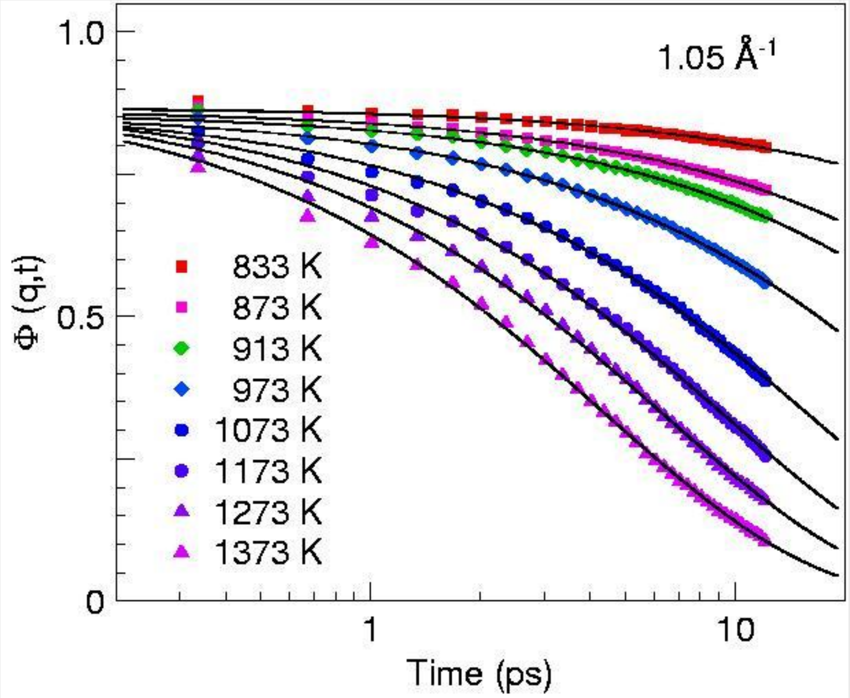
4) Very often $F_s(q,t)$ and F(q,t) are quite similar (similar relaxation times, plateau height,....)

Time correlation functions: 5

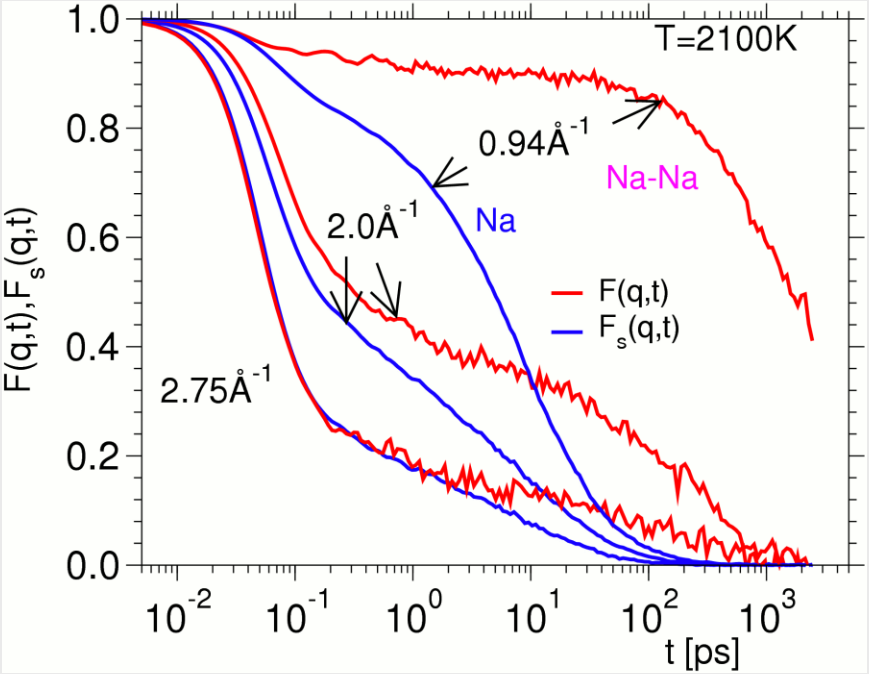
$$F_s(q,t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp\left(i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))\right)\right\rangle$$

$$F(q,t) = \frac{1}{N}\sum_{k=1}^{N}\sum_{j=1}^{N}\langle \exp\left(i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_k(0))\right)\rangle$$

State of the art n-scattering results of Ni in PdNiCuP Meyer *et al*. 2002



Na_2O-$2(SiO_2)$



N.B. Usually n-scattering does not give results in the time domain but in the frequency domain ⇒ one has to Fourier transform the data

In ion-conducting glass-formers the coherent and incoherent functions can be very different

Correlation functions in the frequency domain

- Many experimental techniques do not give information in the time domain but only in the frequency domain (spectroscopy)

$\Rightarrow$ what one measures is $\phi'(\omega)$ and $\phi''(\omega)$, the real and imaginary part of the time-Fourier transform of a time correlation function $\phi(t)$

or

$\chi'(\omega)$ and $\chi''(\omega)$, the real and imaginary part of the dynamic susceptibility

- Fluctuation – Dissipation-Theorem: Important connection between $\phi''(\omega)$ and $\chi''(\omega)$:

$$\chi''(\omega) = \omega\, \phi''(\omega) /(k_B T)$$

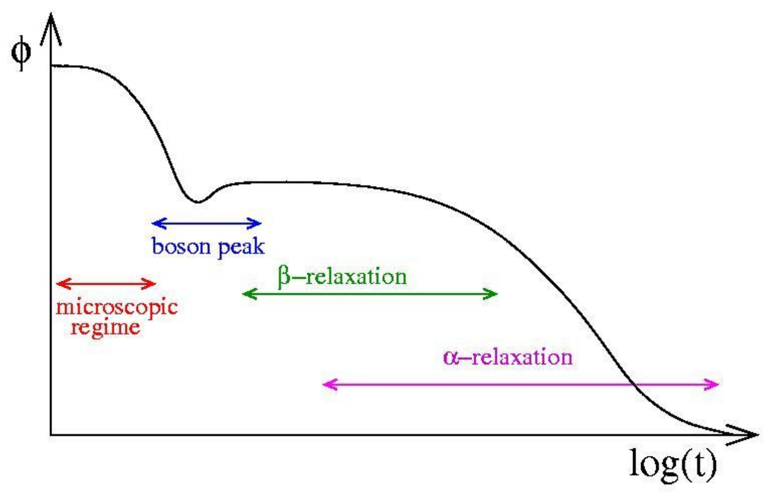
NB: The FDT is valid only in thermal equilibrium! In out of equilibrium situations (e.g. in a glass) one can measure $\chi''(\omega)$ and $\phi''(\omega)$ in order to define an “effective temperature” of the system (see talks by Kurchan and Franz)

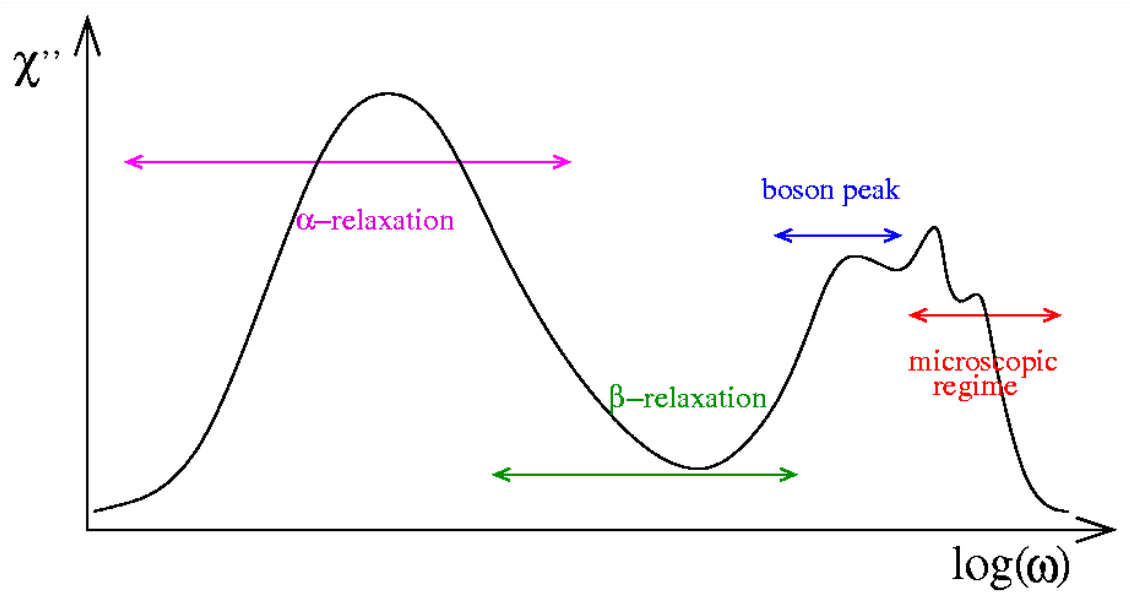
Correlation functions in the frequency domain: 2

- $\phi''(\omega)$: imaginary part of the time-Fourier transform of a time correlation function

  $\chi''(\omega)$: imaginary part of the dynamic susceptibility

  $$\chi''(\omega) = \omega\, \phi''(\omega) / (k_B T)$$





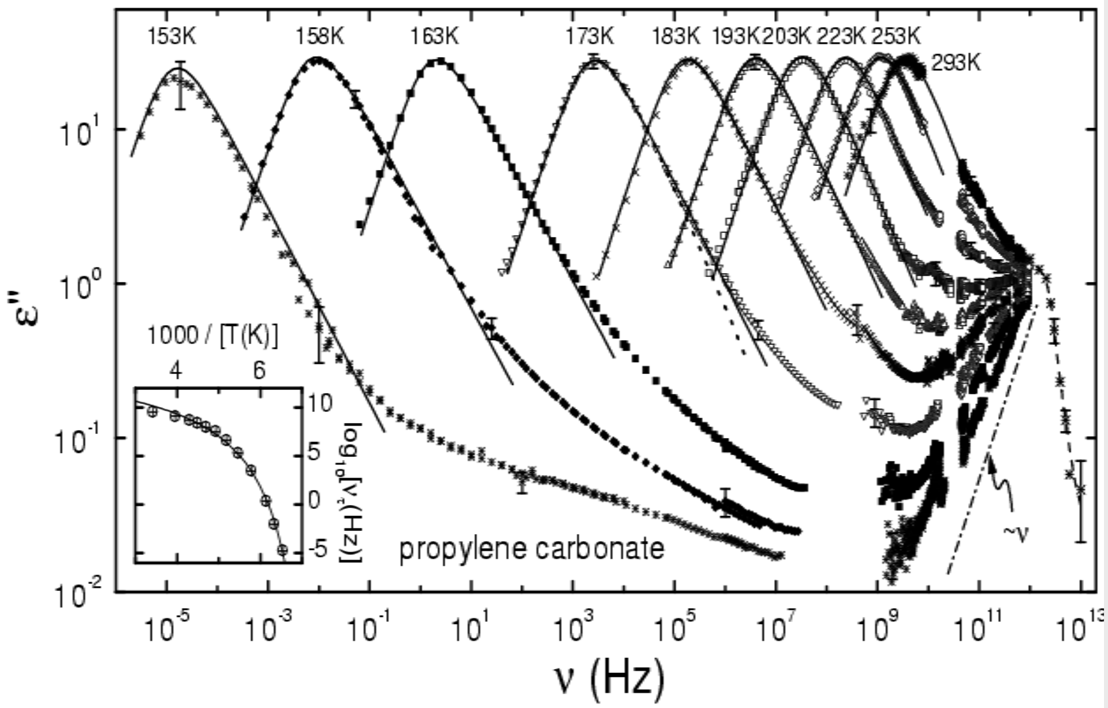
- The various peaks correspond to the different processes seen in the time domain

Correlation functions in the frequency domain: 3

- One of the best techniques to probe the system in a large frequency and temperature range is dielectric measurements

Lunkenheimer *et al.* (2001)

- Problem: what exactly is measured??



Brownian Dynamics

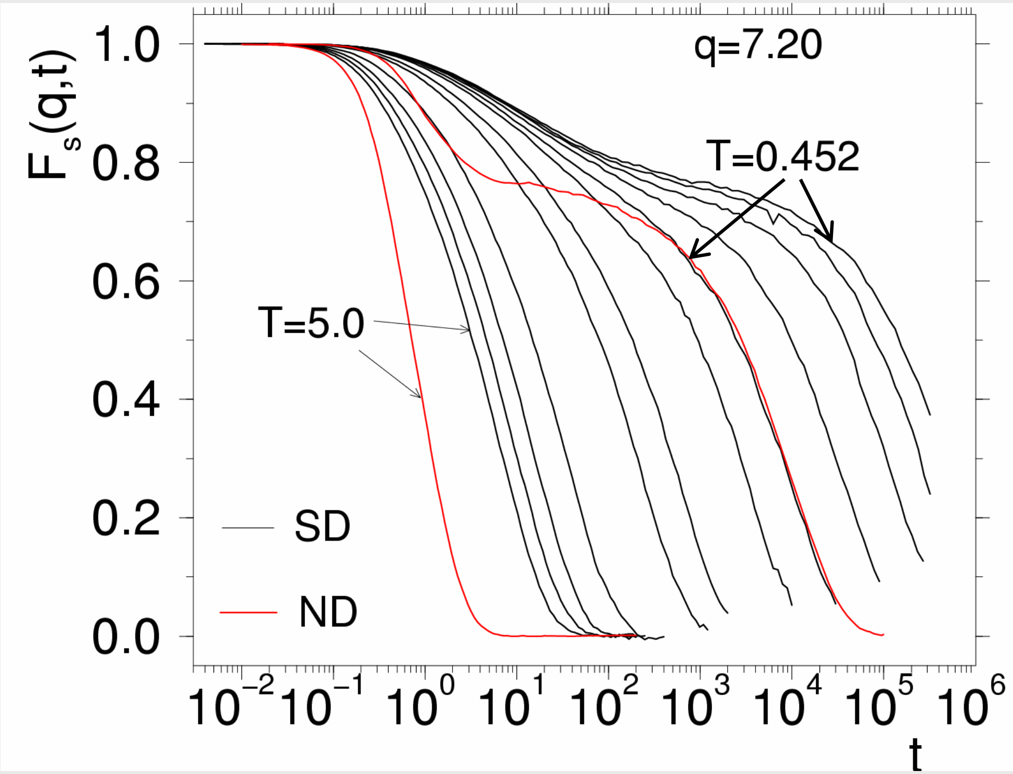
- So far we have discussed Newtonian dynamics which is appropriate for atomic systems. But in colloidal systems the relevant microscopic dynamics is a Brownian dynamics (see talk Sciortino)

$$m\ddot{\mathbf{r}}_i + \nabla_i \sum_j V_{ij} = -\zeta \dot{\mathbf{r}}_i + \mathbf{F}_{B,i}$$

$$\langle \mathbf{F}_{B,i} \rangle = 0$$

$$\langle \mathbf{F}_{B,i}(t) \cdot \mathbf{F}_{B,j}(t') \rangle = 6 k_B T \zeta \delta_{ij} \delta(t - t')$$

Compare the self intermediate scattering function $F_s(q,t)$ of the ND with the one from the SD for a simple liquid



- shape of α- relaxation is independent of microscopic dynamics
- early β- relaxation depends strongly on microscopic dynamics
- SD is much slower than ND

Transport coefficients

- From the mean squared displacement $\langle r^2(t)\rangle = \langle|\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2\rangle$ one can easily obtain the tracer diffusion constant D:

$$D = \lim_{t \to \infty} \langle r^2(t)\rangle / 6t$$ Einstein relation

- From the Green-Kubo relation between stress and viscosity one can obtain the viscosity η:

$$\eta = \frac{1}{k_B T V}\int_0^\infty dt \langle \dot{A}_{\alpha\beta}(t)\dot{A}_{\alpha\beta}(0)\rangle \quad \text{with} \quad \dot{A}_{\alpha\beta} = \sum_{i=1}^{N} m_i v_i^\alpha v_i^\beta + \sum_{i=1}^{N}\sum_{j>i}^{N} F_{ij}^\alpha r_{ij}^\beta \quad \alpha \neq \beta.$$

Recall: Connection between the diffusion constant D of a sphere with radius R that is in a liquid with viscosity η:

$$D = k_B T/(6 \eta R)$$ Stokes-Einstein relation

(NB: Sometime η is replaced by the relaxation time τ)

However, SE is only valid for a macroscopic sphere and not an object of the size of an atom!

Molecules

- Many liquids have not atoms as relevant particles but are formed by molecules; therefore one can consider their rotational degrees of freedom

Let $\mathbf{u}_j$ be a vector that is fixed on the molecule j; One defines the rotational correlation functions

$$C_l(t) = N^{-1} \sum_{i,j} \langle P_l(u_i(t) \cdot u_j(0)) \rangle$$

P_l is the Legendre polynomial of order l

l=1: dielectric experiments

l=2: light scattering experiments

NB: 1)One can also define a self-part: $C_l^s(t) = N^{-1} \sum_i \langle P_l(u_i(t) \cdot u_i(0)) \rangle$

2) Further generalizations: q-dependence of these correlation functions

3) For a macroscopic object one has the Debye-Stokes-Einstein relation between the rotational diffusion constant and the viscosity (or the relaxation time)

Summary

- Structure:
  - g(r) for short distances
  - S(q) for intermediate and larger distances
  - coordination number, angle distributions, ring statistics for characterizing the structure on intermediate length scale
- Dynamics
  - mean squared displacement $\Rightarrow$ diffusion constant
  - van Hove function
  - intermediate scattering function $\Rightarrow$ relaxation times τ
  - susceptibilities
  - orientational correlation functions