Structure, Dynamics and Response of Liquids: 
Time correlation functions and transport quantities

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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!

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

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

$\Rightarrow g(r)$ is the (non-normalized) probability that two particles are separated by a vector $r$

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

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

- $g(r)$ 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 $g(r)$

\[
g(r) = \frac{1}{4\pi r^2} \frac{1}{N \rho} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \langle \delta(r - |r_j - r_i|) \rangle
\]

- $g(r)$ 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 $\Rightarrow$ define the static structure factor

$$S(q) = \frac{1}{N} \langle \rho \mathbf{q} \cdot \mathbf{r} \rangle = \frac{1}{N} \sum_{j=1}^{N} \sum_{i=1}^{N} \langle \exp[-i \mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \rangle$$

- Using the definition of $g(r)$, one obtains

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

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

- For **isotropic systems** $S(q)$ depends only on the module $q = |\mathbf{q}|$

$$S(q) = 1 + \rho \int_{0}^{\infty} g(R) \frac{\sin(qR)}{qR} 4\pi R^2 dR$$

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

$$g(R) = 1 + \frac{1}{2\pi^2 \rho} \int_{0}^{\infty} [S(q) - 1] \frac{\sin qR}{qR} q^2 dq$$

**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 $q = q_{\text{initial}} - q_{\text{final}}$.

- $S(q)$ of a simple liquid (binary Lennard-Jones mixture)

- NB: The limit $S(q \to 0)$ is related to the isothermal compressibility:

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

with

$$\kappa_T \equiv -(1/V) \left( \frac{\partial V}{\partial p} \right)_T$$
Structure: Multi-component systems

• Consider a system with \( v \) components; number of particles is \( N_1, N_2, \ldots, N_v \)

• The generalization of the radial distribution function is

\[
g_{\alpha\alpha}(\vec{r}) = \frac{N}{\rho N^2_{\alpha}} \sum_i \sum_{j(\neq i)} \langle \delta(\vec{r} + \vec{r}_i - \vec{r}_j) \rangle \quad \alpha \in \{1, \ldots, v\}
\]

\[
g_{\alpha\beta}(\vec{r}) = \frac{N}{\rho N_{\alpha}N_{\beta}} \sum_i \sum_j \langle \delta(\vec{r} + \vec{r}_i - \vec{r}_j) \rangle \quad \text{for} \quad \alpha \neq \beta
\]

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

\[
S_{\alpha\beta}(q) = \frac{f_{\alpha\beta}}{N} \sum_{j=1}^{N_{\alpha}} \sum_{l=1}^{N_{\beta}} \langle \exp[-i q \cdot (\vec{r}_j - \vec{r}_l)] \rangle \quad f_{\alpha\alpha} = 1; \quad f_{\alpha\beta} = 1/2 \quad \text{for} \quad \alpha \neq \beta
\]
Structure: Multi-component systems: 2

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

\[
S_{\text{neu}}(q) = \frac{N}{\sum N_\alpha b_\alpha^2} \sum_{\alpha\beta} b_\alpha b_\beta S_{\alpha\beta}(q)
\]

where the constant \( b_\alpha \) is the “neutron scattering cross section” for an element of type \( \alpha \) (see www for values); N.B. \( b_\alpha \) depends on the isotope.

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

\[
S_{\text{xr}}(q) = \frac{N}{\sum N_\alpha x_\alpha^2(q)} \sum_{\alpha\beta} x_\alpha(q) x_\beta(q) S_{\alpha\beta}(q)
\]

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

NB: For one component systems we have \( S_{\text{neu}}(q) = S_{\text{xr}}(q) = S(q) \)
Structure: Multi-component systems: 3

- Compare $S_{\text{neu}}(q)$ with $S(q)$ for different glass-formers

$S_{\text{neu}}(q) = \sum_{\alpha}^N \sum_{\beta}^N b_\alpha b_\beta S_{\alpha\beta}(q)$

SiO$_2$

Na$_2$O-2(SiO$_2$)

NS2 at 2100K

O–O

Na–Na

NS2

Misawa et al., $T=300$K

simulation, $T=300$K
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 define nearest neighbor \( \Rightarrow \) coordination number (NB: can be measured by NMR).

Coordination numbers in Na\(_2\)O-x(SiO\(_2\)) = NS\(_x\)
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

\[ \langle r^2(t) \rangle = \langle |r_i(t) - r_i(0)|^2 \rangle \]

- Short times: ballistic regime

\[ \langle r^2(t) \rangle \sim t^2 \]

- Long times: diffusive regime

\[ \langle r^2(t) \rangle \sim t \]

- Intermediate times at low T: “cage effect”

With decreasing T, the dynamics slows down quickly since the length of the plateau increases.

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 $G_s(r,t) = \text{probability that a particle has moved a distance } r \text{ in time } t$

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

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 $G_s(r,t) = \text{probability that a particle has moved a distance } r \text{ in time } t$

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

$G_s(r,t)$ for a ion-conducting liquid: $\text{Na}_2\text{O-x(SiO}_2\text{)}$

- 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:

$$G_d(r,t) = N^{-1} \sum_i \sum_{j \neq i} \langle \delta(r - |r_i(t) - r_j(0)|) \rangle$$

N.B. $G_d(r,0) = g(r)$

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 $F_s(q,t) = \langle N^{-1} \sum_j \exp(i \mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))) \rangle$, ...)

• Short times: Microscopic dynamics
• Intermediate times: Motion in the cage (= $\beta$-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 \( F_s(q,t) \)

\[
F_s(q, t) = \frac{1}{N} \left< \sum_{j=1}^{N} \exp \left( i q \cdot (r_j(t) - r_j(0)) \right) \right>
\]

N.B.

1) \( F_s(q,t) \) is the space FT of the self part of the van Hove function \( G_s(r,t) = N^{-1} \sum_i \left< \delta(r - |r_i(t) - r_i(0)||) \right> \)

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

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

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 spatial dynamical heterogeneities \( \Rightarrow \) talk Berthier
Time correlation functions: 3

\[ F_s(q, t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} \exp \left( i q \cdot (r_j(t) - r_j(0)) \right) \right\rangle \]

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

- **High T**: after the microscopic regime the correlation decays in an exponential way
- **Low T**: existence of a plateau at intermediate time (reason: cage effect)
- **N.B.**: plateau can only be seen on a logarithmic time axis

**Intermediate times**: viscoelastic effects, Boson peak

NB: we are above the melting temperature \( T_m = 2000 \text{K} \)!

\( \Rightarrow \) 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 $F(q,t)$:

$$F(q, t) = \frac{1}{N} \sum_{k=1}^{N} \sum_{j=1}^{N} \langle \exp(iq \cdot (r_j(t) - r_k(0))) \rangle$$

N.B.

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

2) $F(q,t)$ can be measured in coherent inelastic neutron- or x-ray scattering experiments: $q = q_{\text{initial}} - q_{\text{final}}$; $t$ 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

\[ F_s(q, t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} \exp \left( i q \cdot (r_j(t) - r_j(0)) \right) \right\rangle \]

\[ F(q, t) = \frac{1}{N} \sum_{k=1}^{N} \sum_{j=1}^{N} \left\langle \exp \left( i q \cdot (r_j(t) - r_k(0)) \right) \right\rangle \]

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

Na\textsubscript{2}O-2(SiO\textsubscript{2})

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

N.B. Usually n-scattering does not give results in the time domain but in the frequency domain \( \Rightarrow \) one has to Fourier transform the data
Correlation functions in the frequency domain

• Many experimental techniques do not give information in the time domain but only in the frequency domain (spectroscopy)
  ⇒ 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 $\chi''(\omega)$:

  $$\chi''(\omega) = \omega \frac{\phi''(\omega)}{k_B T}$$

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
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??

Correlation functions in the frequency domain: 3
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)

\[ m\ddot{r}_i + \nabla_i \sum_j V_{ij} = -\zeta \dot{r}_i + F_{B,i} \]

\[ \langle F_{B,i} \rangle = 0 \]

\[ \langle F_{B,i}(t) \cdot F_{B,j}(t') \rangle = 6k_B T \zeta \delta_{ij} \delta(t - t') \]

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 \( \alpha \)-relaxation is independent of microscopic dynamics

• early \( \beta \)-relaxation depends strongly on microscopic dynamics

• SD is much slower than ND
Transport coefficients

• From the mean squared displacement \( \langle r^2(t) \rangle = \langle |r_i(t) - r_i(0)|^2 \rangle \) one can easily obtain the tracer diffusion constant \( D \):

\[
D = \lim_{t \to \infty} \frac{\langle r^2(t) \rangle}{6t}
\]

Einstein relation

• From the Green-Kubo relation between stress and viscosity one can obtain the viscosity \( \eta \):

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

Recall: Connection between the diffusion constant \( D \) of a sphere with radius \( R \) that is in a liquid with viscosity \( \eta \):

\[
D = \frac{k_B T}{6 \eta R}
\]

Stokes-Einstein relation

(NB: Sometime \( \eta \) is replaced by the relaxation time \( \tau \))

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 \( u_j \) 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: \( C_{ls}(t) = N^{-1} \sum_i \langle P_l(u_i(t) \cdot u_i(0)) \rangle \)

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 $\tau$
  • susceptibilities
  • orientational correlation functions