We have generated sets of (x,y,z) positions for various times at various given thermodynamic conditions (N,V,T,P). Today we focus mostly on time dependence!

**Correlation functions and linear response theory**
- Mean square displacement and diffusion
- Van Hove correlation functions
- Intermediate scattering functions
- Linear response theory, time correlations
- Applications
A) MEAN SQUARE DISPLACEMENT AND DIFFUSION

The mean square displacement is defined as

\[ \langle r^2(t) \rangle = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \langle |r_i(t) - r_i(0)|^2 \rangle, \]

- performed in NVE or NVT.
- do not use periodic boundary conditions

Gives a direct description of the dynamics.

A-B Lennard-Jones liquid

Bauchy et al., PRL 2013

Kob PRE 2000

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Atomic modeling of glass – LECTURE 6 TIME CORRELATION
More insight into the msd...

\[ \text{GeO}_2 \]

Ballistic régime
msd \( \sim t^2 \)
Short time

Caging régime (LT)

Diffusive régime
Long times

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Atomic modeling of glass – LECTURE 6 TIME CORRELATION
Behavior with temperature

Usually, a gentle Arrhenius behavior: \( D = \exp\left[-\frac{E_A}{k_B T}\right] \)

- Species dependent. Na diffuses faster than Si or O in silicates

\[ \text{GeO}_2 \]

Micoulaut et al. PRE 2006

Bauchy et al. Chem Geol. 2013

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Behavior of the diffusion constant with other thermodynamic variables

- Dependence on V or P.

- To be comparable with experiment, should be calculated at P=0.

- Usually at fixed V (e.g. V_g) and P non-zero

Figure 3: Density dependence of the diffusion coefficient, $D$, shown for eight isotherms. The curves from top to bottom correspond to temperatures $T$ (in K) of: 400, 350, 320, 300, 280, 260, 240 and 220. The solid lines are fifth-order polynomial fits to the data, and are simply guides to the eye. The diffusion coefficient was calculated from the long-time behaviour of the mean squared displacement of the water molecules, $\langle r^2(t) \rangle$, using the Einstein relationship $6D = \delta \langle r^2(t) \rangle / \delta t$.

Errington et al. Nature 2001

Bauchy et al., PRB 2011

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To go further in correlation study, one can follow correlation both in space and
time. This information is richer, but the price to pay is the calculation of a two-
variable correlation function, at least.
We introduce these functions because they are also available in experiments,
essentially form neutron scattering.

**B) VAN HOVE CORRELATION FUNCTION**

We first introduce a density correlation function \( G(\mathbf{r}, \mathbf{r}', t) \) defined from the local atomic
densities:

\[
\rho G(\mathbf{r}, \mathbf{r}'; t) = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r}' + \mathbf{r} - \mathbf{r}_i(t))\delta(\mathbf{r} - \mathbf{r}_j(0))\right\rangle
\]

or:

\[
\rho G(\mathbf{r}, \mathbf{r}'; t) = \left\langle \rho(\mathbf{r}' + \mathbf{r}, t)\rho(\mathbf{r}', 0)\right\rangle
\]

For an homogeneous system, \( G \) depends only on the relative distance. Integration gives:

\[
G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0))\right\rangle
\]
At \( t=0 \), we have

\[
G'(\mathbf{r}, t) = \frac{1}{N} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \rangle
\]

 Except a singularity at the origin, the Van Hove correlation function is proportional to the pair correlation function \( g(r) \). We can split the function into two parts, self and distinct:

\[
G'(\mathbf{r}, 0) = \frac{1}{N} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(0)) \rangle = \delta(\mathbf{r}) + \rho g(\mathbf{r})
\]

At \( t=0 \), we have

\[
G(\mathbf{r}, 0) = G_s(\mathbf{r}, 0) + G_d(\mathbf{r}, 0)
\]

which can be established at non-zero times:

\[
G_s(\mathbf{r}, t) = \frac{1}{N} \langle \sum_{i=1}^{N} \delta((\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)) \rangle
\]

\[
G_d(\mathbf{r}, t) = \frac{1}{N} \langle \sum_{i \neq j} \delta(\mathbf{r} + \mathbf{r}_j(0) - \mathbf{r}_j(t)) \rangle
\]
**Physical interpretation:**

- The Van Hove function is the probability density of finding a particle $i$ in the vicinity of $r$ at time $t$, knowing that a particle $j$ is in the vicinity of the origin at time $t=0$.

- The self part $G_s(r,t)$ is the probability density of finding a particle $i$ at time $t$ knowing that this particle was at the origin at time 0. **Probability that a particle has moved a distance $r$ in time $t$ (dynamics).**

\[
G_s(r,t) = \frac{1}{N} \langle \sum_{i=1}^{N} \delta((r + r_i(0) - r_i(t))) \rangle
\]

- The distinct part $G_d(r,t)$ is the probability density of finding a particle $j$ different from $i$ at time $t$ knowing that the particle $i$ was at the origin at time $t=0$. **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.** And $G_d(r,0)=g(r)$.

\[
G_d(r,t) = \frac{1}{N} \langle \sum_{i \neq j}^{N} \delta(r + r_j(0) - r_j(t)) \rangle
\]
Normalization of the functions leads to:

\[ \int d\mathbf{r} G_s(\mathbf{r}, t) = 1 \quad \int d\mathbf{r} G_d(\mathbf{r}, t) = N - 1 \]

Integration over space, \( G_d(r,t) \) is able to count the remaining particles.

In the long-time limit, the system looses memory of the initial configuration and the correlation functions become independent of the distance:

\[ \lim_{r \to \infty} G_s(\mathbf{r}, t) = \lim_{t \to \infty} G_s(\mathbf{r}, t) \simeq \frac{1}{V} \simeq 0 \]
\[ \lim_{r \to \infty} G_d(\mathbf{r}, t) = \lim_{t \to \infty} G_s(\mathbf{r}, t) \simeq \frac{N - 1}{V} \simeq \rho \]
Examples: Self part in Na silicates

Kob, PRB 2000

- At short times, $G_s(r,t) \sim \delta(r)$
- Small times: rattling and hopping motion on the length scale of nearest neighbors.
- Spatial extent of the motion is determined by thermodynamic conditions: $T$ (viscous slowing down) or $P$ (motion blocked by the high density).

Bauchy, PRB 2011

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Atomic modeling of glass – LECTURE 6 TIME CORRELATION
Examples: Distinct part in a binary A-B mixture

- At high temperature, the correlation hole at $r=0$ is quickly filled up
- At low temperature, correlation hole survives at long time

Kob and Andersen, PRE 1995
C) DYNAMIC STRUCTURE FACTOR

Fourier (time) transform of the intermediate scattering function (see next lectures)

\[ S(k, \omega) = \int dt F(k, t)e^{i\omega t} \int d\omega S(k, \omega) = S(k) \]

Neutron weighted dynamic structure factor 
(similar to static one):

\[ S_n(q, \omega) = \frac{1}{N \langle b^2 \rangle} \int -\infty \rightarrow \infty \frac{dt}{2\pi} e^{-i\omega t} \sum_{i=1}^{N} \sum_{j=1}^{N} b_i b_j \langle e^{i q \cdot r_j(t)} e^{-i q \cdot r_i(0)} \rangle \]

Access to partial dynamic structure factors:

\[ S_{\alpha\beta}(q, \omega) = \frac{1}{\sqrt{N_{\alpha}N_{\beta}}} \int -\infty \rightarrow \infty \frac{dt}{2\pi} e^{-i\omega t} \sum_{i \in \alpha} \sum_{j \in \beta} \langle e^{i q \cdot r_j(t)} e^{-i q \cdot r_i(0)} \rangle \]

- Can be compared to measurements extracted from coherent inelastic neutron scattering.

Differential cross-section \((d^2\sigma/d\omega d\Omega)\) proportional to \(S(q, \omega)\)

Jin and Vashishta PRB 1993
D) LINEAR RESPONSE THEORY

- Goal: Having MD generated trajectories at our disposal, we want to compute viscosity, electrical or thermal conductivity, mechanical properties, etc. Use of linear response theory

- General idea (Onsager): Disturbance in a system created by a weak external perturbation decays in the same way as a spontaneous fluctuation in equilibrium.

- Linear response theory: link between time correlation functions and response to weak perturbations (Green-Kubo’s fluctuation-dissipation relations)

- Static response (e.g. polarization, electric current) to a constant weak applied field.
  - Property characterized by a dynamic variable A.
  - Change in the Hamiltonian $H_0 - \lambda B(p^N, q^N)$
  - External perturbation brings the system from Ensemble average $\langle A \rangle_0$ to $\langle A \rangle_0 + \langle \Delta A \rangle$. 

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• External perturbation brings the system from Ensemble average $<A>_0$ to $<A>_0+<\Delta A>$.

• The Ensemble average $<A>$ for this perturbated $A$ is:

$$<A>_0 + <\Delta A> = \frac{\int d\Gamma \exp[-\beta(\mathcal{H}_0 - \lambda B)]A}{\int d\Gamma \exp[-\beta(\mathcal{H}_0 - \lambda B)]}$$

$\Gamma$ is the integration over phase space variables $(q^N, p^N)$

• $<A>$ can be expressed as a linear Taylor expansion: $<A>=<A>_0+\lambda(d<A>/d\lambda)_{\lambda=0}$ involving the quantity:

$$(\frac{\partial <\Delta A>}{\partial \lambda})_{\lambda=0} = \beta \{<AB>_0 - <A>_0 <B>_0\}$$

☐ Similarly, we can compute the **dynamic response**

❖ Preparation of the system under a weak constant perturbation. One thus has $<A>=<A>_0+<\Delta A>$

❖ At $t=0$, the perturbation is switched off. Response $\Delta A$ decays to zero.

❖ Ensemble average of $\Delta A$ at time $t$ is given by:

$$<\Delta A(t)> = \frac{\int d\Gamma \exp[-\beta(\mathcal{H}_0 - \lambda B)]A(t)}{\int d\Gamma \exp[-\beta(\mathcal{H}_0 - \lambda B)]}$$

with $A(t)$ the value of $A$ at time $t$ in a system starting at point $\Gamma$. 

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Atomic modeling of glass – LECTURE 6 TIME CORRELATION
In the limit \( \lambda = 0 \) (and assuming that \( \langle A \rangle_0 = 0 \)), we can simplify to:

\[
\langle \Delta A(t) \rangle = \frac{\int d\Gamma \exp[-\beta(H_0 - \lambda B)]A(t)}{\int d\Gamma \exp[-\beta(H_0 - \lambda B)]}
\]

The decay of \( \Delta A \) of the system is determined by a time correlation function describing the decay of spontaneous fluctuations of \( A \) in equilibrium under an external perturbation \( B \).

**E) TIME CORRELATION FUNCTION**

- Let us consider two time dependent signals \( A \) and \( B \). The general time correlation between them is given by:

\[
C(t) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(t_0)B(t_0 + t) dt_0 = \langle A(t_0)B(t_0 + t) \rangle
\]

\( A=B \): auto-correlation. Otherwise cross-correlation which is the case in linear response.
At equilibrium, the correlation is invariant under time translation, i.e.

$$C(t) = \langle A(t_0) B(t_0 + t) \rangle = \langle A(t_0 + s) B(t_0 + s + t) \rangle$$

NB: Glasses $C(t)$ is not time invariant so that $t$ depends on $t_0 = t_w$ (waiting time)

In the limit of no delay time, $C(0)$ is the static correlation function

Can be normalized to the value at $t_0$:

$$\hat{C}(t) = \frac{\langle A(t_0) B(t_0 + t) \rangle}{\langle AB \rangle}$$

$$C(0) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(t_0) B(t_0) \, dt_0 = \langle A(t_0) B(t_0) \rangle = \langle AB \rangle$$
G) APPLICATIONS-1: ELECTRICAL CONDUCTIVITY

Hamiltonian of the system with vector potential is given by:
\[ \mathcal{H}' = \sum_{i=1}^{N} \frac{1}{2m_i} \left( p_i - \frac{e_i}{c} A \right)^2 + \mathcal{U}_{\text{pot}}. \]

A being a gauge field.

I remind that from in Classical Electromagnetism, the generalized momentum \( p \) of a particle with mass \( m \) and charge \( q \) moving at a velocity \( v \) in a vector potential \( A \) is \( p = mv + e_i A \).

- The vector potential is switched off at \( t=0 \). The electrical field is an infinitesimal spike (delta function) given that:
  \[ E = -\frac{1}{c} \dot{A} \quad \text{and} \quad E(t) = \frac{1}{c} A \delta(t) \]

- At the first order, we can write:
  \[ \mathcal{H}' = \mathcal{H}_0 - \sum_{i=1}^{N} \frac{e_i}{cm_i} \mathbf{p}_i \cdot \mathbf{A} + \mathcal{O}(A^2) \]
  \[ = \mathcal{H}_0 - \frac{A}{c} \int \mathbf{d}r \sum_{i=1}^{N} \frac{e_i}{m_i} \mathbf{p}_i \delta(r_i - r) \]
  \[ = \mathcal{H}_0 - \frac{A}{c} \int \mathbf{d}r \mathbf{j}(r), \quad \text{with } \mathbf{j}(r) \text{ the current density} \]
From the expression of the perturbated Hamiltonian, we obtain the correlation function:

$$\mathcal{H}' = \mathcal{H}_0 - \frac{A}{c} \int dr \, j(r)$$

we can write the average current density as:

$$\langle j(t) \rangle = \frac{\int d\Gamma e^{-\beta \left( \mathcal{H}_0 - \frac{A}{c} \int dr' j(r', t) \right)} j(r)}{\int d\Gamma e^{-\beta \mathcal{H}_0}}$$

and, expanding at small vector $A$, we have:

$$\langle j(t) \rangle = \frac{A}{c V k_B T} \int dr dr' \langle j(r, 0) j(r', t) \rangle$$

Remember that we have Ohm’s law ($j = \sigma E$) and for the response function:

$$\langle \Delta A(t) \rangle = \int_{-\infty}^{t} dt' \chi_{AB}(t - t') f(t')$$

so that ($E(t)$ is a Dirac function):

$$\langle j(t) \rangle = \int_{-\infty}^{t} dt' \sigma(t - t') E(t') = \sigma(t) \frac{A}{c}.$$
Example-1: Electrical conductivity in amorphous aluminia

Computation of the current from the atomic velocities:

$$J(t) = \sum_i Z_i e v_i(t)$$

Normalized current autocorrelation function:

$$\psi(t) = \frac{\langle J(t) \cdot J(0) \rangle}{\langle J(0) \cdot J(0) \rangle}$$

Frequency dependent conductivity

$$\sigma(\omega) = \frac{\langle J(0)^2 \rangle}{3Vk_B T} \int_0^{\infty} \psi(t)e^{i\omega t} dt$$

---

Vashishta et al. JAP 2008

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Atomic modeling of glass – LECTURE 6 TIME CORRELATION
Example-2: Electrical conductivity in an aluminosilicate liquid

- Plot of $\sigma(t)$ following:

$$\sigma(t) = \frac{1}{V k_B T} \int \! drdr' \langle j(r,0)j(r', t) \rangle$$

- Access to $\sigma_{dc}$

$$\sigma(\omega = 0) = \frac{1}{V k_B T} \int_0^\infty \! dt \int \! drdr' \langle j(r,0)j(r', t) \rangle$$

- Behavior with temperature (Arrhenius)

Figure 4. (a) Ionic conductivity due to Na in NaAlSiO$_4$ determined from simulations at four temperatures, calculated according to Equations 7 and 8 in text. (b) Ionic conductivity determined in simulations (open squares) in comparison with results of laboratory measurements by Terai (1969).

Spera et al. JCP 2001
Example-3: Beyond linear response theory-usefulness of MD

- The computation of $\sigma(t)$ or $\sigma_{dc}$ and successful comparison with experiment is the starting point (prerequisite) of atomic scale insight of conductivity.

- Channel conduction in silicates

Link with static structure factor
Typical distance related to $q=0.9\text{Å}^{-1}$

Prasada Rao et al. SS Ionics 2011
Meyer et al. PRL 2004

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Atomic modeling of glass – LECTURE 6 TIME CORRELATION
F) APPLICATIONS-2: THERMAL CONDUCTIVITY

Similar treatment to electrical conductivity.

- Define a heat current: \( \mathbf{J} = \sum_i E_i \mathbf{v}_i + \frac{1}{2} \sum_{i>j \text{ pairs}} \mathbf{r}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j) \)

- with \( E_i \), energy of atom \( i \)

- Compute the autocorrelation function:

\[
\kappa = \frac{1}{3Vk_B T^2} \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle \, dt
\]

FIG. 4. Thermal conductivity vs temperature for amorphous silicon. Solid circles are from Allen and Feldman (Ref. 5) and open circles are from experiment (Ref. 17). Open circles with error bars are the present calculations. *Lee et al.*, PRB 1991

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Jund and Jullien, PRB 1999
F) APPLICATIONS-3: VISCOSITY

- Shear cannot be interpreted in terms of an external field acting on all particles.

- Use of a canonical transformation corresponding to uniform shear transforming linearly the coordinates from $r^N$ to $r'^N$ with $r'_i = h_{ij} r_j$ and $h_{ij} = 1 + \varepsilon_{ij}$

- This means that we transform the Hamiltonian from:

  $$\mathcal{H}_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(r^N)$$

  to:

  $$\mathcal{H}_1 = \sum_{i=1}^{N} \frac{1}{2m_i} \mathbf{p}'_i \cdot G^{-1} \cdot \mathbf{p}'_i + U(r'^N)$$

  with $G$ the metric tensor defined as: $G \equiv \mathbf{h}^T \cdot \mathbf{h}$

- Effect of uniform shear, e.g. $\varepsilon_{xy} = \varepsilon$ otherwise 0.

- Assume equilibration of the system with Hamiltonian $H_1$ (i.e. under shear) and then switch off $\varepsilon$ at $t=0$ (now left with $H_0$).
Assume equilibration of the system with Hamiltonian $H_1$ (i.e. under shear) and then switch off $\epsilon$ at $t=0$ (now left with $H_0$).

The system experiences a $\delta$-function spike in the shear rate, i.e. one has:

$$\frac{\partial \nu_x}{\partial y} = -\epsilon \delta(t)$$

Time-dependent response of the shear stress, $\sigma_{xy}(t)$ to the sudden change from $H_1$ to $H_0$:

$$\langle \sigma_{xy}(t) \rangle = -\epsilon \frac{1}{\sqrt{k_B T}} \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle$$

where $\sigma_{xy}$ (tensor) can be computed via:

$$\sigma_{\alpha\beta} = \frac{1}{V} \sum_{i=1}^{N} \left[ \frac{(p_i \cdot \hat{e}_\alpha)(p_i \cdot \hat{e}_\beta)}{m_i} + (q_i \cdot \hat{e}_\alpha)(F_i \cdot \hat{e}_\beta) \right]$$

Remember (lecture 5) that pressure is:

$$p = \frac{1}{3V} \sum_{i=1}^{N} \left[ \frac{p_i^2}{m_i} + q_i \cdot F_i \right]$$
Again, remember that: $\langle \Delta A(t) \rangle = \int_{-\infty}^{t} dt' \chi_{AB}(t - t') f(t')$

with $f(t')$ the δ-function of the shear rate.

We find that

$$\sigma_{xy} = \frac{\partial v_x}{\partial y} \times \frac{1}{V k_B T} \int_{0}^{\infty} dt \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle$$

Then, we remember **Newton’s law for viscosity**.
Under laminar flow, the force exerted by a fluid in the x-direction is proportional to the velocity gradient, the constant of proportionality being the shear viscosity.

The shear stress is thus: $\sigma_{xy} = \eta \frac{\partial v_x}{\partial y}$ and, by identification:

$$\eta = \frac{1}{V k_B T} \int_{0}^{\infty} dt \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle$$
**G) APPLICATIONS-3: VISCOSITY**

**Example-1: Viscosity of a silicate liquid (NS2) and MORB under pressure**

NPT (P=0), then NVE

![Graph showing viscosity vs. 1/T for NS2 and MORB](image)

*Fig. 3. Simulated viscosity of the NS2 liquid at zero pressure (filled red squares), compared to experimental data (red circles) from Bockris et al. (1955), together with simulated viscosity of the MORB liquid at zero pressure (filled black squares), compared to experimental data (broken black curve) from Villeneuve et al. (2008). The dotted line is a high temperature Arrhenius fit for the MORB data whereas the solid line is a TVF fit (see text for parameters).*

Bauchy et al. Chem. Geol. 2013

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Atomic modeling of glass – LECTURE 6 TIME CORRELATION
G) APPLICATIONS-3: VISCOSITY

Example-1: Viscosity of a silicate liquid (NS2) and MORB under pressure

- Checking for empirical relationships

Eyring (1948): \( \eta = k_B T / \lambda D \)

With \( \lambda \) a jump distance (d_{O-O} \approx \text{a few A})

- Compute (MD) D and \( \eta \)
- Valid only at high viscosity

- Detecting anomalies (minima in viscosity)
Example-2: Viscosity of silica

FIG. 10. Main figure: Arrhenius plot of the shear viscosity from the simulation (filled squares). The dashed line is a fit with an Arrhenius law to our low-temperature data. The open circles are experimental data from Urbain et al. [34]. Inset: Temperature dependence of the left hand side of Eq. (12) to check the validity of the Stokes-Einstein relation.

Horbach and Kob, PRB 1999
**Conclusion:**

- Dynamic quantities can be estimated from Molecular Dynamics
  - Time-dependent structural correlations
  - Transport coefficients (linear response theory)

- Insight into the glass transition phenomenon (see next lectures)

- Agreement with experiments is less obvious (as compared to structure)

**Next time:** Force fields and limitations