Structural quantities

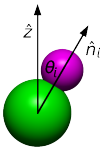
Correlation functions

- radial distribution function (RDF, also pair correlation/distribution function), $g(r)$ = probability of finding a particle at distance r (from another particle), normalized to ideal gas
- structure factor (diffraction → Fourier transform of $g(r)$)
- angular correlation function – good for small nonspherical molecules
- time autocorrelation functions

Order parameters

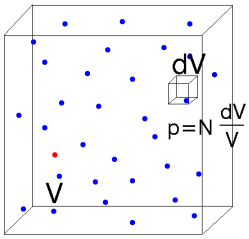
- Ordering in the z-direction: $\langle \sum_i \cos\theta_i \rangle$: ↑ vs. ↓
- For symmetric molecules: $\left\langle \sum_i \left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right)\right\rangle$: ↕ vs. ↔
- Nematic liquid crystal – the "director" is not known:

$$Q_{\alpha\beta} = \left\langle \sum_i \left(\frac{3}{2}\hat{n}_{\alpha,i}\hat{n}_{\beta,i} - \frac{1}{2}\delta_{\alpha\beta}\right)\right\rangle, \quad \text{eigenvector of the max. eigenvalue = director}$$

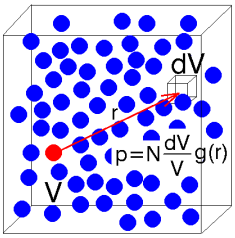


- Formulas detecting local order (e.g., tetrahedral around water molecules), onset of crystallization, etc.

Structure of fluids – correlation functions



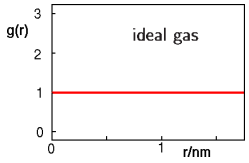
randomly distributed molecules (ideal gas)

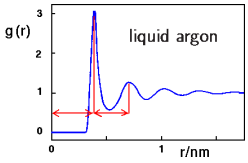


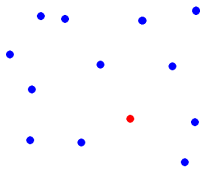
liquid

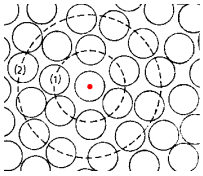
$g(r)$ = pair correlation function = radial distribution function = probability density of finding a particle r apart from another particle, normalized so that for randomly distributed particles (ideal gas) it is 1

Structure of fluids – correlation functions

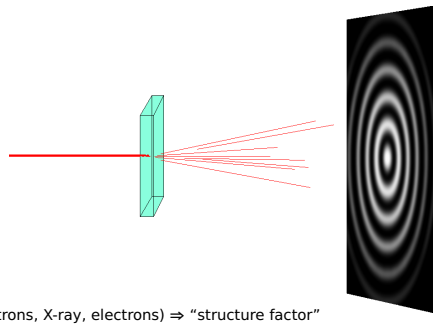






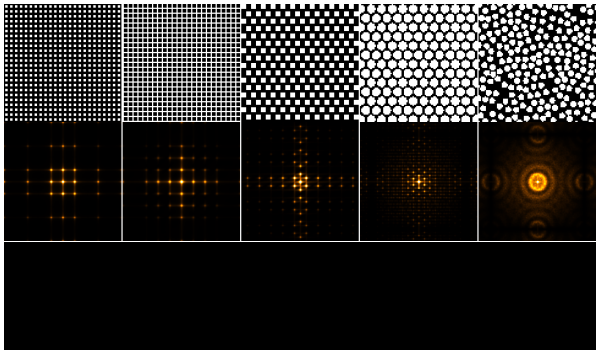


How to obtain structure – experiment

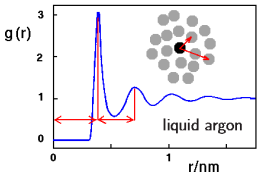


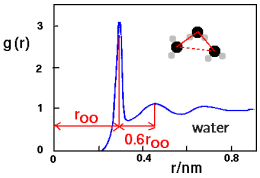
- Diffraction (neutrons, X-ray, electrons) ⇒ "structure factor"
- inverse Fourier transform ⇒ RDF

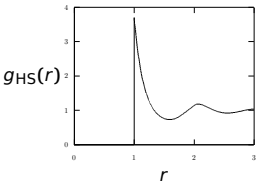
How to obtain structure



Argon, hard spheres, water







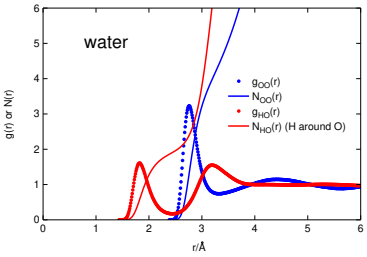
- The structure of simple fluid (argon, HS) is organized by shells.
- The structure of water is determined by the tetrahedral geometry of hydrogen bonds.
- After several molecular diameters, the correlations decay to zero.

Running coordination number

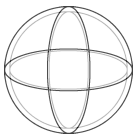
Also "cumulative radial distribution function" $\rho = N/V$ = number density

$$N(r) = 4\pi\rho \int_0^r g(r')r'^2 \mathrm{d}r'$$

For $r_{\min}$ = first minimum on the RDF curve, $N(r_{\min})$ = "coordination number" = averaged number of molecules in the first shell



RDF from simulations – simple



Histogram of the number of particle pairs, $\mathcal{N}_i$, so that

$$r \in [r_i - \Delta r/2, r_i + \Delta r/2) \quad \text{alternatively: } \mathcal{I}_i = [r_i, r_i + \Delta r)$$

The volume of the shell

$$\Delta V_i = \frac{4\pi}{3}\left[\left(r_i + \frac{\Delta r}{2}\right)^3 - \left(r_i - \frac{\Delta r}{2}\right)^3\right]$$

Mean number of molecules around a selected particle in case of uniformly distributed molecules (ideal gas, $\rho = N/V$):

$$\rho \Delta V_i$$

Sum over all particles (1/2 to count each pair just once):

$$\mathcal{N}_i^{\text{id. gas}} = \frac{N}{2}\rho\Delta V_i$$

Radial distribution function:

$$g(r_i) = \frac{\langle \mathcal{N}_i \rangle}{\mathcal{N}_i^{\text{id. gas}}} = \frac{2\langle \mathcal{N}_i \rangle}{N\rho\Delta V_i}$$

SIMOLANT – installation (Windows)

- http://www.vscht.cz/fch/software/simolant
  or Google simolant
- Download `simolant-win32.zip`
- Create a folder and unpack SIMOLANT there.
  Do not run directly from `simolant-win32.zip`!
- Run `simolant.exe`

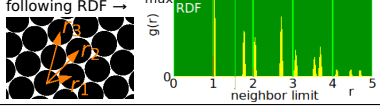
Hint: The calculated data are exported to file `simolant.txt` with a decimal point. If you like decimal comma (useful with Czech localization), click ,, in panel "Measure".

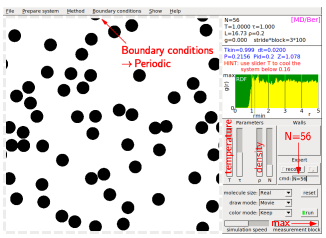
Hint: If you restart SIMOLANT, the old `simolant.txt` is renamed to `simolant.bak`. The export name `simolant` can be changed by Menu: File → Protocol name..

Simolant: observe RDF by yourself

[simolant] 10/22
s08/3

- Set in menu: Boundary conditions → Periodic
- Type 'magic number' N=209 to input field "cmd:" (slow computer: N=56)
- Slide "measurement block" to max, watch $g_{\text{gas}}(r)$
- Increase density (slider "ρ") and observe the changes in RDF for liquid
- Repeat with a lower temperature "T", combine different ρ and T
- Crystal: Set max ρ, cool slowly to $T = 0$, try heat/cool if not well crystallized
  Hint: "color mode" → Neighbors to visualize crystal defects
- You should get the following RDF →





- Apparently $r_3/r_1 = 2$ because r_3 is the second neighbor ●●●
- Similarly, $r_2/r_1 = \sqrt{3}$

Radial distribution function in the NVT ensemble

3D (e.g., in periodic b.c.), good for a homogebeous and isotropic liquid:

$$g(r) \equiv g(r_{12}) = \frac{N(N-1)}{\rho^2 Q_{\mathrm{NVT}}} \int \dots \int \exp[-\beta U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)]\, \mathrm{d}\vec{r}_3 \dots \mathrm{d}\vec{r}_N$$

Equivalently

$$g(r) = \left(1 - \frac{1}{N}\right) V \langle \delta(\vec{r}_{12} - \vec{r}) \rangle$$

For a mixture:

$$g_{ij}(r) = V \langle \delta(\vec{r}_{12} - \vec{r}) \rangle$$

Normalization (fluid):

$$\lim_{N\to\infty, r\to\infty} g(r) = 1$$

NB: ideal gas at finite N: $g(r) = 1 - 1/N$ (e.g., in periodic b.c.)

Number of particles around one chosen particle (in NVT):

$$\int_V \rho g(\vec{r}) \mathrm{d}\vec{r} = N - 1$$

Calculation of RDF in simulations – exact

Histogram of the count of pairs of particles, $\mathcal{N}_i$, so that $r \in \mathcal{I}_i$

$$\mathcal{I}_i = [r_i - \Delta r/2, r_i + \Delta r/2), \quad \text{optionally } \mathcal{I}_i = [r_i, r_i + \Delta r)$$

$$r_i = i\Delta r, \; i = 1, \dots, i_{\max}$$

$$\begin{aligned}
\langle \mathcal{N}_i \rangle &= \frac{1}{Q_{\mathrm{NVT}}} \sum_{j<k} \int_{r_{jk} \in \mathcal{I}_i} \exp[-\beta U(\vec{r}^N)] \mathrm{d}\vec{r}^N \\
&= \frac{1}{Q_{\mathrm{NVT}}} \binom{N}{2} V \int_{r_{12} \in \mathcal{I}_i} \left\{ \int \exp[-\beta U(\vec{r}^N)] \mathrm{d}\vec{r}_3 \dots \mathrm{d}\vec{r}_N \right\} \mathrm{d}\vec{r}_{12} \\
&= \frac{N}{2} \rho \int_{\mathcal{I}_i} g(r) \mathrm{d}\vec{r} \\
&\approx \frac{N^2}{2V} g(r_i) \Delta V_i
\end{aligned}$$

The formula again:

$$g(r_i) = \frac{2\langle \mathcal{N}_i \rangle}{N \rho \Delta V_i}$$

Correlation function and thermodynamics

For simple fluid (point particles interacting by a pair spherically symmetric potential):

Residual internal energy:

$$\langle U \rangle = \frac{1}{Q_{\mathrm{NVT}}} \int \sum_{i<j} u_{ij}(r_{ij}) \mathrm{e}^{-\beta U} \mathrm{d}\vec{r}_1 \dots \mathrm{d}\vec{r}_N$$

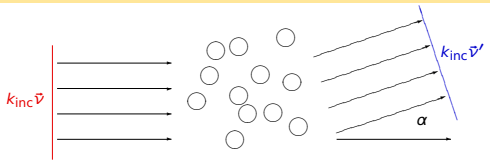
$$\langle U \rangle = \binom{N}{2} \frac{V}{Q_{\mathrm{NVT}}} \int \mathrm{e}^{-\beta U} 4\pi r_{12}^2 \mathrm{d}r_{12} u(r_{12}) \mathrm{d}\vec{r}_3 \dots \mathrm{d}\vec{r}_N$$

$$\langle U \rangle = \frac{N}{2} \rho \int u(r) g(r) \mathrm{d}\vec{r} = 2N\pi\rho \int u(r) g(r) r^2 \mathrm{d}r$$

Pressure:

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi}{3} \beta\rho \int g(r) u'(r) r^3 \mathrm{d}r$$

Structure factor



- Distance of atom $\vec{r}_j$ from plane $\vec{\nu} \cdot \vec{r} = 0$ is $\vec{\nu} \cdot \vec{r}_j$ (for $|\vec{\nu}| = 1$).
- Distance from wave source (wave plane of eq. $\vec{\nu} \cdot \vec{r} = \mathrm{const}$) via atom r_j to the detector ($\vec{\nu}' \cdot \vec{r} = \mathrm{const}$) is $\vec{\nu} \cdot \vec{r}_j - \vec{\nu}' \cdot \vec{r}_j + \mathrm{const}$
- Wave vector $\vec{k}_{\mathrm{inc}} = k_{\mathrm{inc}} \vec{\nu}$, $k_{\mathrm{inc}} = 2\pi/\lambda$
- Formally the incident wave is (but phase)

$$\exp[\,i(k_{\mathrm{inc}}\vec{\nu} - k_{\mathrm{inc}}\vec{\nu}') \cdot \vec{r}_j] = \exp[\,i\vec{k} \cdot \vec{r}_j]$$

where

$$\vec{k} = k_{\mathrm{inc}}\vec{\nu} - k_{\mathrm{inc}}\vec{\nu}', \qquad k = |\vec{k}| = 2\sin(\alpha/2) k_{\mathrm{inc}} \approx \alpha k_{\mathrm{inc}}$$

Structure factor

Waves scattered by all atoms interfere:

$$K = \sum_{j=1}^{N} \exp[\,i(k_{\mathrm{inc}}\vec{\nu} - k_{\mathrm{inc}}\vec{\nu}') \cdot \vec{r}_j] = \sum_{j=1}^{N} \exp[\,i\vec{k} \cdot \vec{r}_j], \qquad \text{signal} \propto \langle |K|^2 \rangle$$

Definition of the structure factor (pure compound):

$$S(\vec{k}) = \left\langle \frac{1}{N} \left| \sum_{j=1}^{N} \exp(-i\vec{k} \cdot \vec{r}_j) \right|^2 \right\rangle$$

It is a function of vector $\vec{k}$, we may imagine it in the periodic b.c. in a cube of edge L:

$$\vec{k} = \frac{2\pi\vec{n}}{L}, \; \vec{n} \in \mathbb{Z}^3$$

Similarly, a 3D RDF is (not exactly isotropic even for a liquid)

$$g(\vec{r}_{12}) = \frac{N(N-1)}{\rho^2 Q_{\mathrm{NVT}}} \int_{L^3} \dots \int_{L^3} \exp[-\beta U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)]\, \mathrm{d}\vec{r}_3 \dots \mathrm{d}\vec{r}_N$$

Structure factor and RDF

In a periodic box $V = L^3$; $\vec{k} = 2\pi\vec{n}/L$:

$$\begin{aligned}
S(\vec{k}) &= \left\langle \frac{1}{N} \left| \sum_{j=1}^{N} \exp(-i\vec{k} \cdot \vec{r}_j) \right|^2 \right\rangle \\
&= \left\langle \frac{1}{N} \sum_{j=1}^{N} \sum_{l=1}^{N} \exp(-i\vec{k} \cdot \vec{r}_j) \exp(i\vec{k} \cdot \vec{r}_l) \right\rangle \\
&= 1 + \frac{1}{N} \left\langle \sum_{j<l}^{N} [\exp(-i\vec{k} \cdot \vec{r}_{jl}) + \exp(i\vec{k} \cdot \vec{r}_{jl})] \right\rangle \\
&= 1 + \rho \int_{L^3} g(\vec{r}) \cos(\vec{k} \cdot \vec{r}) \mathrm{d}\vec{r}
\end{aligned}$$

The integral diverges as $V \to \infty \Rightarrow$ we subtract $0 = \int_V \cos(\vec{k} \cdot \vec{r}) \mathrm{d}\vec{r}$, $\vec{k} = 2\pi\vec{n}/L$
(other method: convergence factor $\exp(-\alpha k^2)$, $\lim_{\alpha \to 0}$)

$$S(\vec{k}) = 1 + \rho \int_V [g(\vec{r}) - 1] \cos(\vec{k} \cdot \vec{r}) \mathrm{d}\vec{r} \overset{V \to \infty}{=} 1 + \rho \int [g(\vec{r}) - 1] \cos(\vec{k} \cdot \vec{r}) \mathrm{d}\vec{r}$$

Structure factor and RDF

Since $g(\vec{r}) = g(-\vec{r})$, we have

$$S(\vec{k}) - 1 = \rho \int [g(\vec{r}) - 1] \cos(\vec{k} \cdot \vec{r}) \mathrm{d}\vec{r} = \rho \int [g(\vec{r}) - 1] \mathrm{e}^{-i\vec{k} \cdot \vec{r}} \mathrm{d}\vec{r}$$

and the 3D inverse Fourier transform is

$$g(\vec{k}) - 1 = \frac{1}{8\pi^3 \rho} \int [S(\vec{k}) - 1] \mathrm{e}^{i\vec{k} \cdot \vec{r}} \mathrm{d}\vec{k}$$

Once again using $S(\vec{k}) = S(-\vec{k})$:

$$g(\vec{k}) - 1 = \frac{1}{8\pi^3 \rho} \int [S(\vec{k}) - 1] \cos(\vec{k} \cdot \vec{r}) \mathrm{d}\vec{k}$$

The $k \to 0$ limit:

$$\begin{aligned}
&NVT: \quad S(0) = 0 \\
&\mu VT: \quad S(0) = 1 + \rho \int [g(\vec{r}) - 1] \mathrm{d}\vec{r} = k_{\mathrm{B}} T \left(\frac{\partial \rho}{\partial p} \right)_T \quad \text{(compressibility equation)}
\end{aligned}$$

Isotropic structure factor

Let's choose $\vec{k} = (0, 0, k)$ and spherical coordinates (ϕ, θ, r), then $\vec{k} \cdot \vec{r} = kr\cos\theta$ and (g and S are odd functions)

$$\begin{aligned}
S(k) - 1 &= \rho \int [g(\vec{r}) - 1] \cos(\vec{k} \cdot \vec{r}) \mathrm{d}\vec{r} \qquad (\text{subst. } z = \cos\theta) \\
&= \rho \int_0^\infty r^2 \mathrm{d}r \int_0^{2\pi} \mathrm{d}\phi \int_{-1}^{1} [g(r) - 1] \cos(krz) \mathrm{d}z \\
&= \frac{4\pi\rho}{k} \int_0^\infty r [g(r) - 1] \sin(kr) \mathrm{d}r
\end{aligned}$$

In the same way we can evaluate the inverse Fourier transform

$$\begin{aligned}
g(\vec{k}) - 1 &= \frac{1}{8\pi^3 \rho} \int [S(\vec{k}) - 1] \cos(\vec{k} \cdot \vec{r}) \mathrm{d}\vec{k} \\
&= \frac{1}{2\pi^2 r\rho} \int_0^\infty k [S(k) - 1] \sin(kr) \mathrm{d}k
\end{aligned}$$

$S(k)$ from simulations

$S(\vec{k})$ in simulations can be calculated directly by the same code as the k-space part of the Ewald summation. If needed, we may sphericalize it:

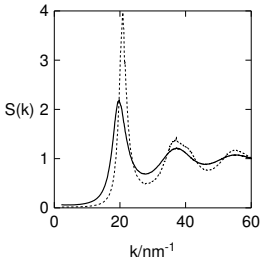
$$S(k) = \sum_{k=|\vec{k}|} S(\vec{k}) / \sum_{k=|\vec{k}|} 1$$

$S(k)$ can be obtained by the inverse Fourier transform of $g(r)$. The RDF $g(r)$ must have a long range and/or it has to be filled (by 1) for long distances.

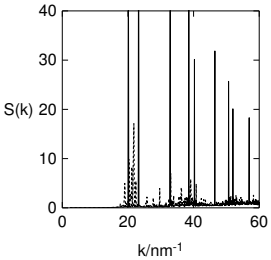
If one wishes, 3D $S(\vec{k})$ can be obtained by the inverse Fourier transform from RDF $g(\vec{r})$ and vice versa

- Simulation-based $S(k)$ for a mixture (where individual site-site RDFs need not be available) allows for a direct comparison with the experiment
- $S(k)$ and $S(\vec{k})$ may detect unwanted crystallization of a supercooled system

Structure factor



— liquid - - - glass ($T = 0$)



— crystal - - - crystallite
(both cooled to $T = 0$)

Structure factor for multiatomic systems

Structure factor for a “mixture” of atoms (b_j = coherent scattering length)

$$S(k) = 1 + N\frac{\langle|Q(\vec{k})|^2\rangle - \sum_j b_j^2}{\left(\sum_j b_j\right)^2}$$

$$Q(\vec{k}) = \sum_j b_j \exp[-2\pi i\vec{k}\cdot\vec{r}_j/L]$$

$$S = \sum_I \sum_J w_{IJ} S_{IJ}, \quad w_{IJ} = \frac{N_I b_I N_J b_J}{(\sum_I N_I b_I)^2}$$

N_I = number of atoms of type I ($\sum_I N_I b_I = \sum_j b_j$)

Reverse Monte Carlo

Input: experimental RDF

Output: $u(r)$ so that the RDF is best reproduced

Not unique – other conditions on $u(r)$ needed