

Correlation functions

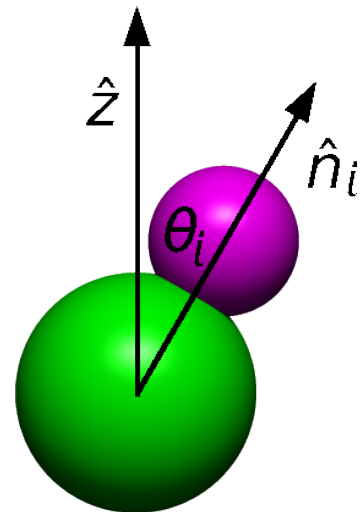
- radial distribution function (RDF, also pair correlation/distribution function), $g(r)$ = probability of finding a particle at distance r (from another particle), normalized to ideal gas
- structure factor (diffraction \rightarrow Fourier transform of $g(r)$)
- angular correlation function – good for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

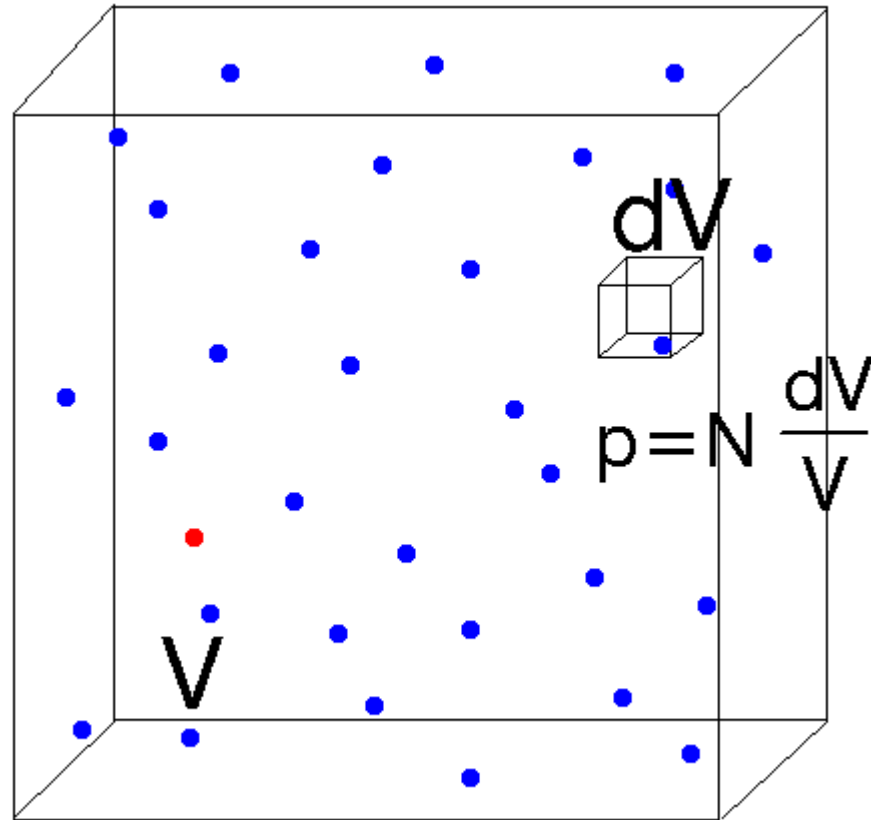
Order parameters

- Ordering in the z-direction: $\langle \sum_i \cos \theta_i \rangle$: \uparrow vs. \downarrow
- For symmetric molecules: $\langle \sum_i \left(\frac{3}{2} \cos^2 \theta_i - \frac{1}{2} \right) \rangle$: \uparrow vs. \leftrightarrow
- Nematic liquid crystal – the “director” is not known:

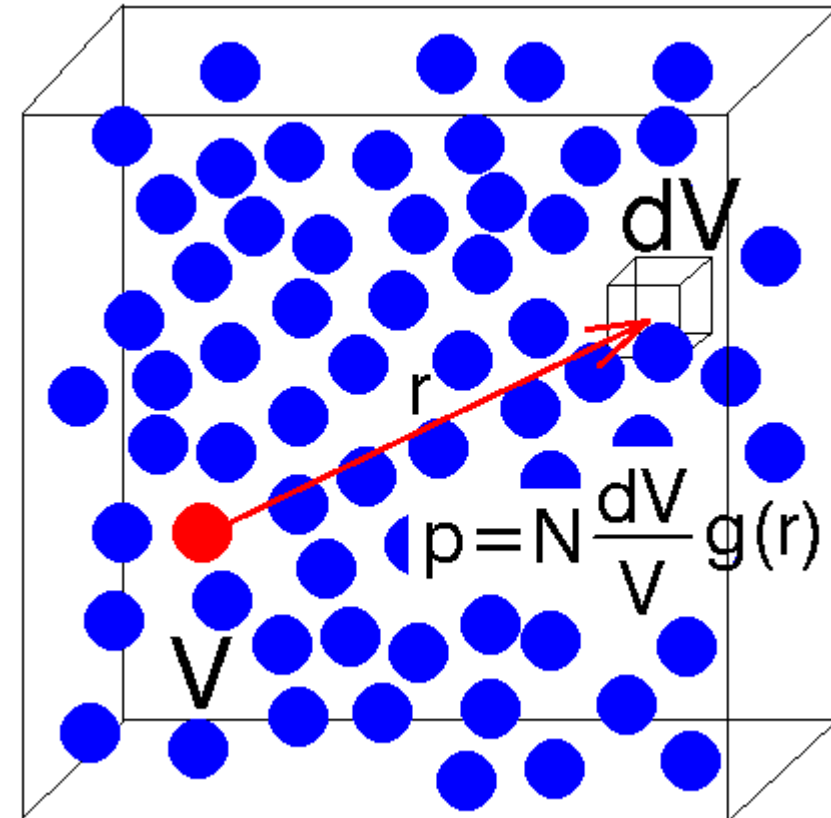
$$Q_{\alpha\beta} = \left\langle \sum_i \left(\frac{3}{2} \hat{n}_{\alpha,i} \hat{n}_{\beta,i} - \frac{1}{2} \delta_{\alpha\beta} \right) \right\rangle, \quad \text{eigenvector of the max. eigenvalue} = \text{director}$$

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



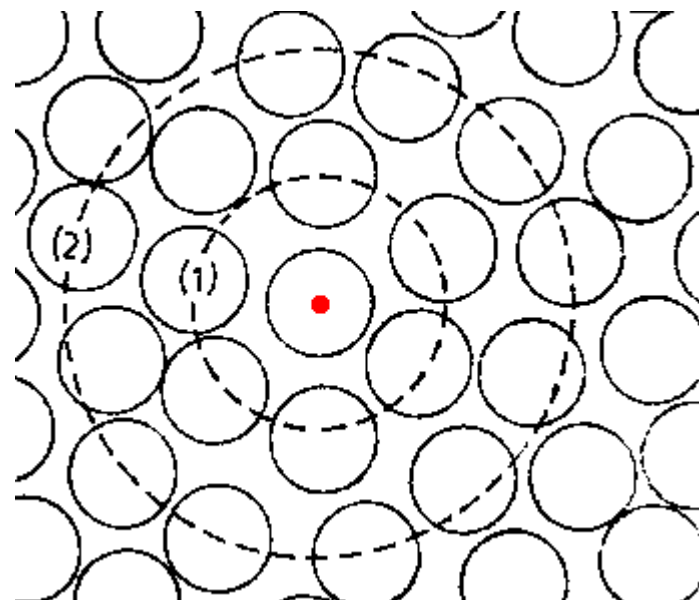
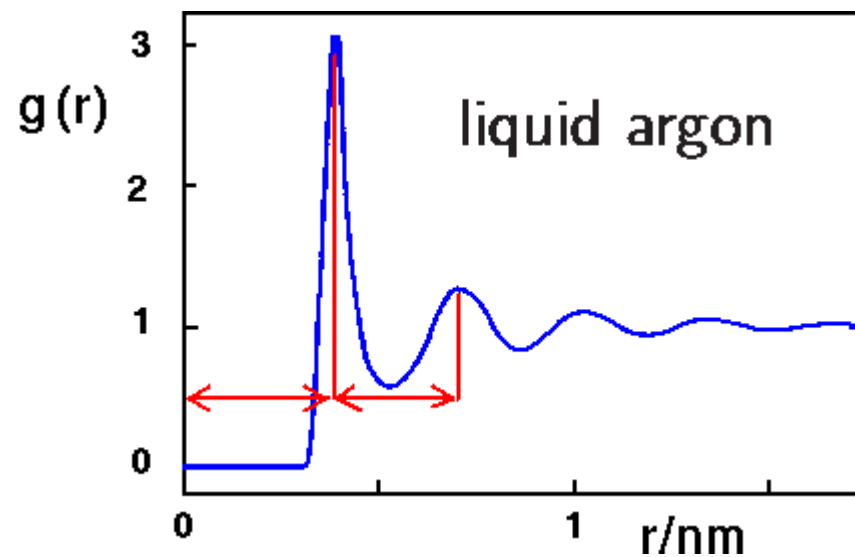
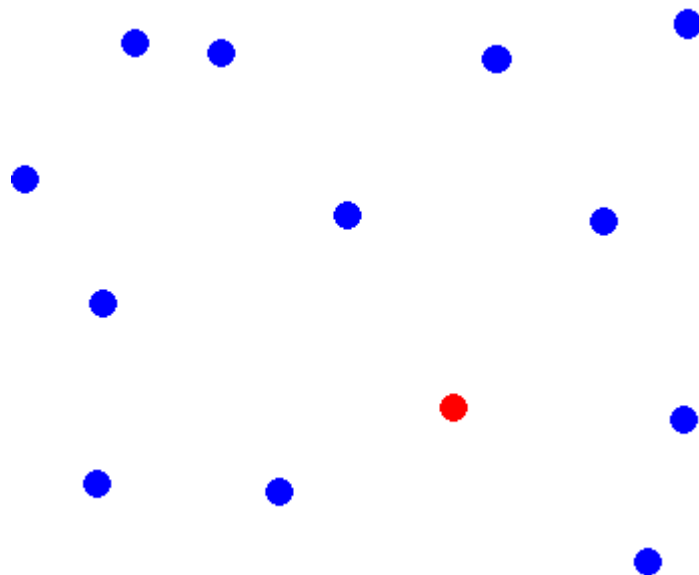
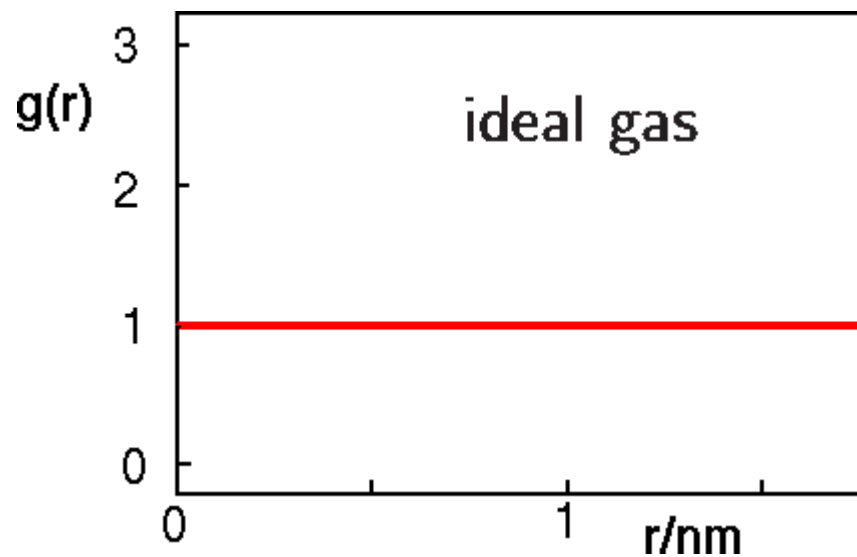


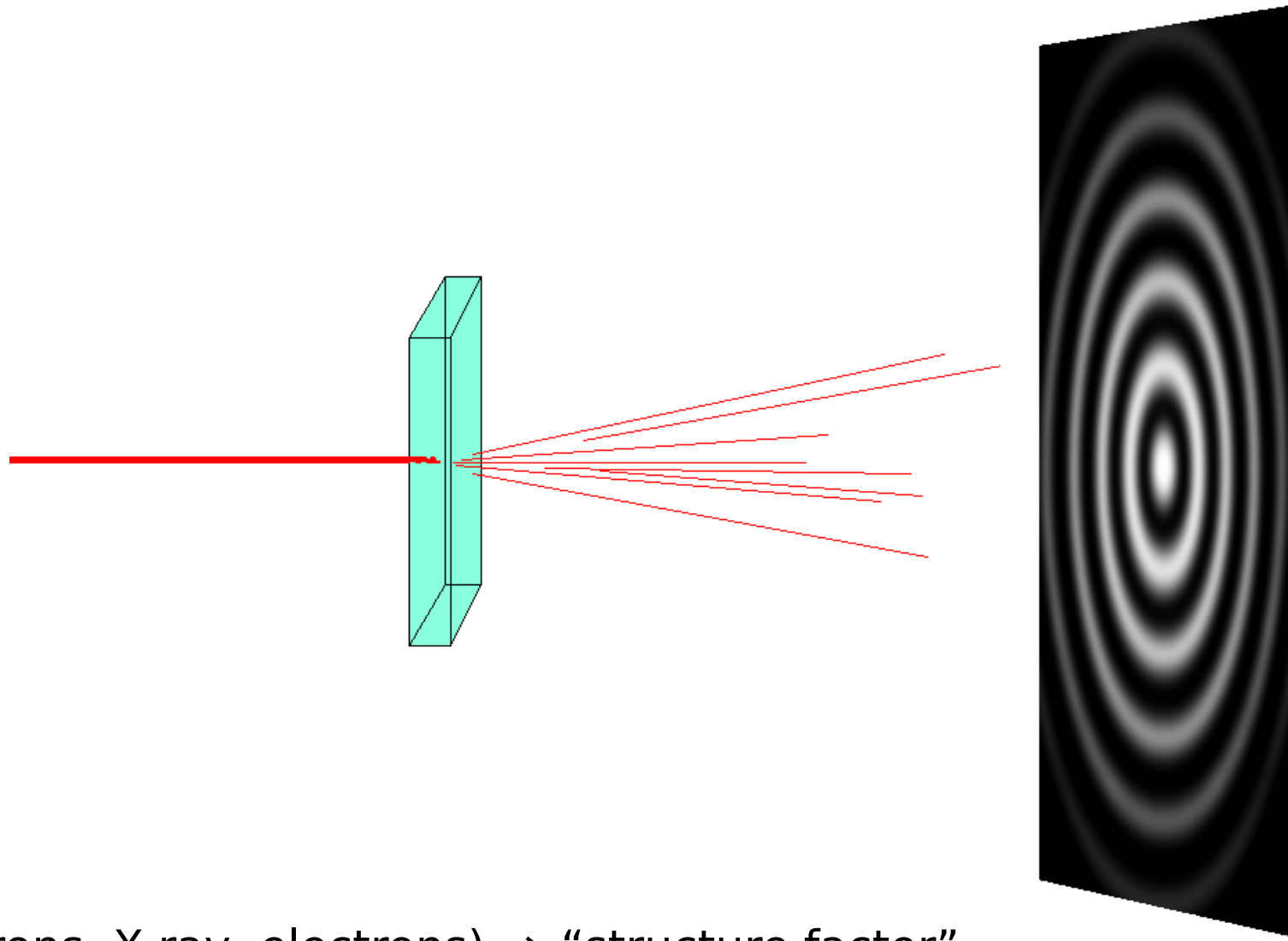
randomly distributed molecules
(ideal gas)



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



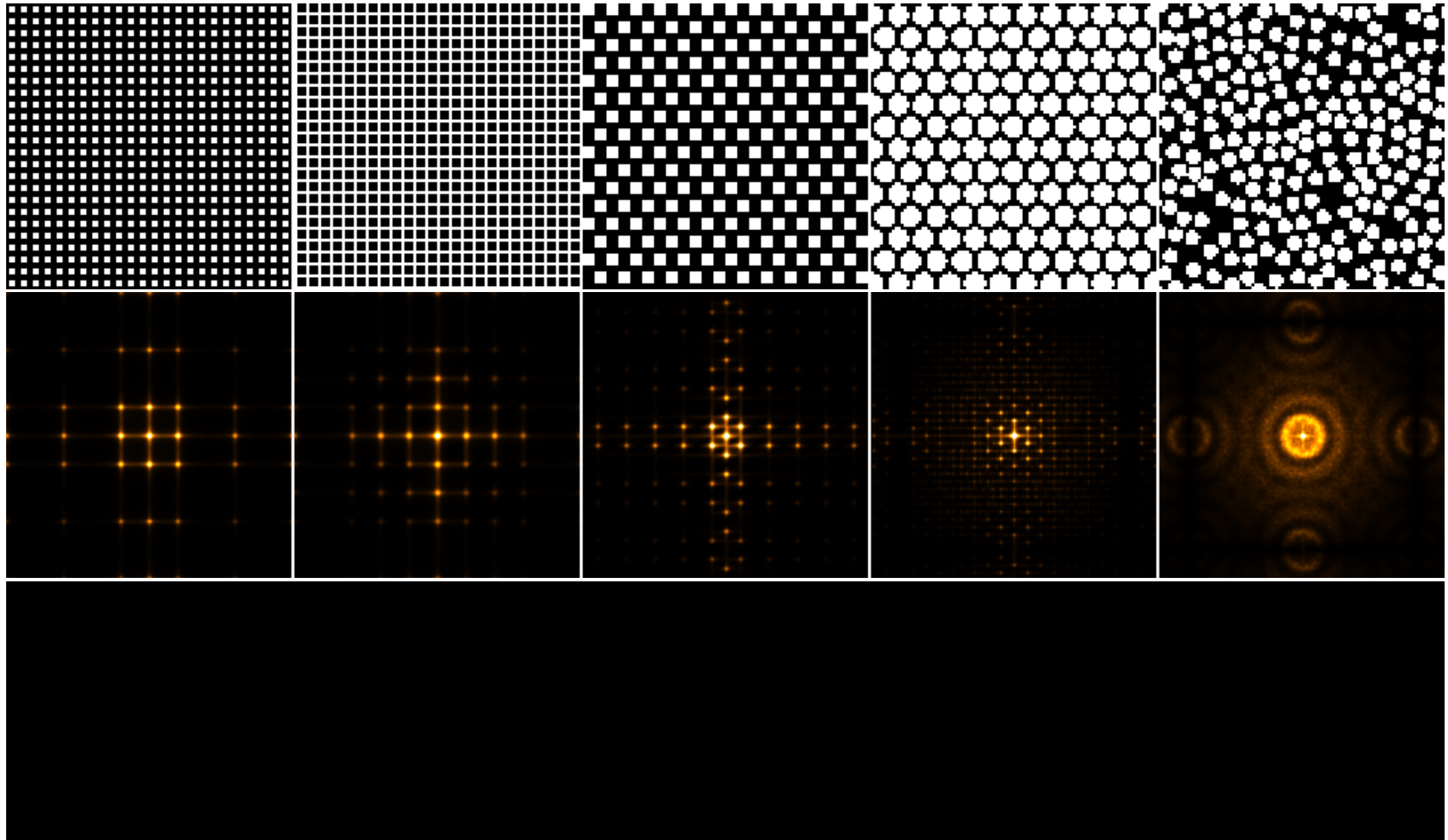


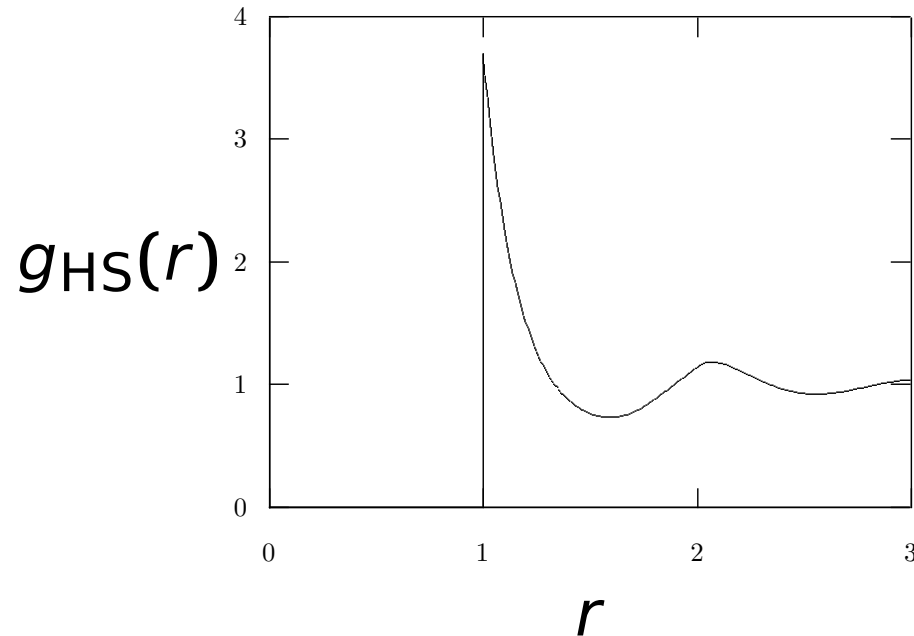
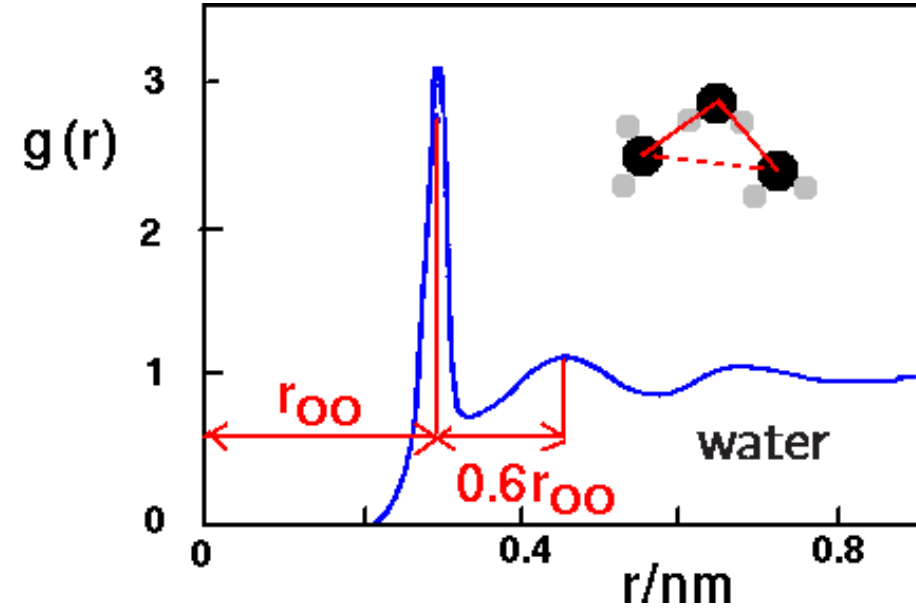
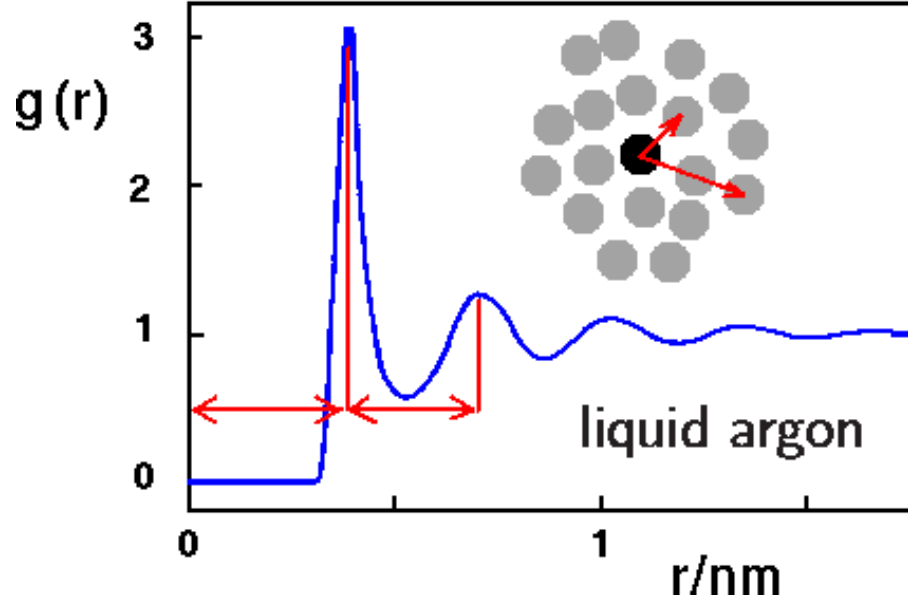
● Diffraction (neutrons, X-ray, electrons) \Rightarrow “structure factor”

● inverse Fourier transform \Rightarrow RDF

How to obtain structure

5/22
s08/3





- 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

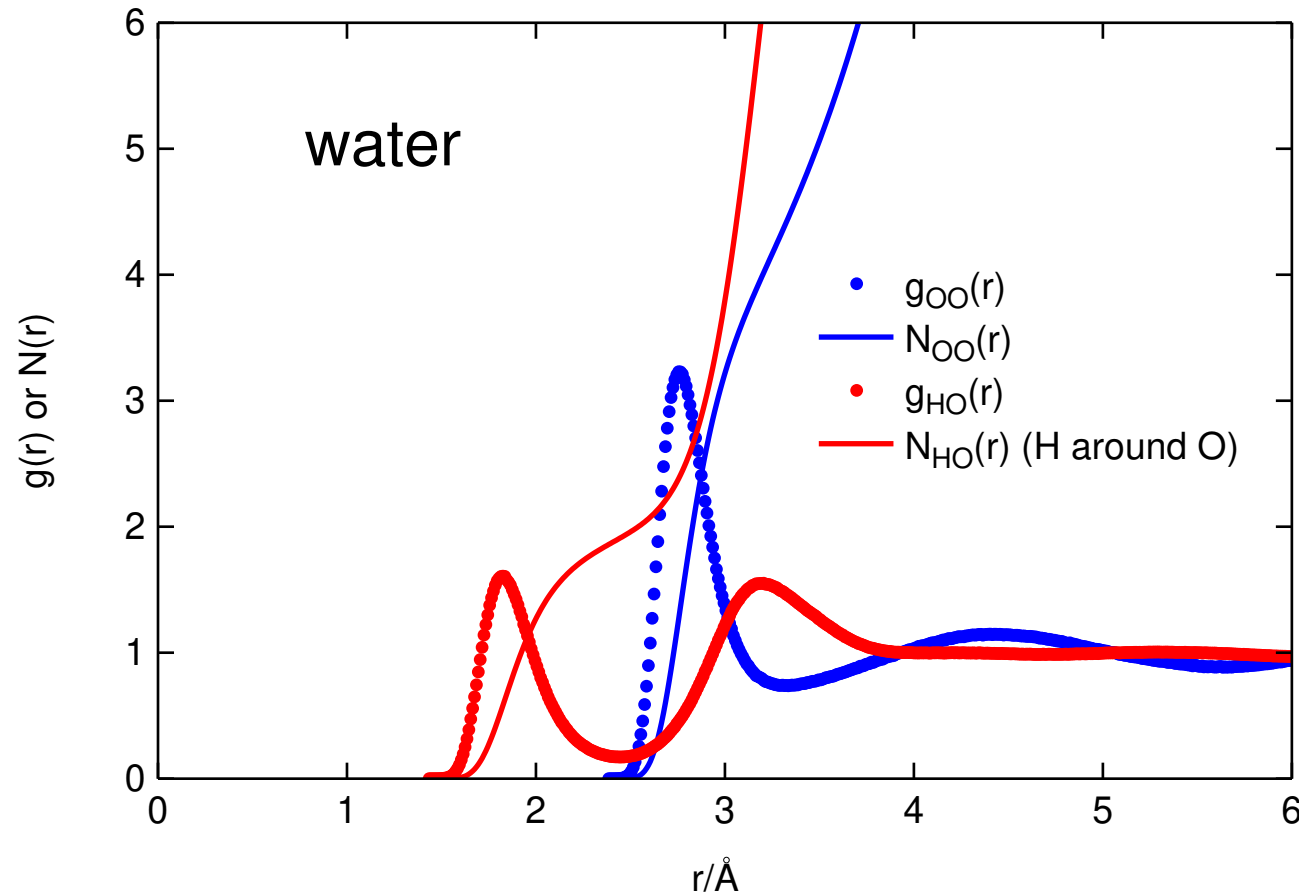
7/22
s08/3

Also “cumulative radial distribution function”

$\rho = N/V =$ number density

$$N(r) = 4\pi\rho \int_0^r g(r')r'^2 dr'$$

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

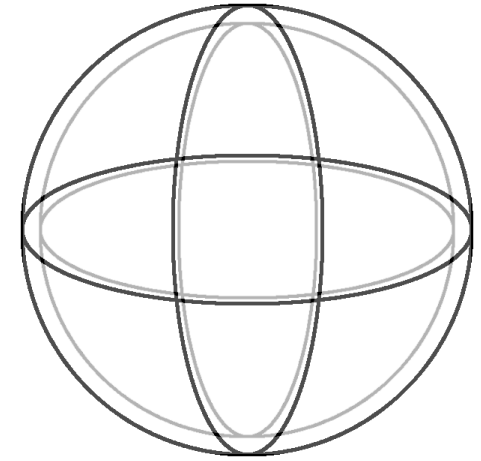


Histogram of the number of particle pairs, \mathcal{N}_i , so that

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

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:

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

- <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`

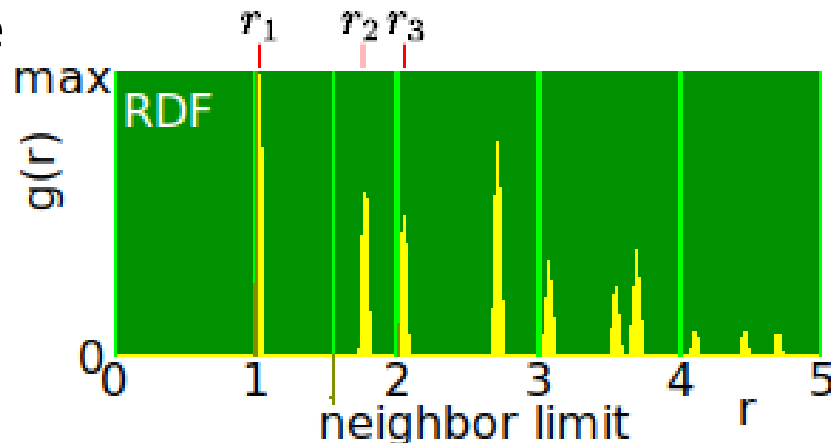
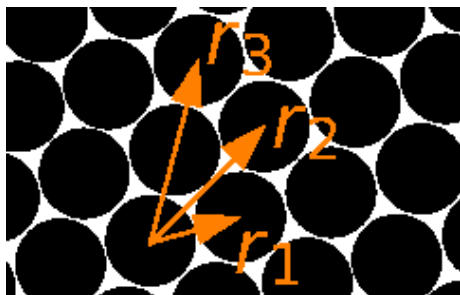
Hint: The calculated data are exported to file `simolant.txt` with a decimal point. If you like decimal comma (useful with Czech localization), click , in panel “Measure”.

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

- 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 →



A screenshot of the Simolant software interface. The main window shows a simulation box with black spheres representing particles. A red arrow points to the top of the box with the text "Boundary conditions → Periodic". The right-hand side contains a control panel with various parameters and sliders. The parameters section shows: N=56, T=1.0000, $\tau=1.000$, L=16.73, $\rho=0.2$, g=0.000, stride*block=3*100. The walls section shows N=56. The expert section has a "reco" button and a "cmd: [N=56]" field. The bottom section has sliders for "temperature", "density", and "simulation speed", and a "max" slider for "measurement block".

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

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

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

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):

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

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):

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

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

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

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

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

The formula again:

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

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

Residual internal energy:

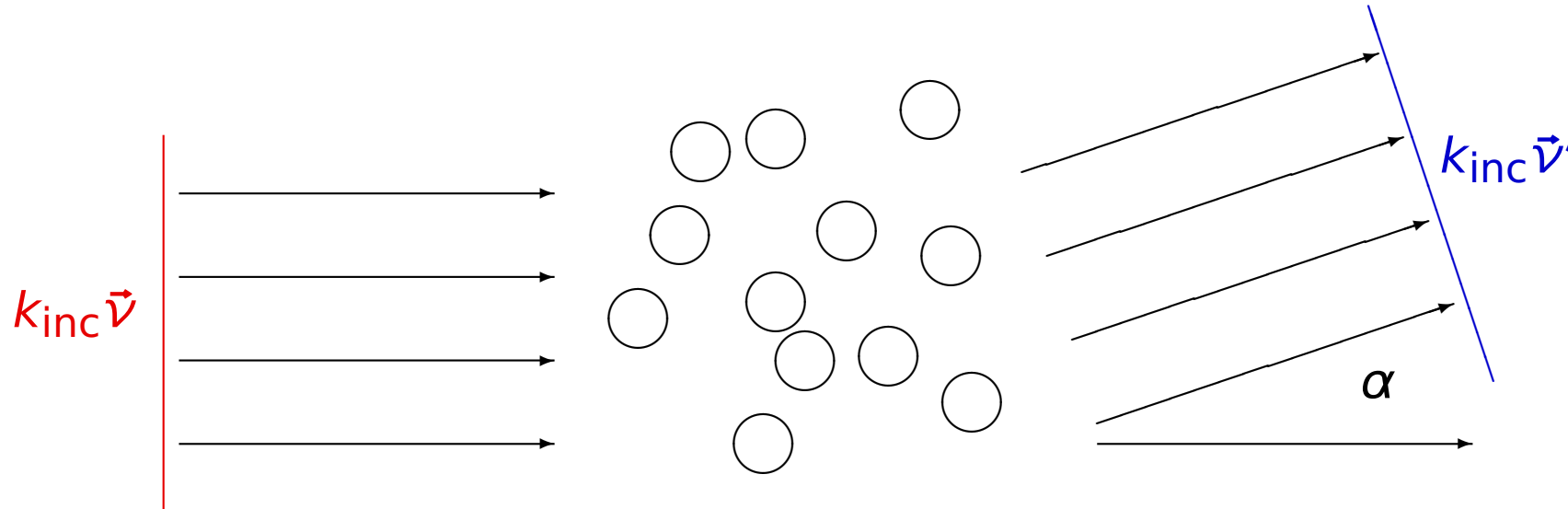
$$\langle U \rangle = \frac{1}{Q_{\text{NVT}}} \int \sum_{i < j} u_{ij}(r_{ij}) e^{-\beta U} d\vec{r}_1 \dots d\vec{r}_N$$

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

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

Pressure:

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



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

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

where

$$\vec{k} = k_{\text{inc}} \vec{v} - k_{\text{inc}} \vec{v}', \quad k = |\vec{k}| = 2 \sin(\alpha/2) k_{\text{inc}} \approx \alpha k_{\text{inc}}$$

Waves scattered by all atoms interfere:

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

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 :

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

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

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

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

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

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

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

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

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

and the 3D inverse Fourier transform is

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

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

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

The $k \rightarrow 0$ limit:

$$NVT: S(0) = 0$$

$$\mu VT: S(0) = 1 + \rho \int [g(\vec{r}) - 1] d\vec{r} = k_B T \left(\frac{\partial \rho}{\partial p} \right)_T \quad (\text{compressibility equation})$$

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)

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

In the same way we can evaluate the inverse Fourier transform

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

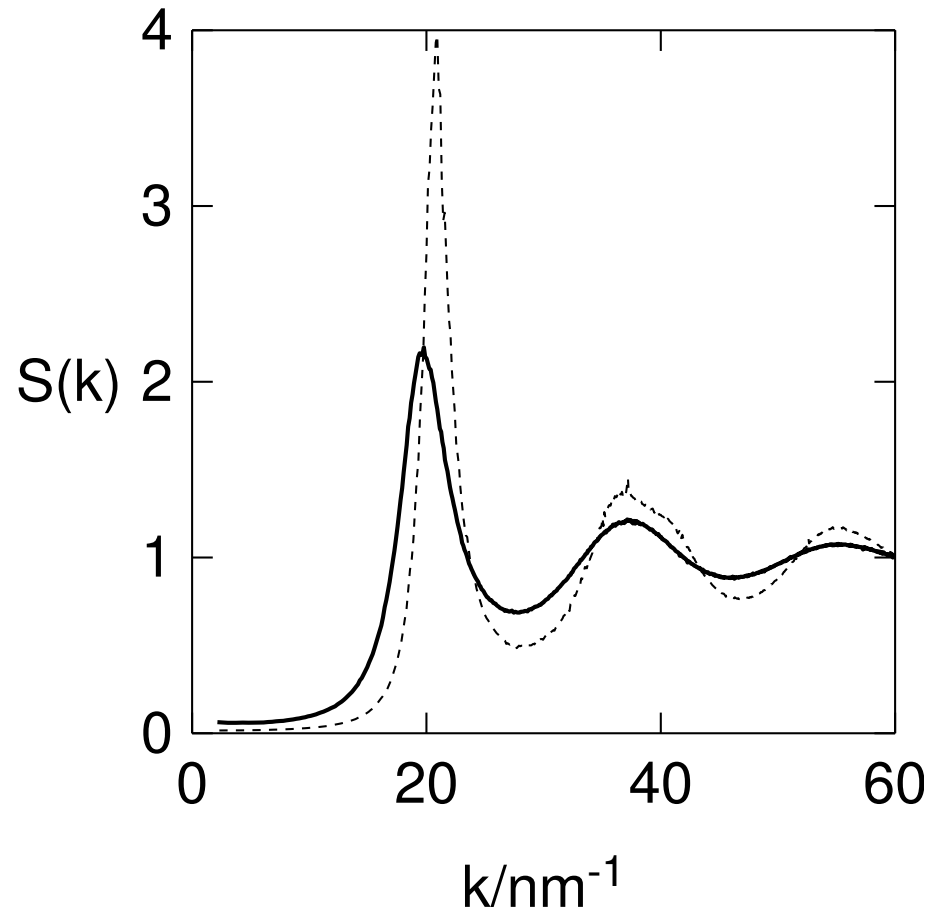
$S(\vec{k})$ in simulations can be calculated directly by the same code as the k-space part of the Ewald summation. If needed, we may sphericalize it:

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

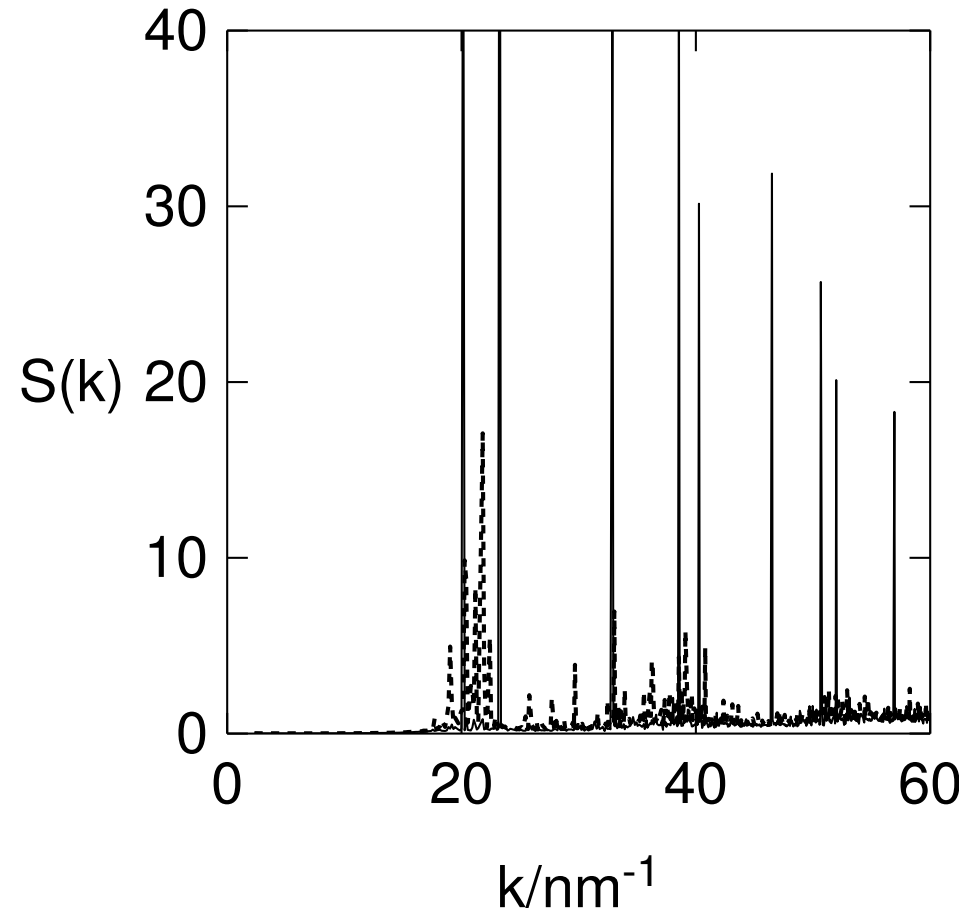
$S(k)$ can be obtained by the inverse Fourier transform of $g(r)$. The RDF $g(r)$ must have a long range and/or it has to be filled (by 1) for long distances.

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



— liquid - - - glass ($T = 0$)



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

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

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

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

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

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

Input: experimental RDF

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

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