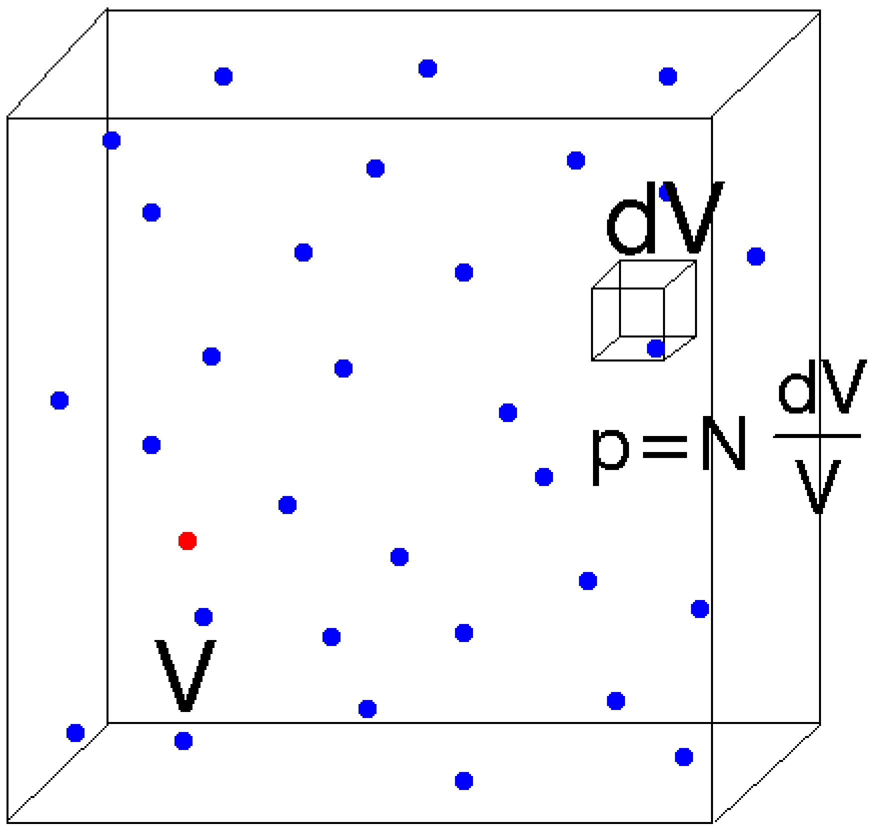
Structural quantities

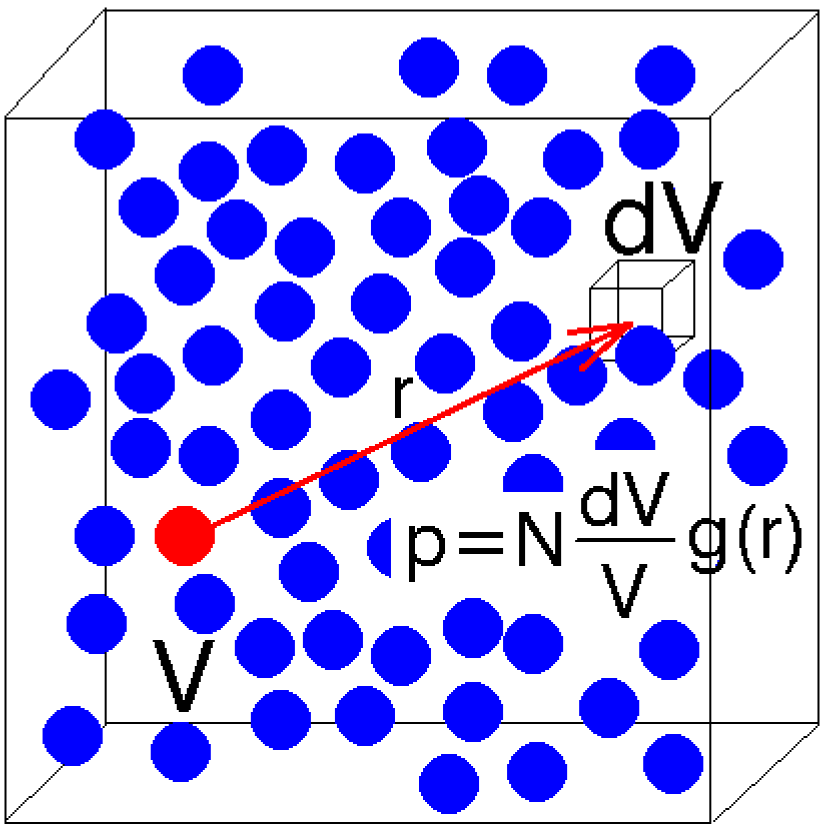
Correlation functions:

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

Structure of fluids – correlation functions



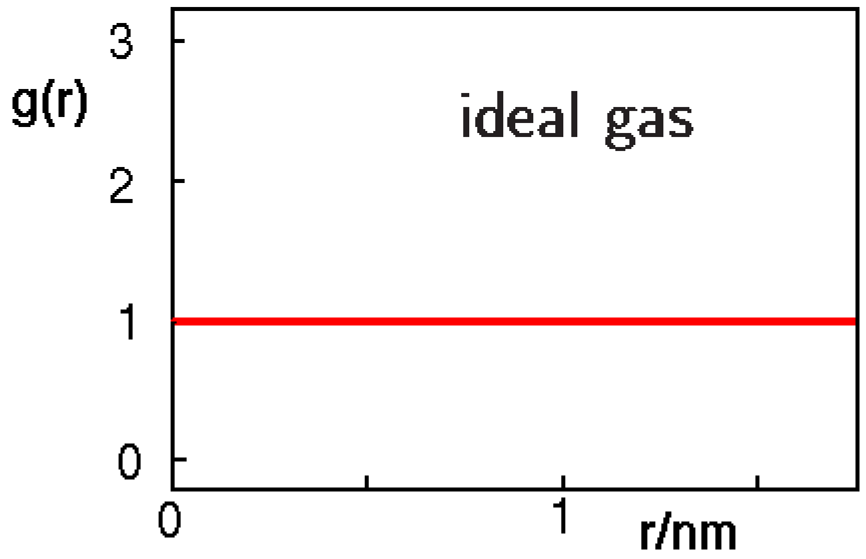
randomly distributed molecules
(ideal gas)

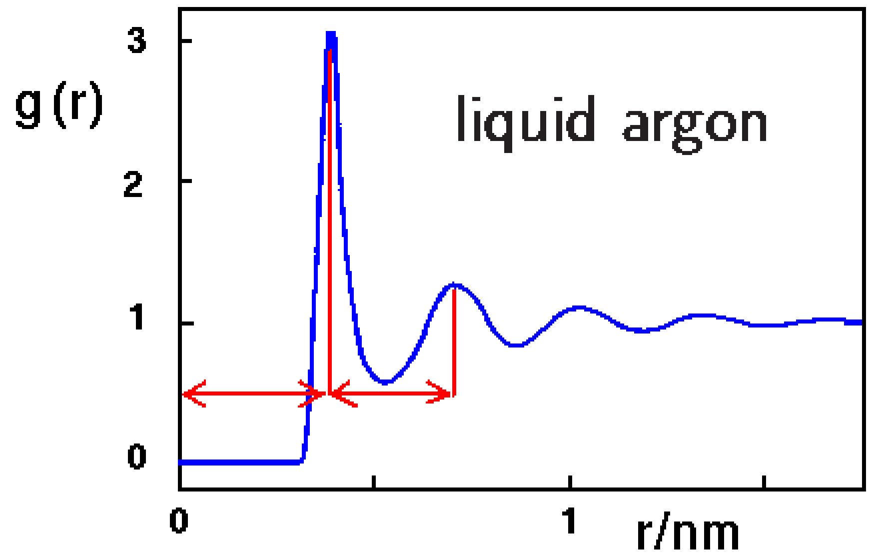


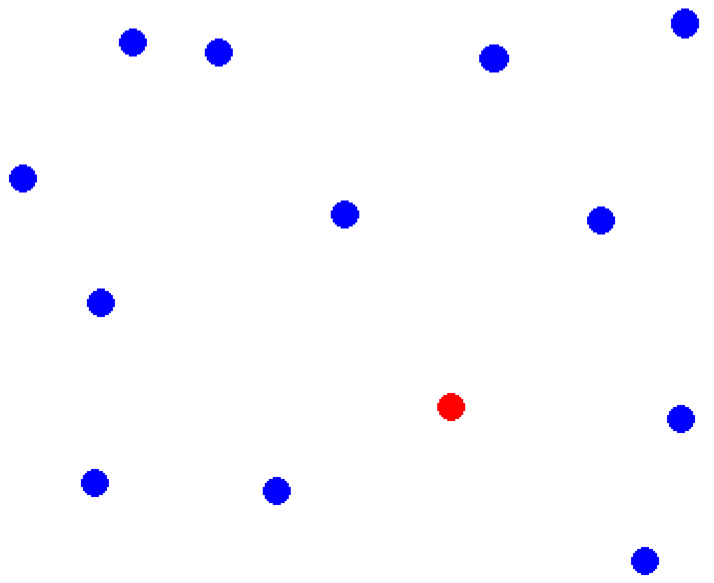
liquid

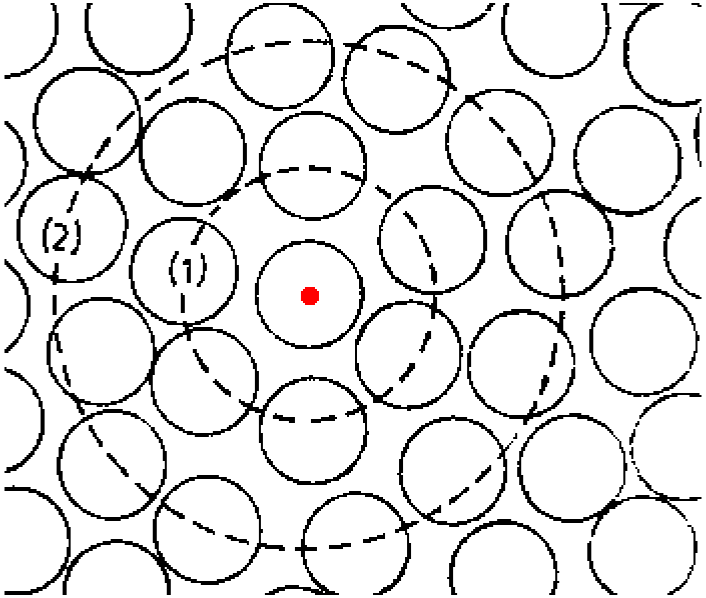
$g(r)$ = pair correlation function = radial distribution function = probability density of finding a particle r apart from another particle, normalized so that for randomly distributed particles (ideal gas) it is 1

Structure of fluids – correlation functions

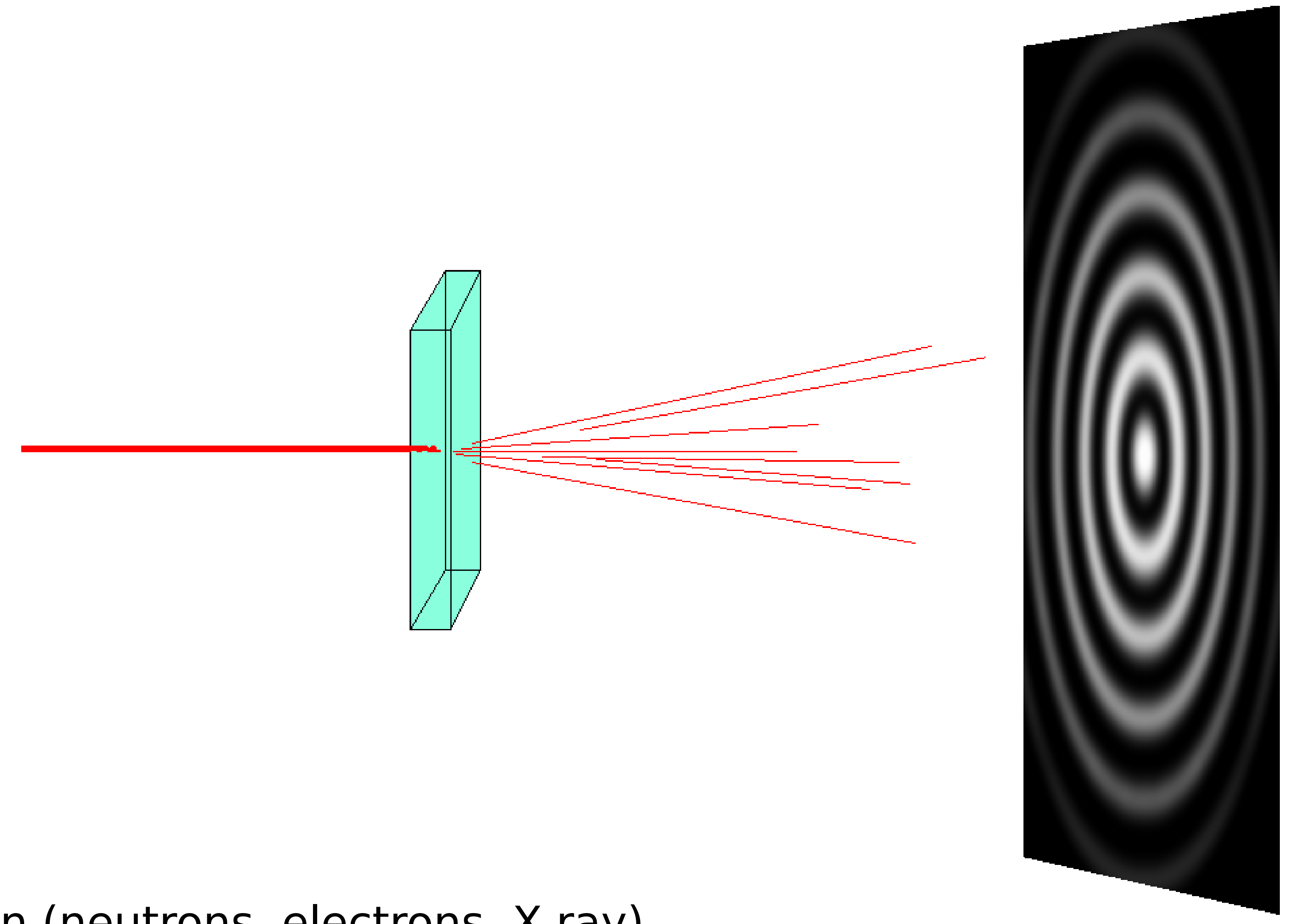






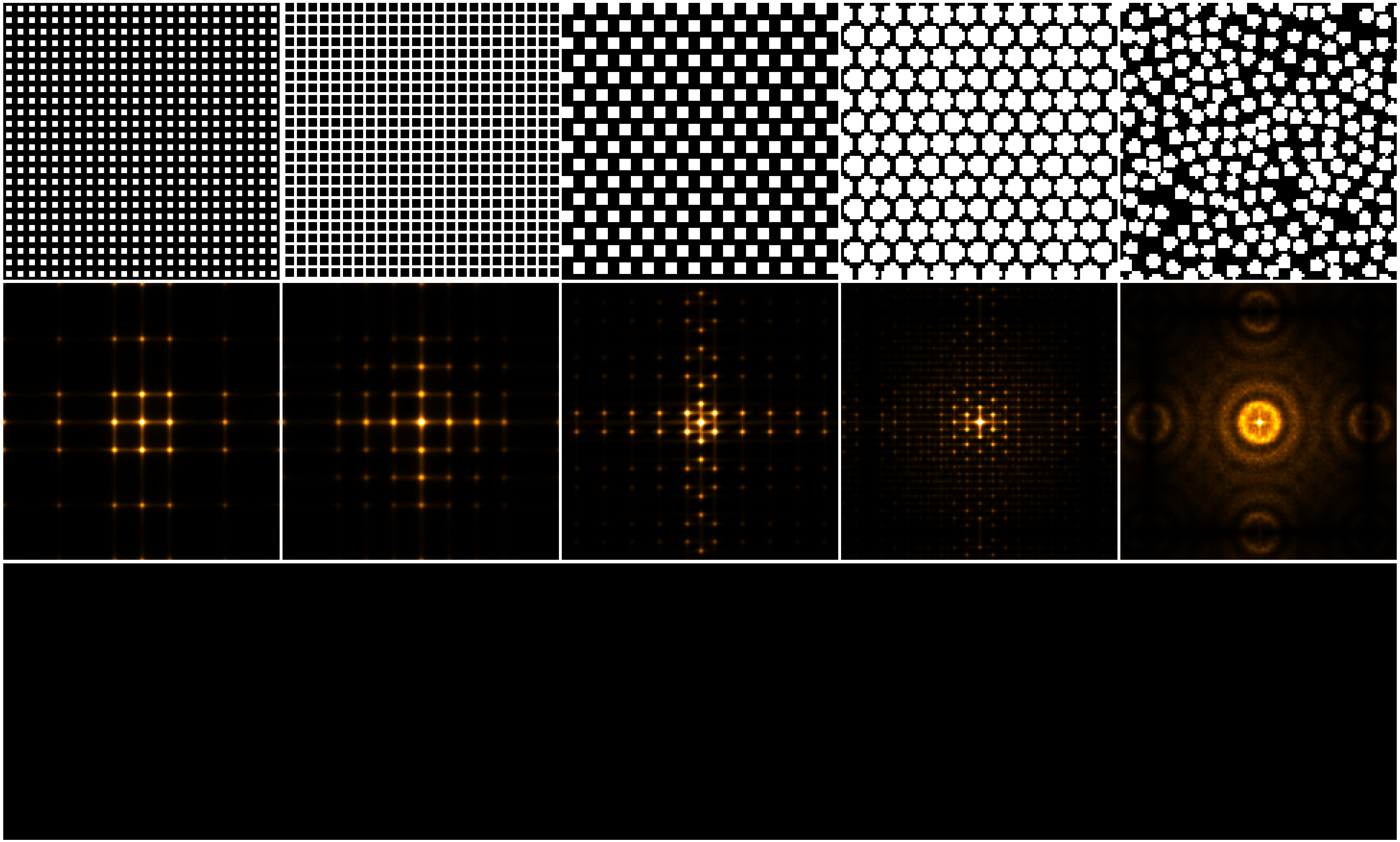


How to obtain structure – experiment

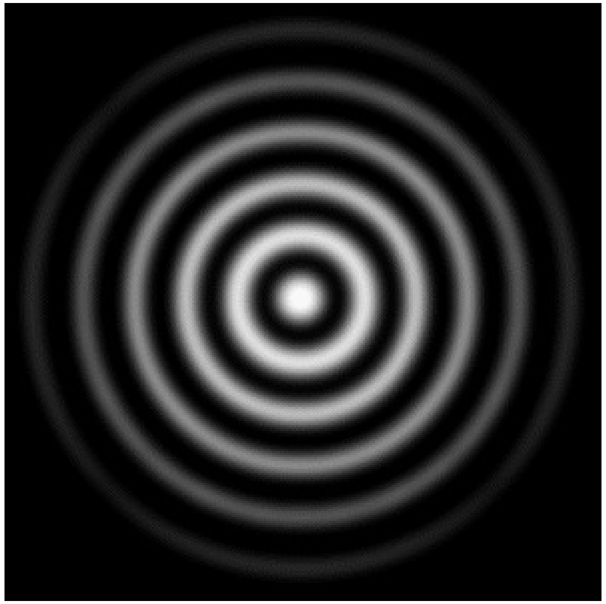


- Diffraction (neutrons, electrons, X-ray)
  ⇒ “structure factor”

How to obtain structure

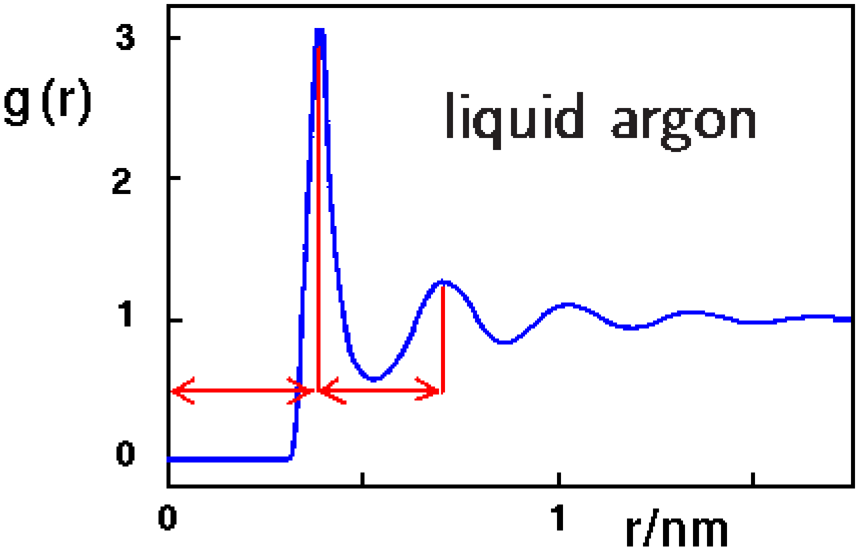


Correlation function from structure factor

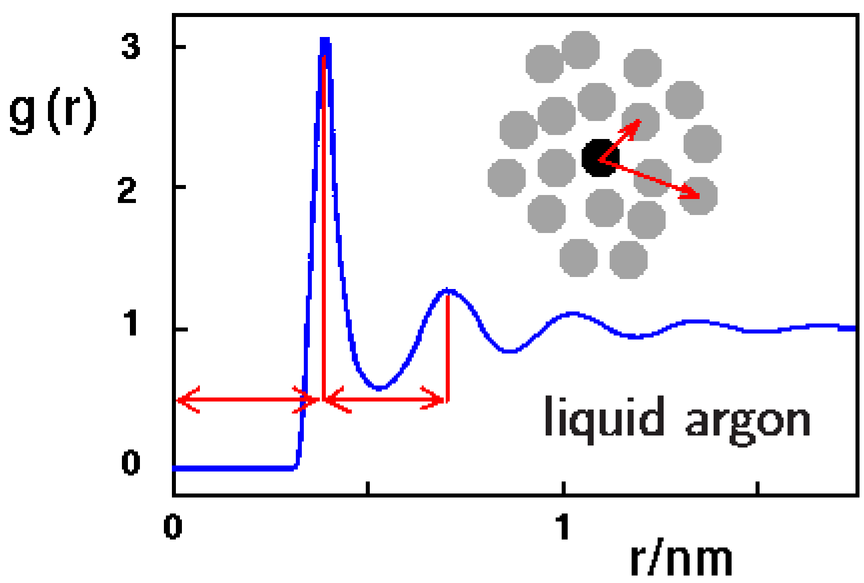


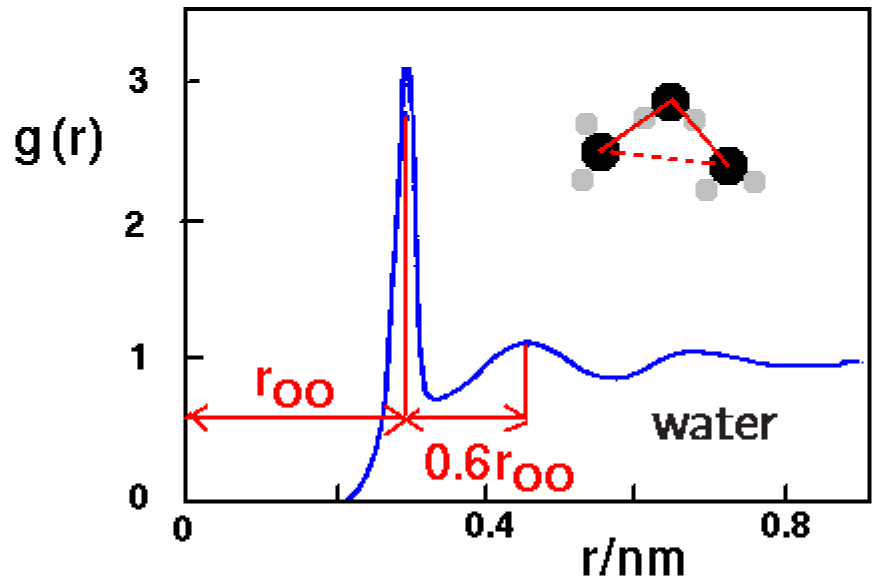
inverse
Fourier
transform

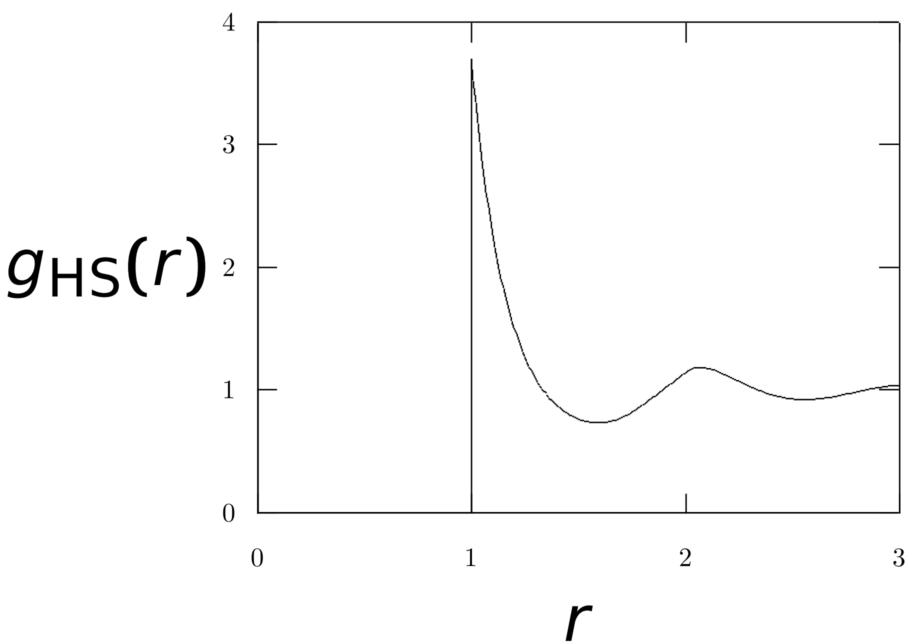
⟶



Argon, hard spheres, water







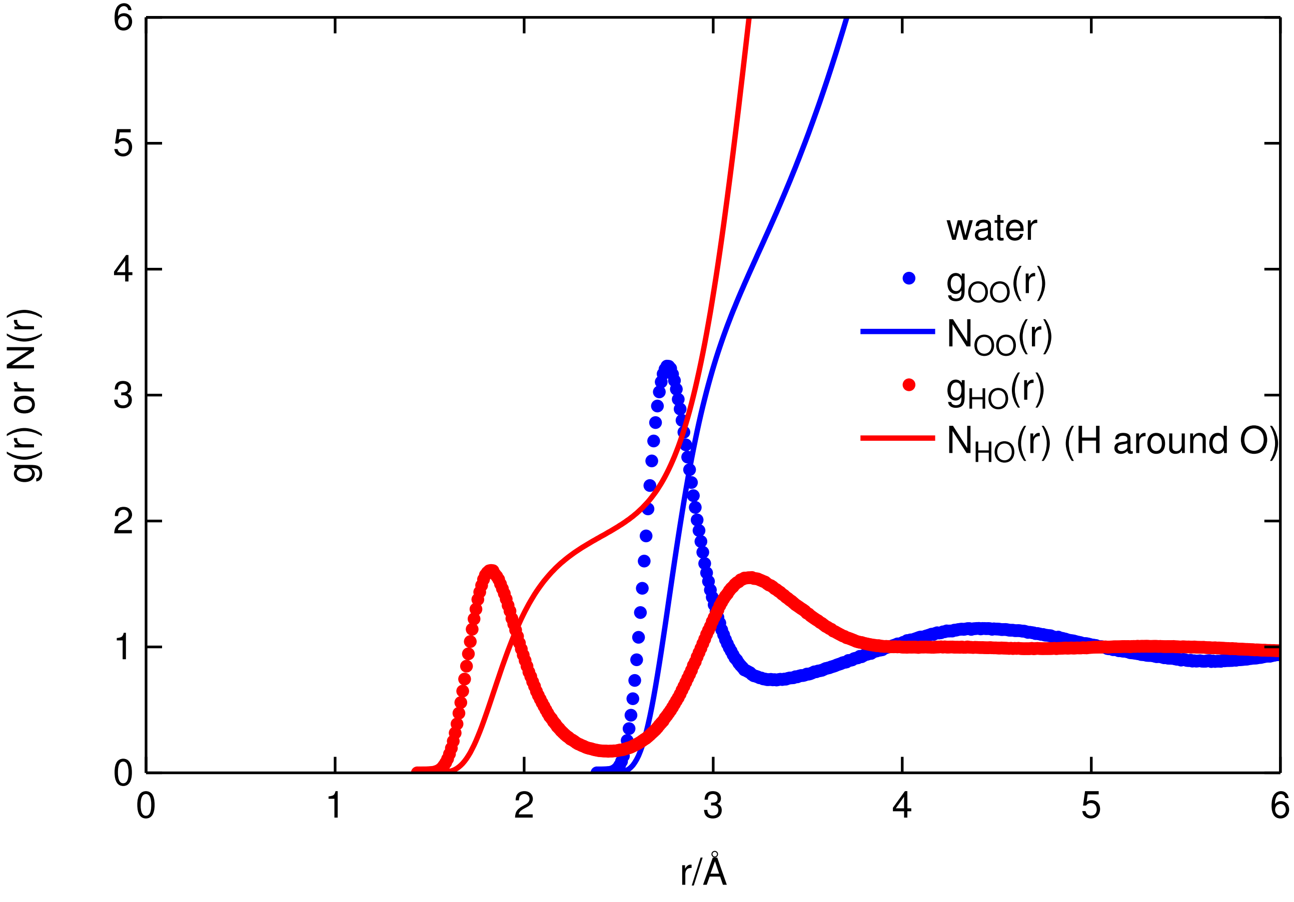
- The structure of simple fluid (argon, HS) is organized by shells.
- The structure of water is determined by the tetrahedral geometry of hydrogen bonds.
- After several molecular diameters, the correlations decay to zero.

Running coordination number

Also “cumulative radial distribution function”

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

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

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

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, $\rho = N/V$):

$$\frac{1}{2}\rho \Delta V_i$$

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:

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

Radial distribution function in the NVT ensemble

3D (e.g., in periodic b.c.):

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

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 $r \in \mathcal{I}_i$

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

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

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

The formula again:

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

For simple fluid with pair forces only:

Residual internal energy:

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

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

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

Pressure:

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