Structural quantities

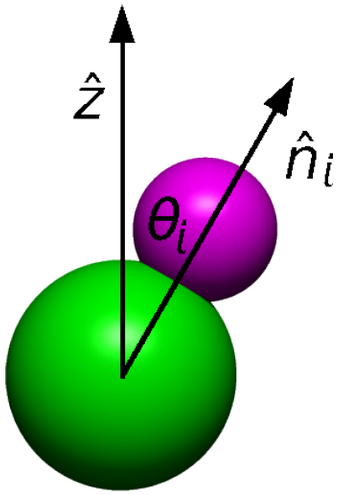
Correlation functions

- 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

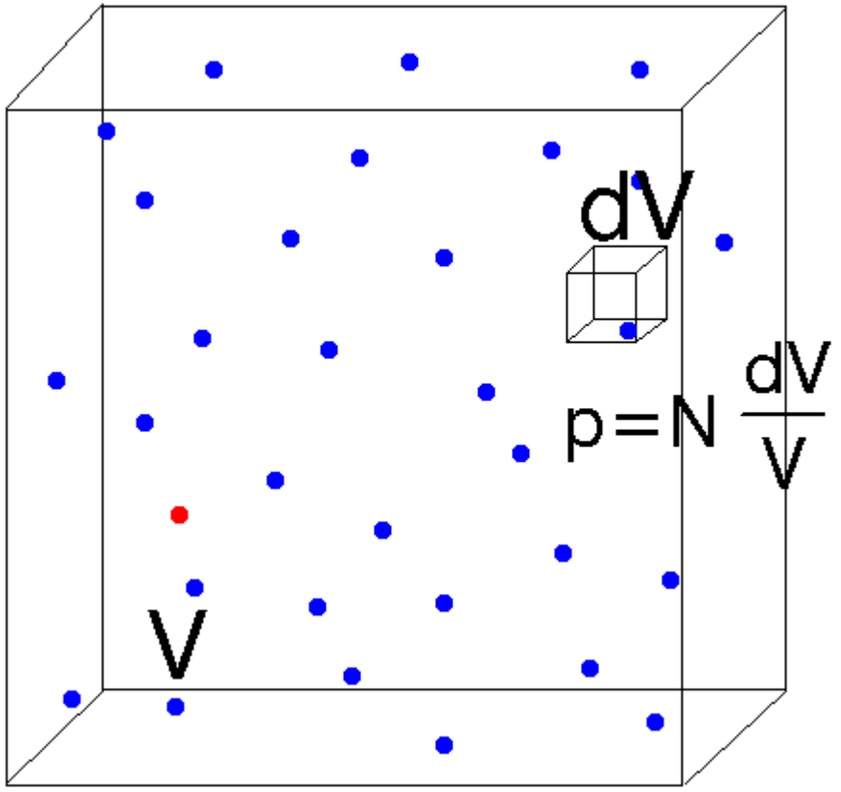
- Ordering in the z-direction: $\left\langle \sum_i \cos\theta_i \right\rangle$: ↑ vs. ↓
- For symmetric molecules: $\left\langle \sum_i \left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2} \right) \right\rangle$: ↕ vs. ↔
- Nematic liquid crystal – the “director” is not known:

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

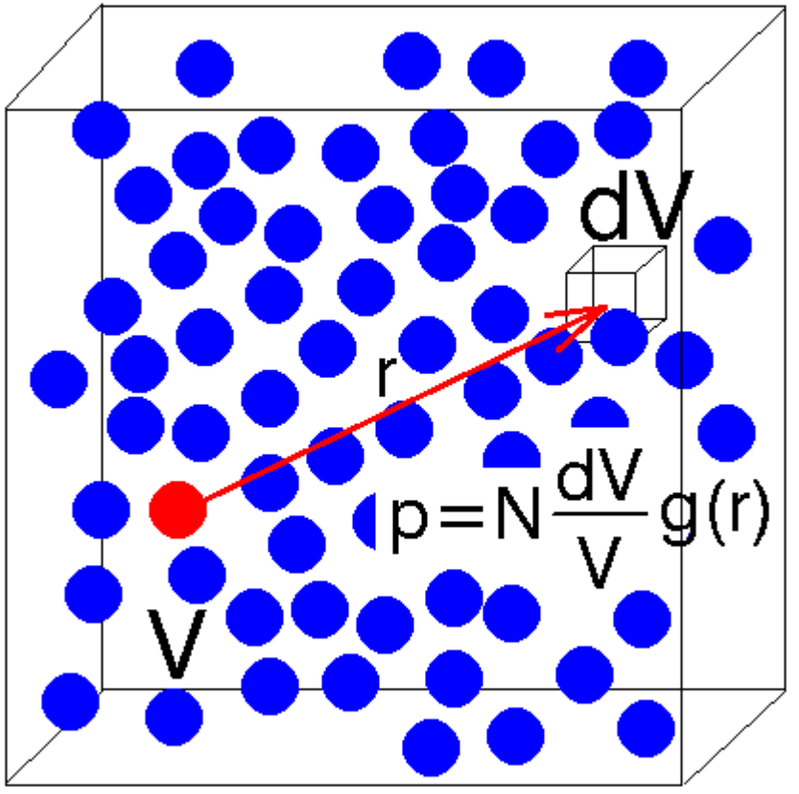


- Formulas detecting local order (e.g., tetrahedral around water molecules), onset of crystallization, etc.

Structure of fluids – correlation functions



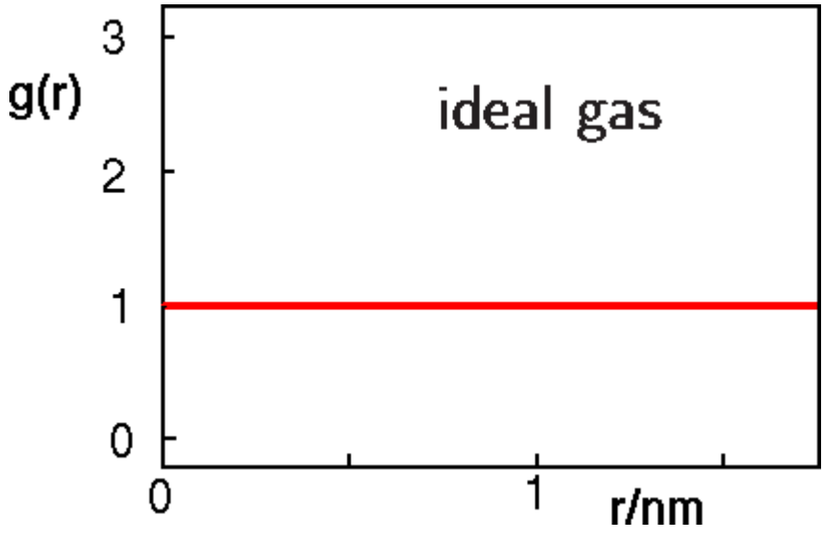
randomly distributed molecules
(ideal gas)

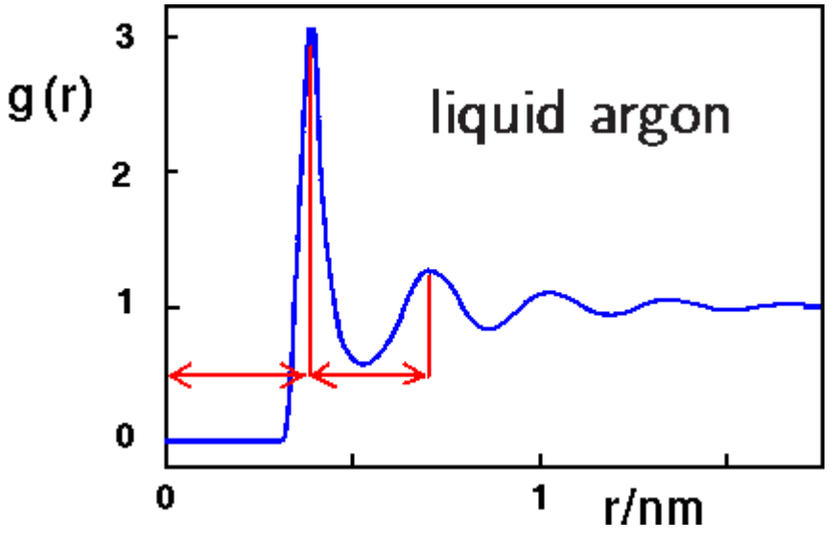


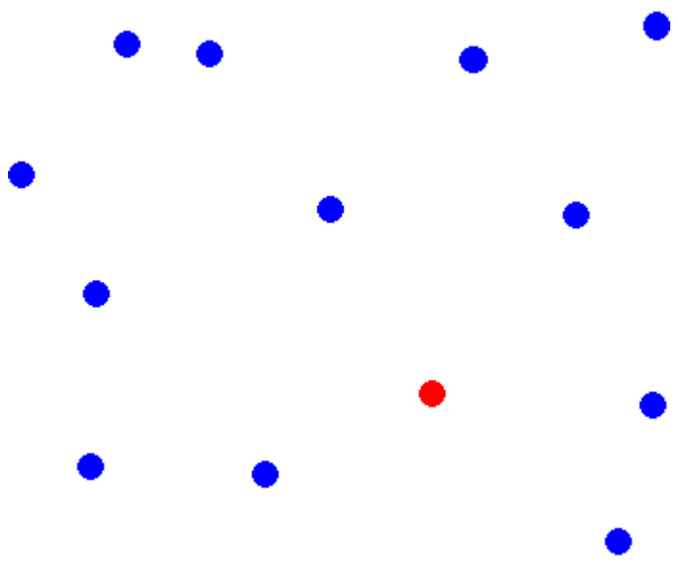
liquid

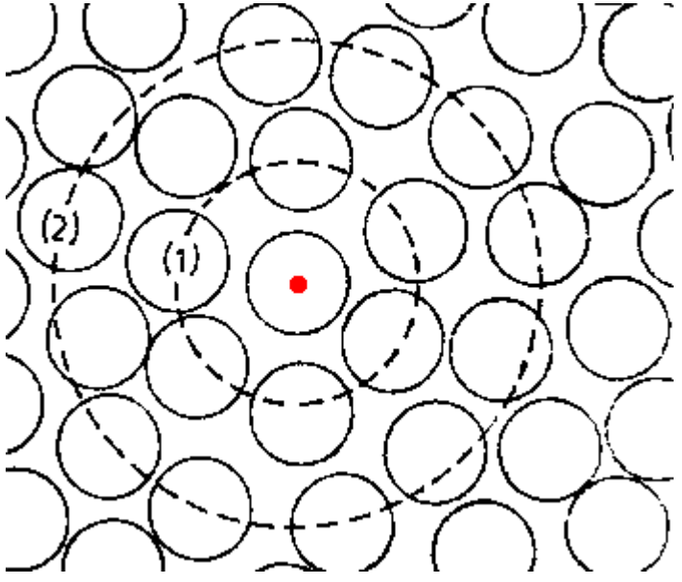
$g(r)$ = pair correlation function = radial distribution function = probability density of finding a particle r apart from another particle, normalized so that for randomly distributed particles (ideal gas) it is 1

Structure of fluids – correlation functions

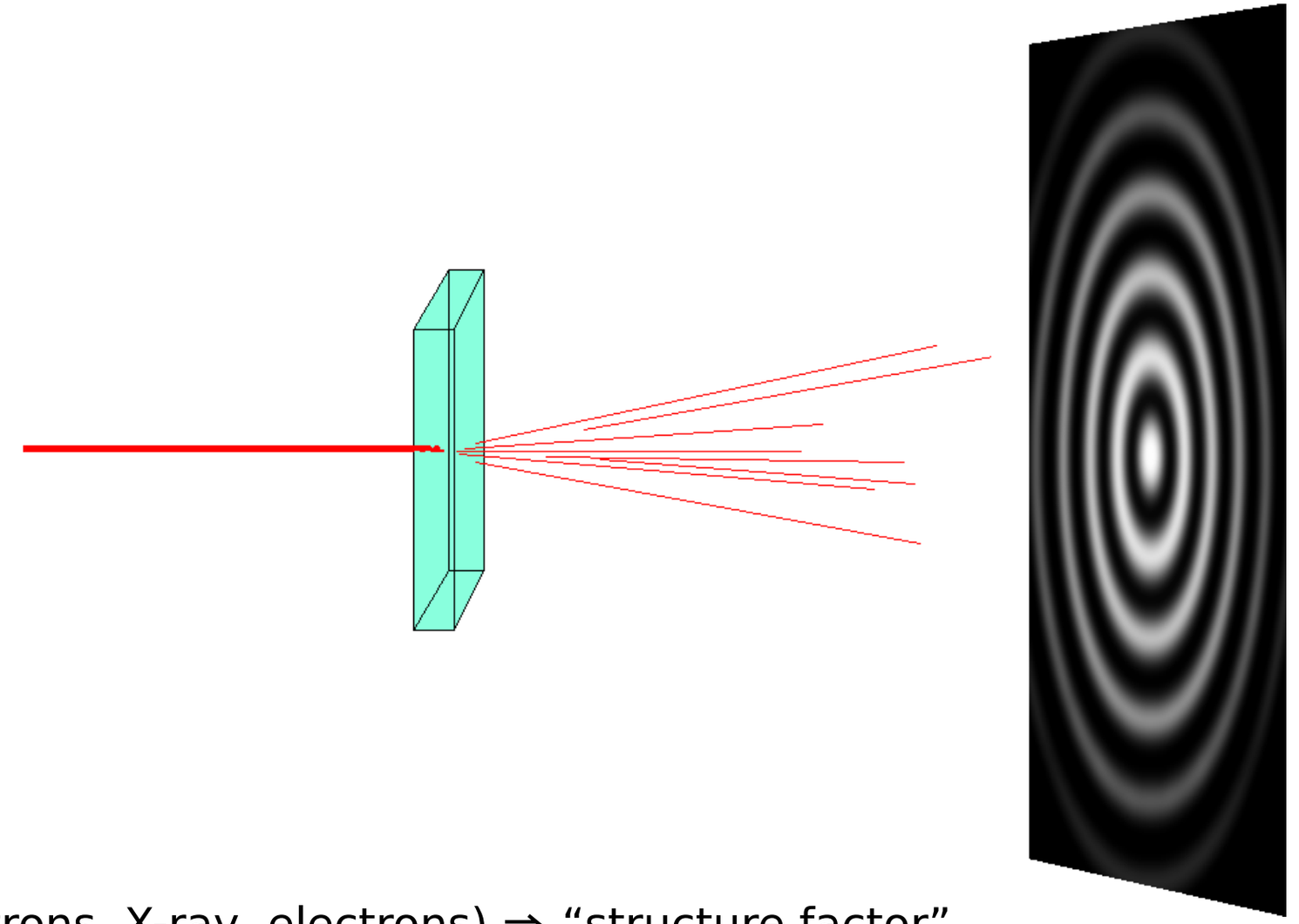






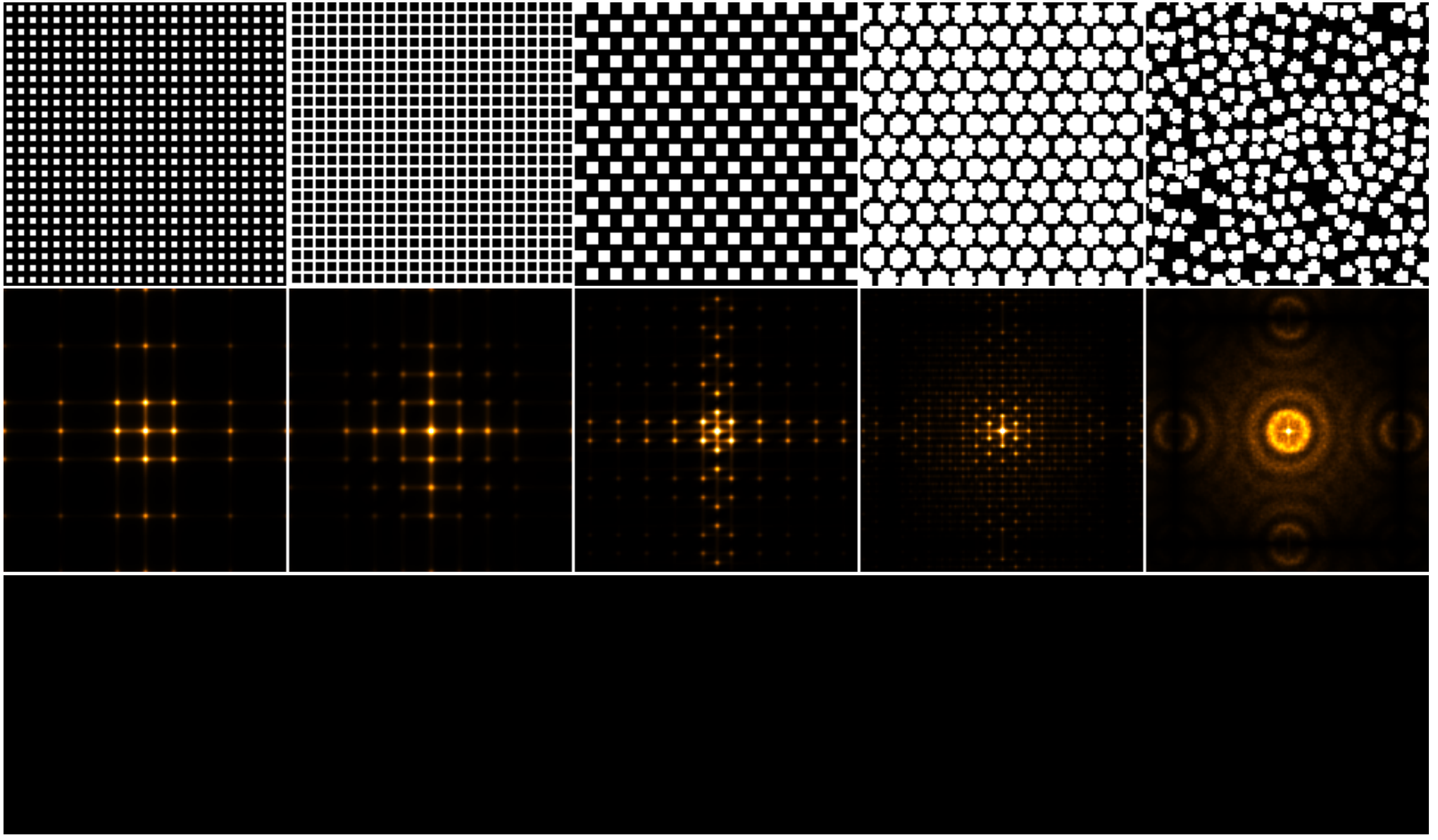


How to obtain structure – experiment

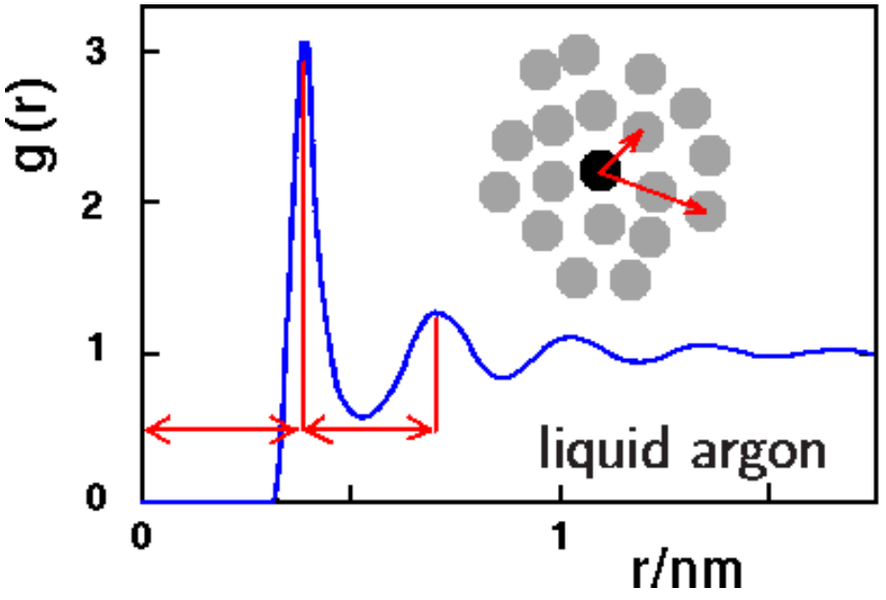


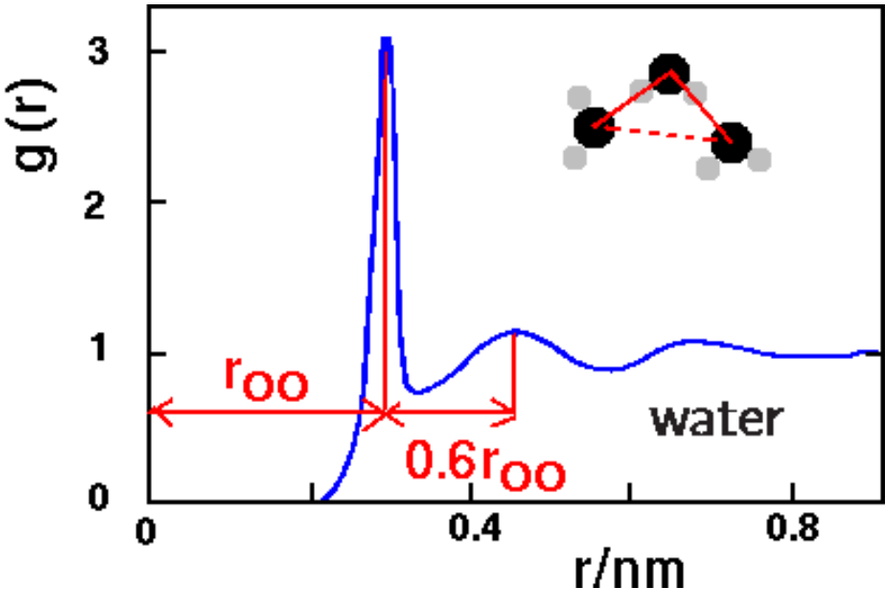
- Diffraction (neutrons, X-ray, electrons) ⇒ “structure factor”
- inverse Fourier transform ⇒ RDF

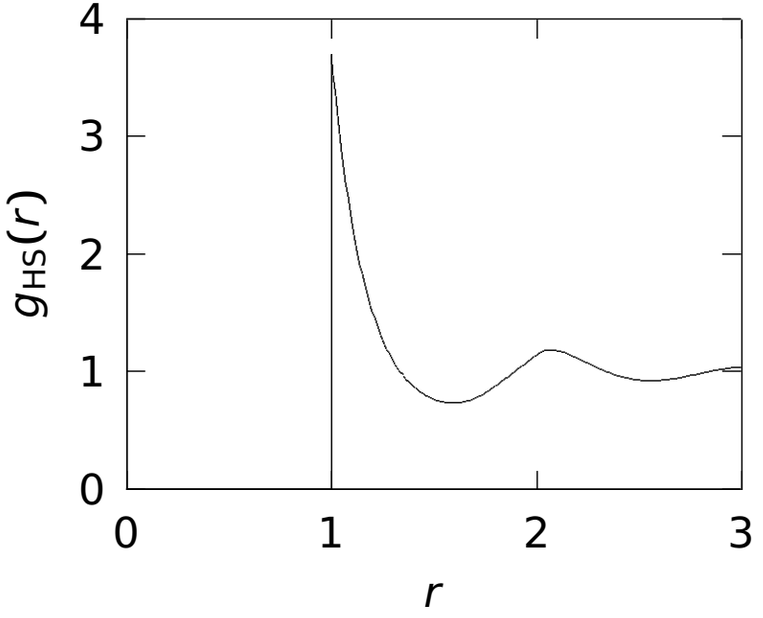
How to obtain structure



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.

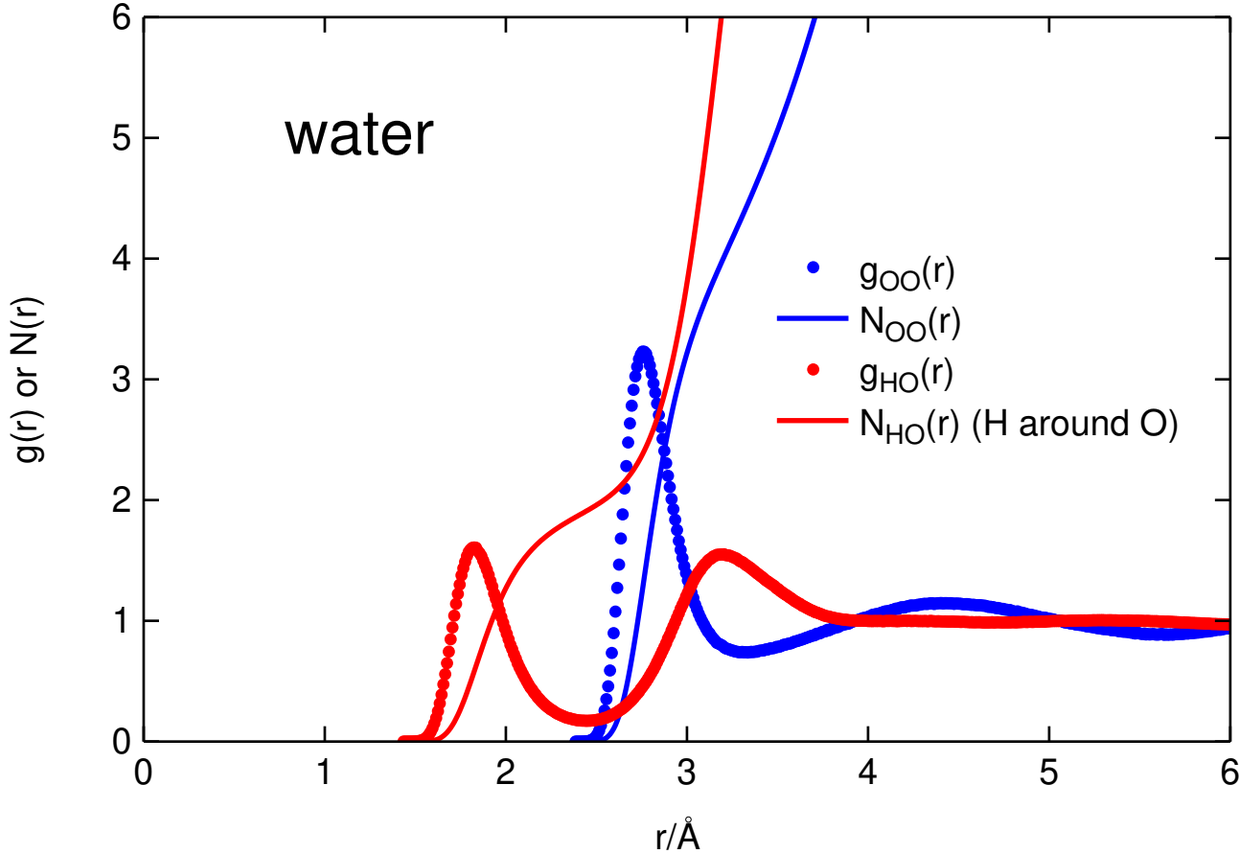
Running coordination number

Also “cumulative radial distribution function”

$\rho = N/V$ = number density

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

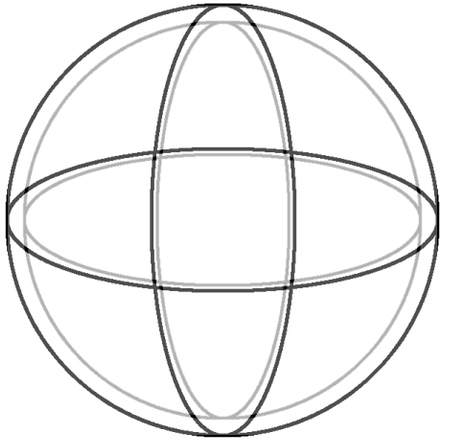
For r_{min} = first minimum on the RDF curve, $N(r_{\mathrm{min}})$ = “coordination number” = averaged number of molecules in the first shell



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)

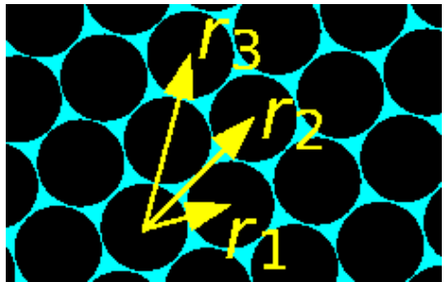
- http://old.vscht.cz/fch/software/simolant
  or Google simolant
- Download `simolant-win32.zip`
- **Create a folder** and unpack SIMOLANT there.
  Do not run directly from `simolant-win32.zip!`
- Run `simolant.exe`

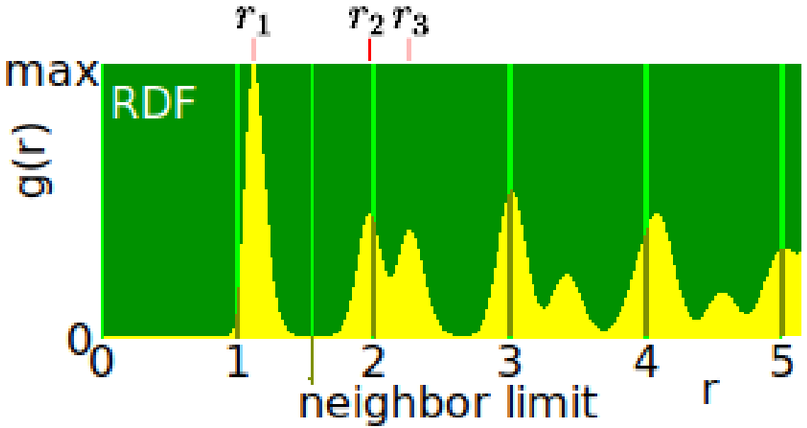
Hint: The calculated data are exported to file `simolant.txt` with a decimal point. If you like decimal comma (useful with Czech localization), click `.,` in panel “Measure”.

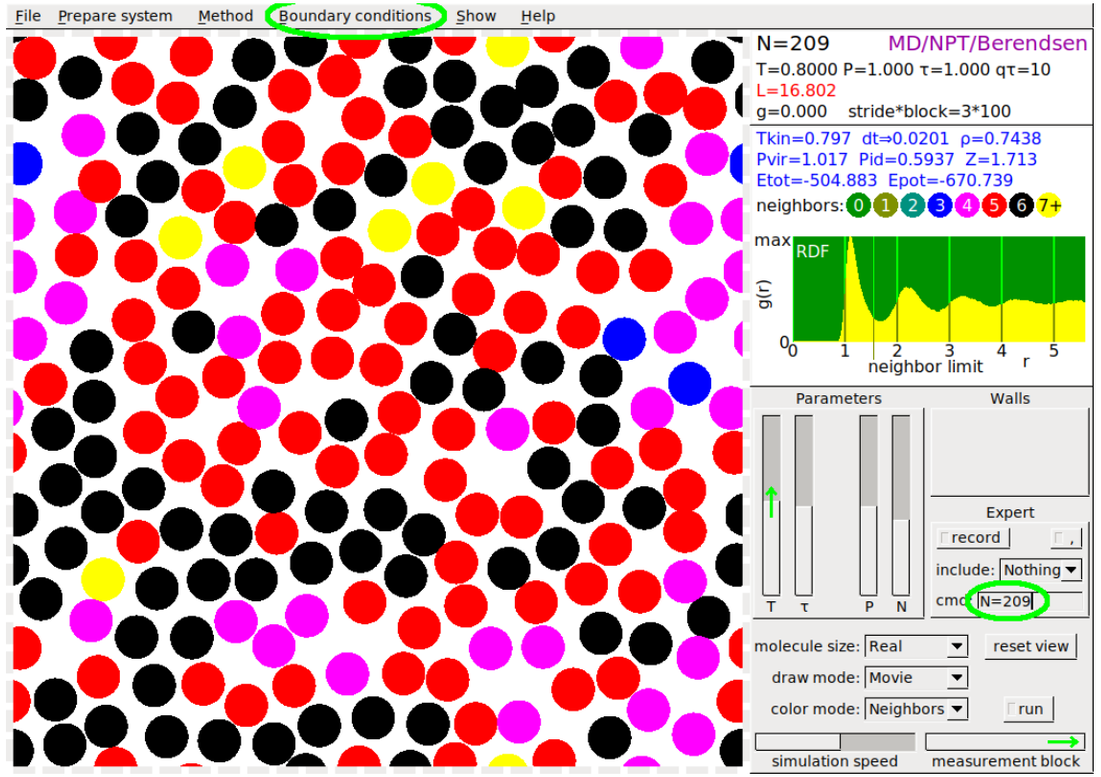
Hint: If you restart SIMOLANT, the old `simolant.txt` is renamed to `simolant.bak`. The export name `simolant` can be changed by Menu: File → Protocol name..

Simolant: observe RDF by yourself

- Menu: Boundary conditions → Periodic
- Menu: Method → Molecular dynamics NPT (Berendsen)
- Type ‘magic number’ N=209 to input field “cmd:” (slow computer: N=56, RDF will be truncated)
- Slide “measurement block” to max, watch $g_{\mathrm{gas}}(r)$
- Hint: Set “color mode” → Neighbors
- Increase temperature (slider “T”) to max ($T = 5$). The first peak should be smaller.
- Decrease temperature; at $T \approx 0.8$, you should observe liquid (may take some time to equilibrate).
- Decrease temperature below 0.4: a crystal should form. Try to heat/cool if there are defects.
- You should get the following RDF →







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