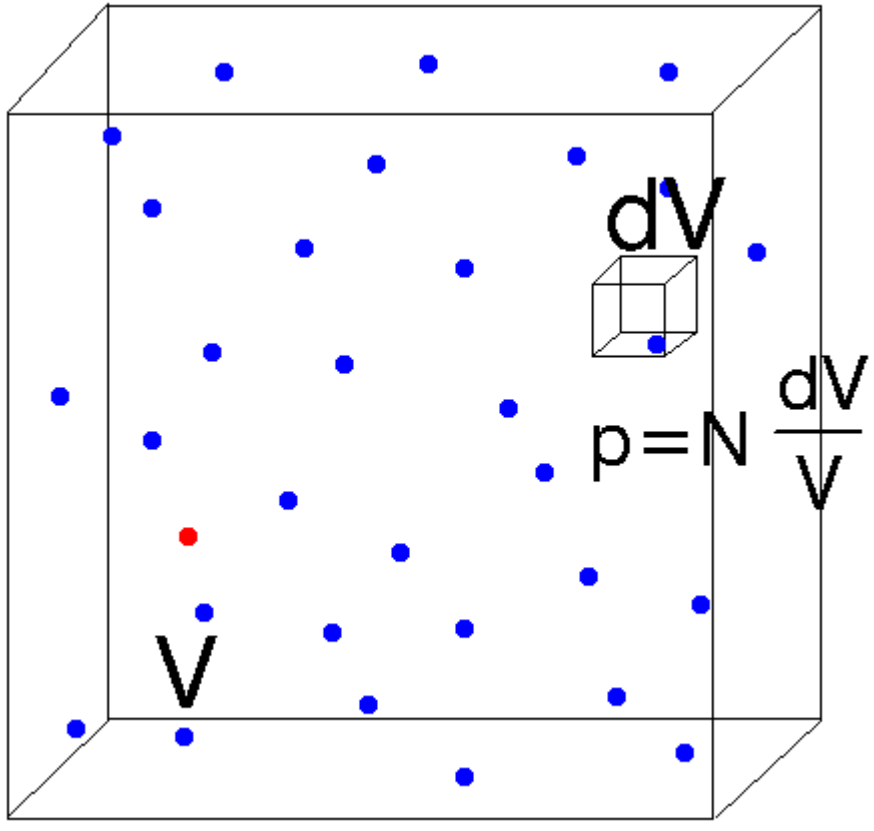
Structural quantities

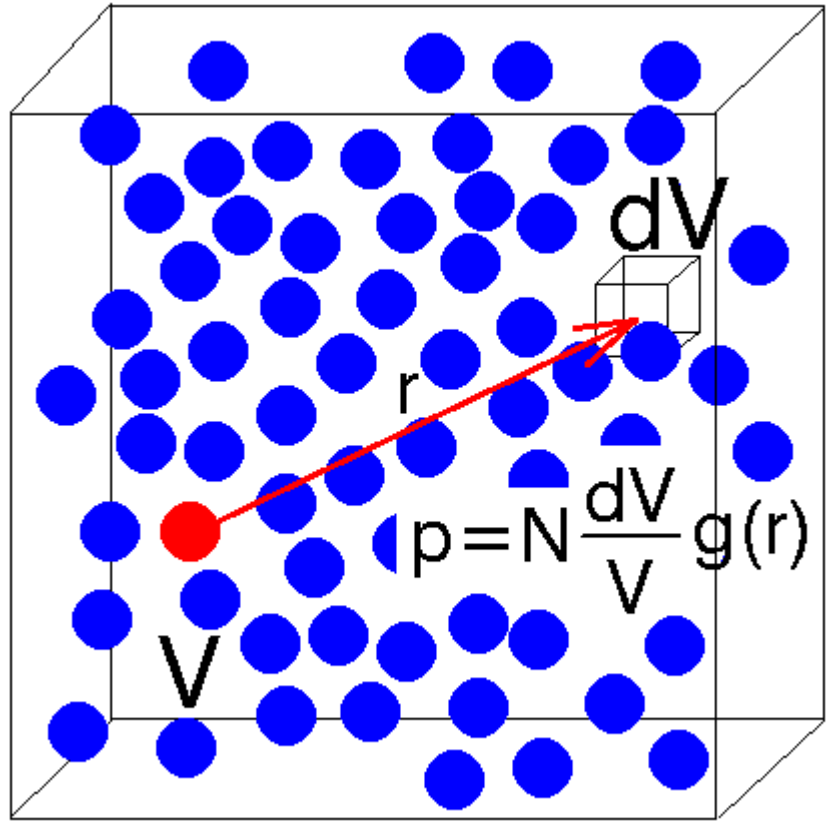
Correlation functions:

- 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

Structure of fluids – correlation functions



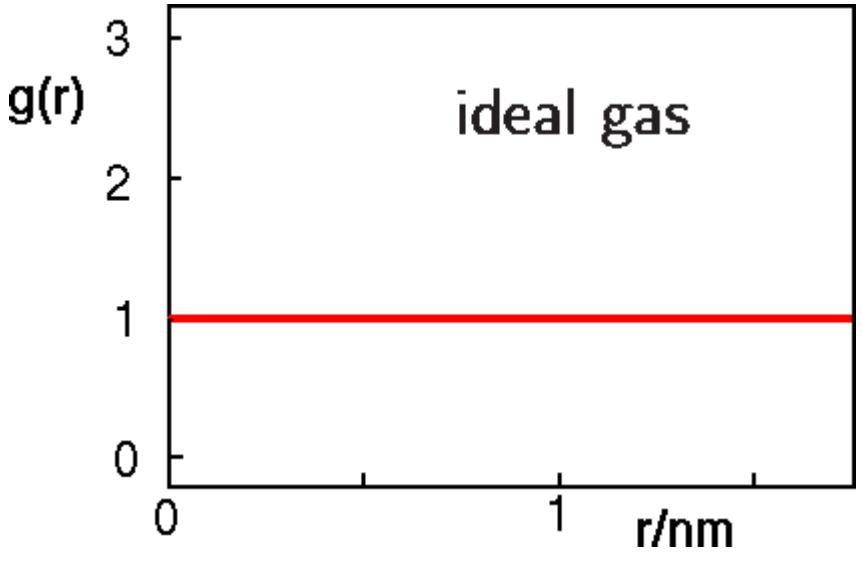
randomly distributed molecules
(ideal gas)

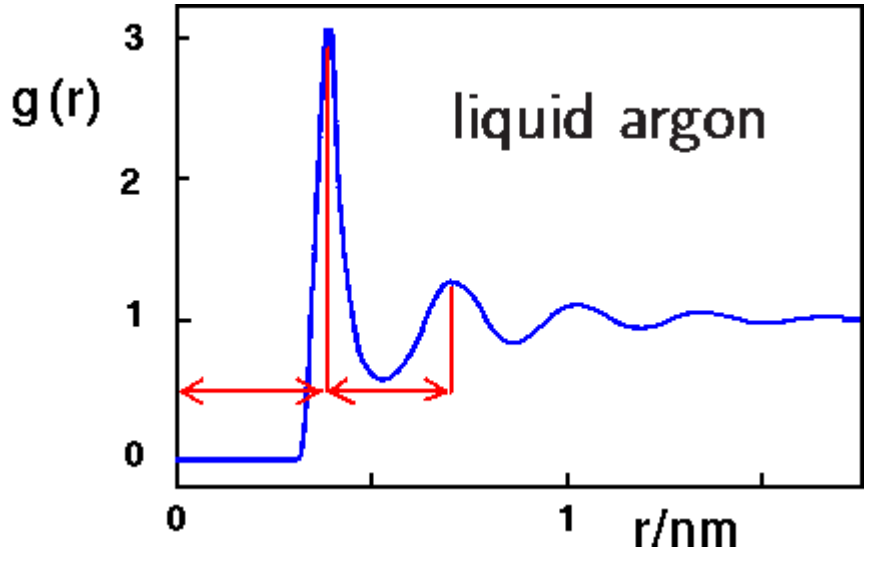


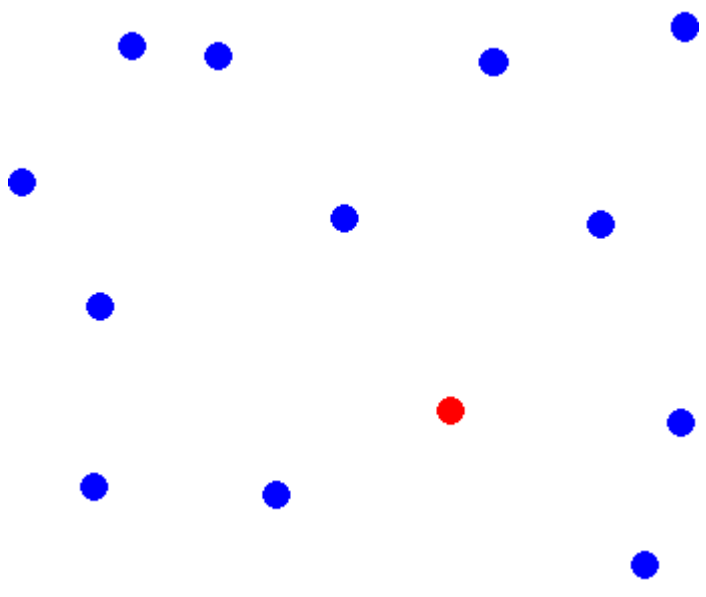
liquid

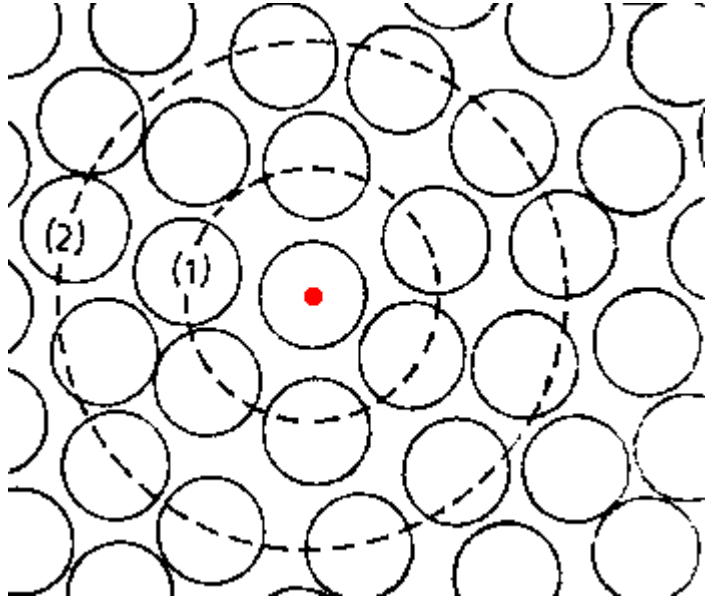
$g(r)$ = pair correlation function = radial distribution function = probability density of finding a particle r apart from another particle, normalized so that for randomly distributed particles (ideal gas) it is 1

Structure of fluids – correlation functions

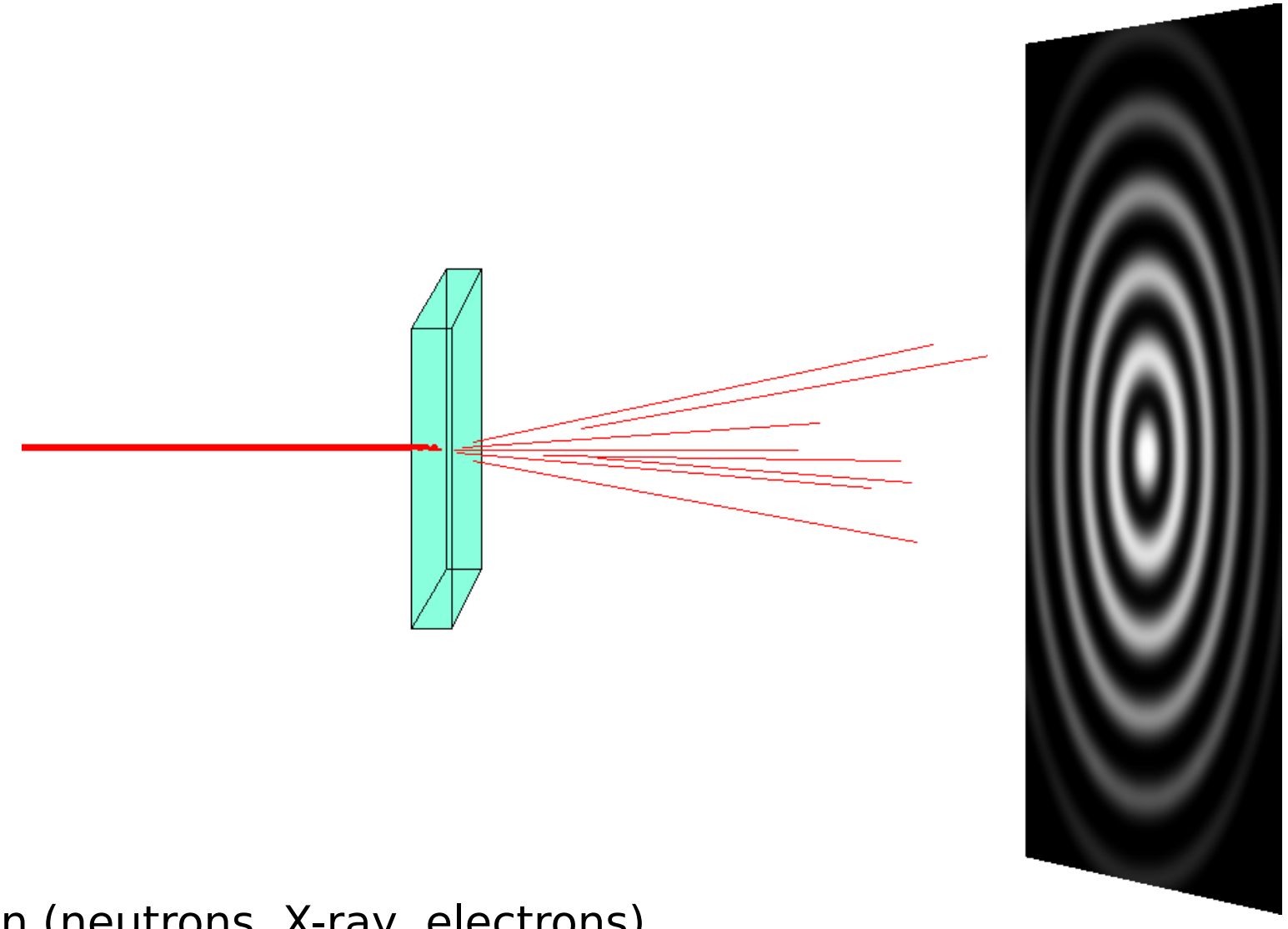






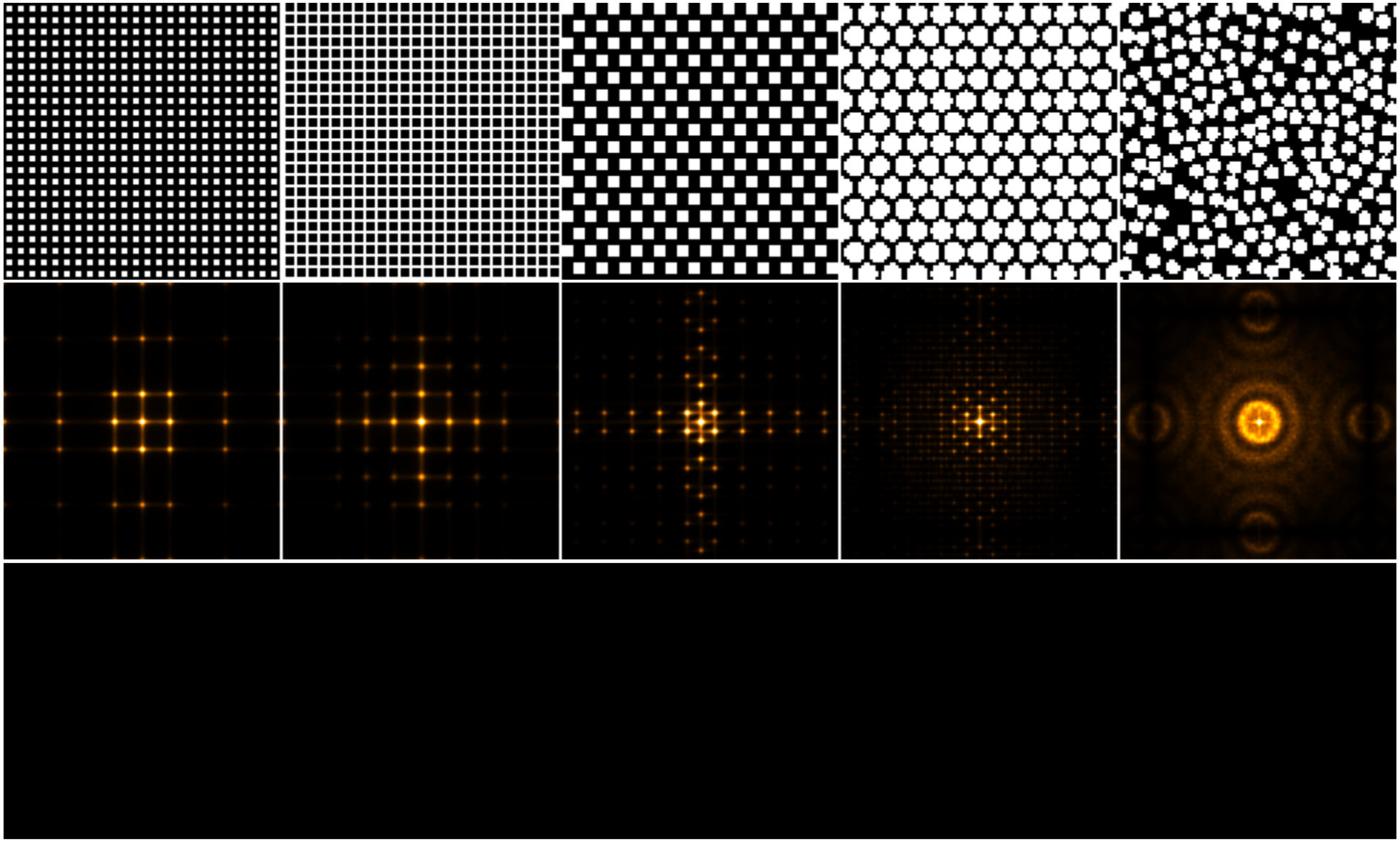


How to obtain structure – experiment

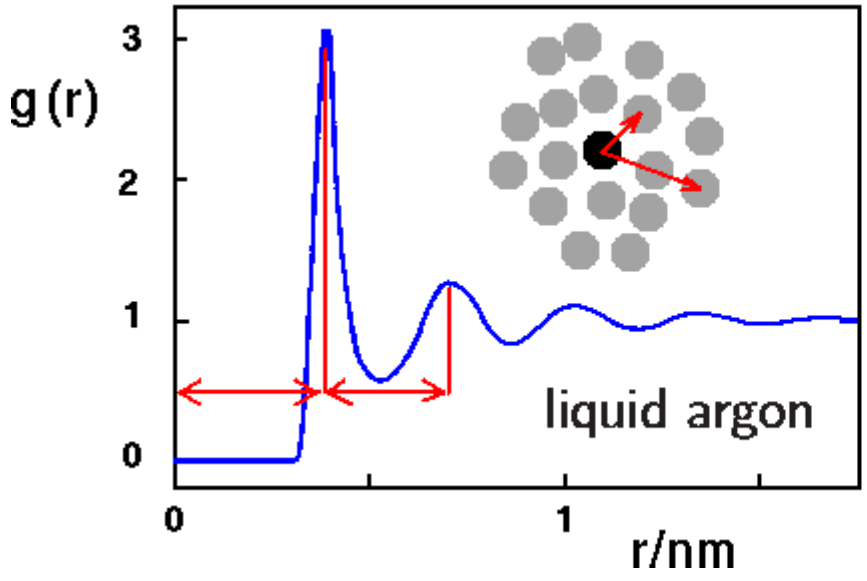


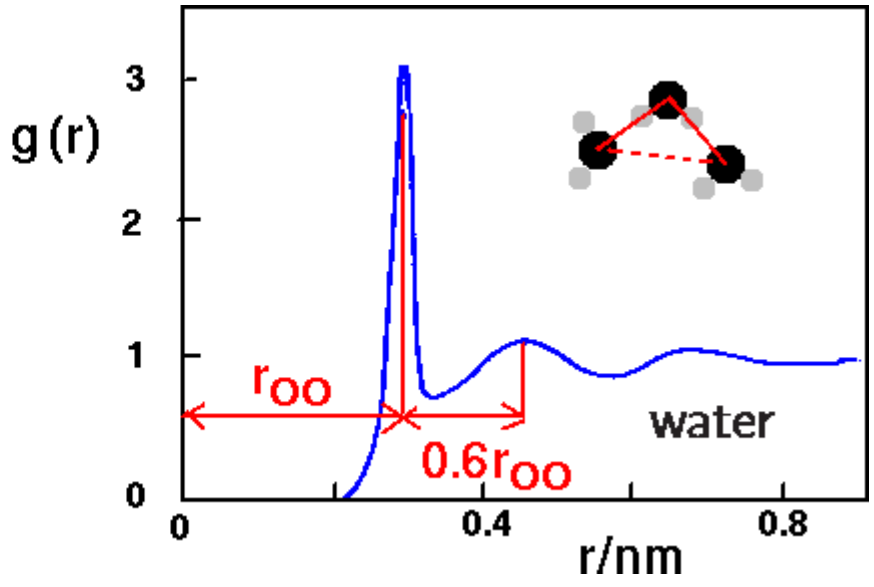
- Diffraction (neutrons, X-ray, electrons)
  ⇒ “structure factor”
- inverse Fourier transform ⇒ RDF

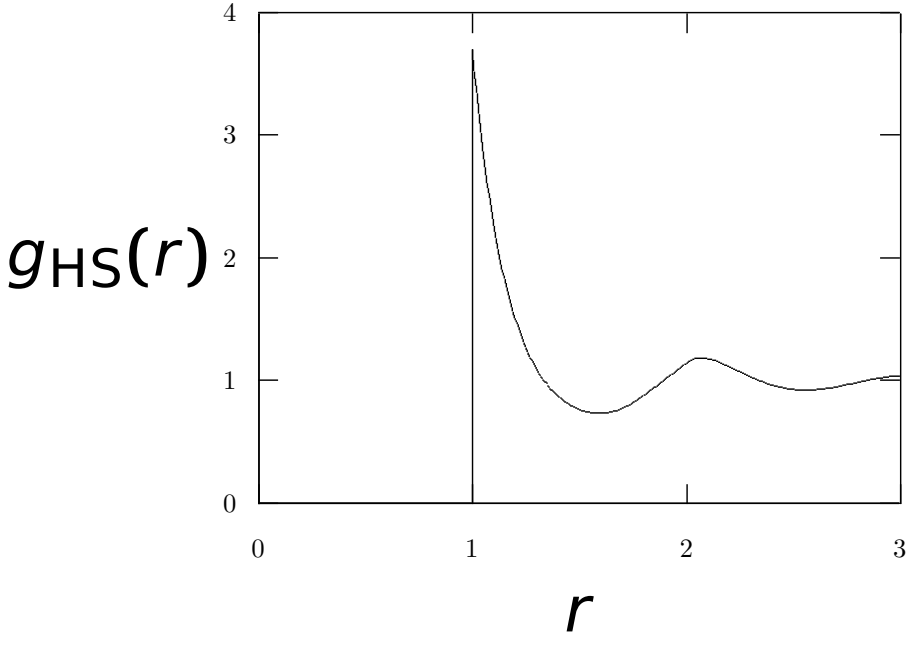
How to obtain structure



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.

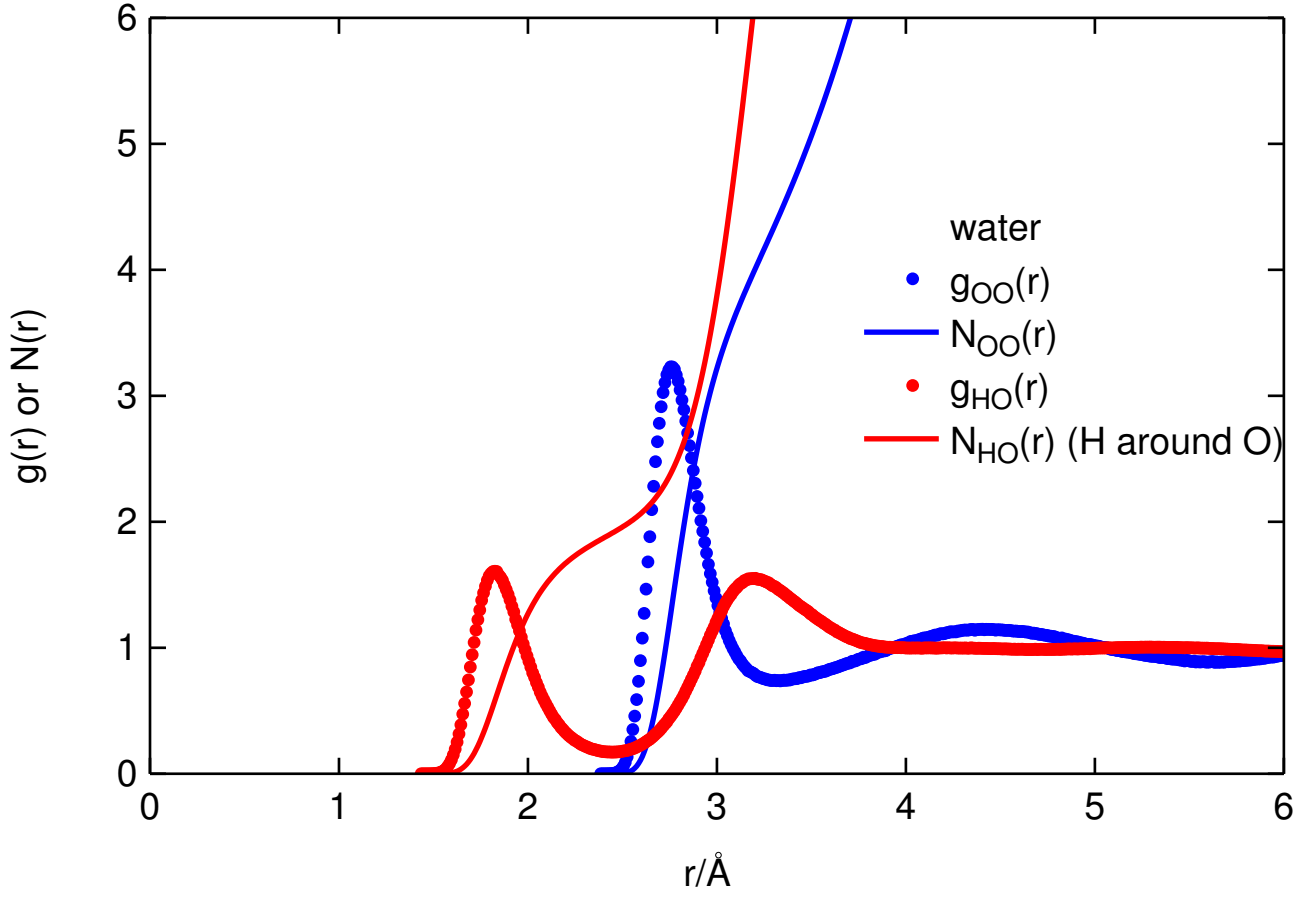
Running coordination number

Also “cumulative radial distribution function”

$\rho = N/V$ = number density

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

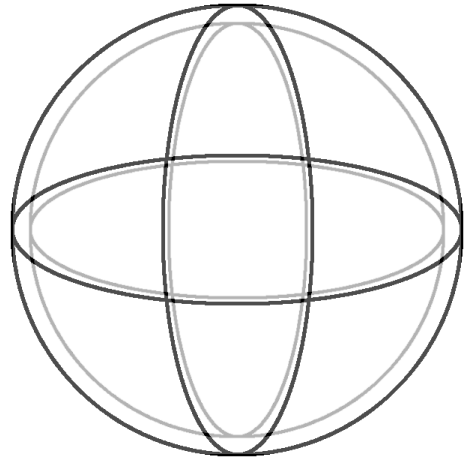
For r_{min} = first minimum on the RDF curve, $N(r_{\mathrm{min}})$ = “coordination number” = averaged number of molecules in the first shell



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)

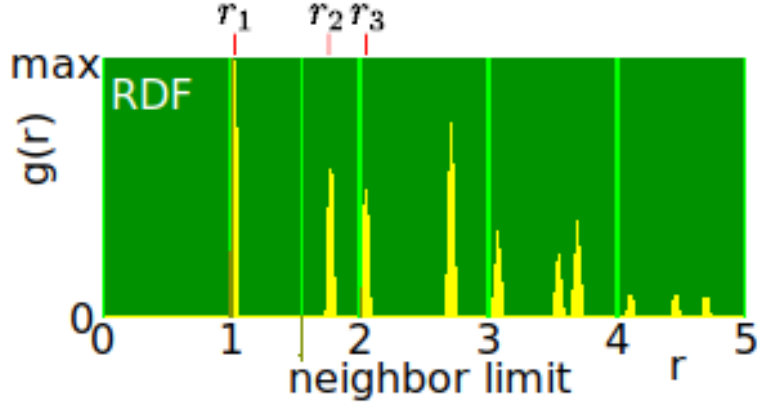
- http://www.vscht.cz/fch/software/simolant
  or Google simolant
- Download `simolant-win32.zip`
- Create a folder and unpack SIMOLANT there.
  Do not run directly from `simolant-win32.zip!`
- Run `simolant.exe`

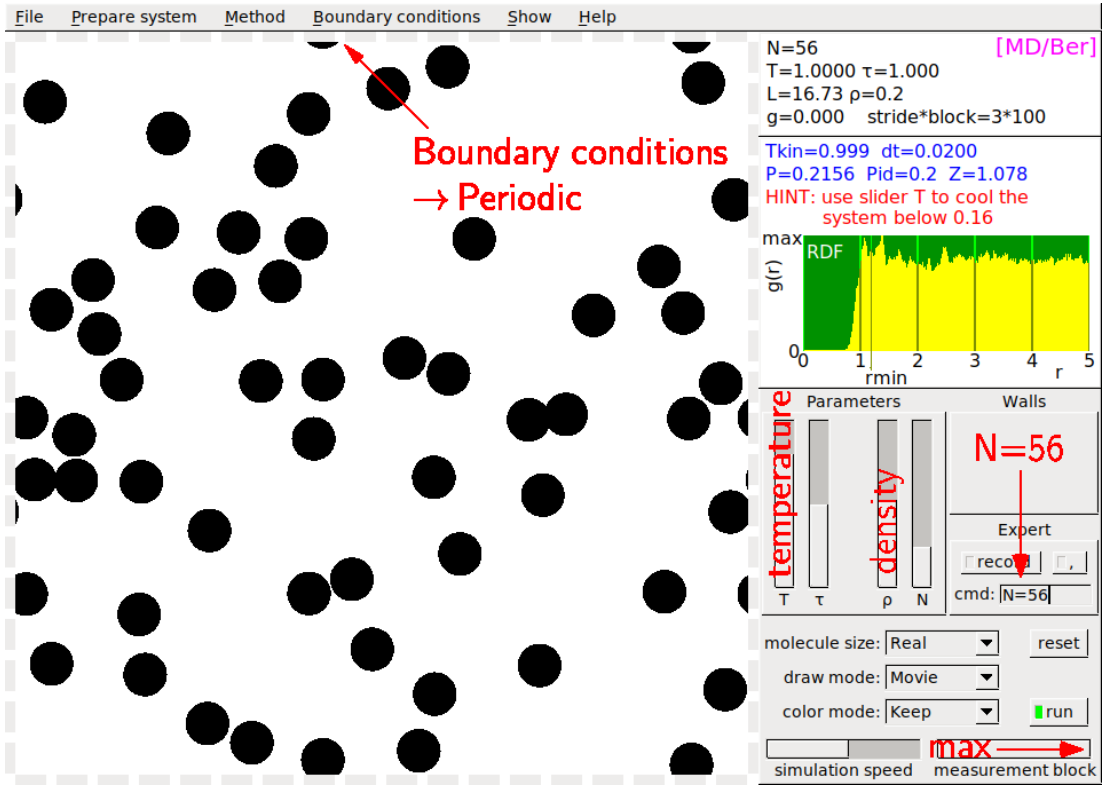
Hint: The calculated data are exported to file `simolant.txt` with a decimal point. If you like decimal comma (useful with Czech localization), click ▮, in panel “Measure”.

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 N=209 to input field “cmd:” (slow computer: N=56)
- Slide “measurement block” to max
- Increase density (slider “ρ”) and observe the changes in RDF
- Repeat with a lower temperature “T”, combine different ρ and T.
- 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 ●●●
- Your homework: calculate r_2/r_1