Structural quantities

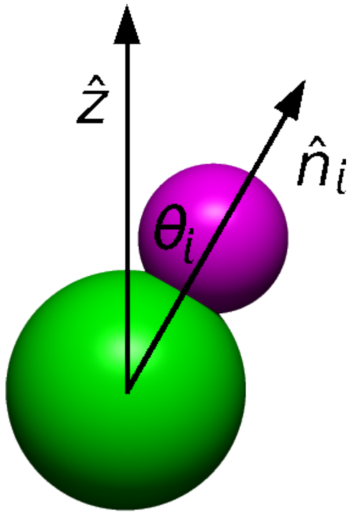
Correlation functions

- 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

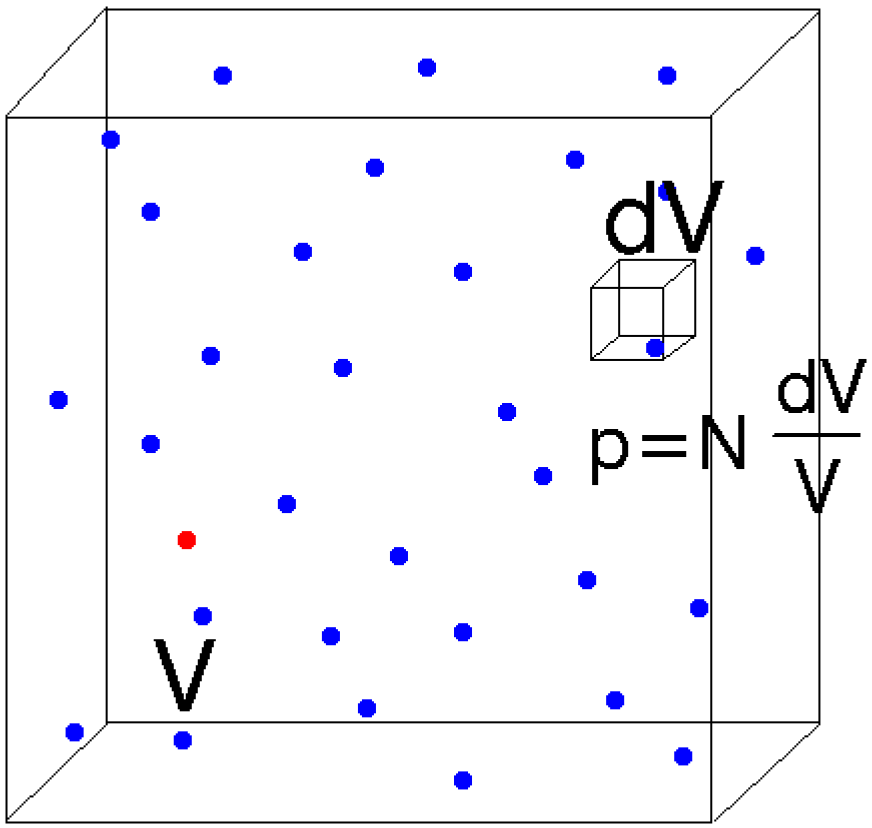
- Ordering in the z-direction: $\left\langle \sum_i \cos\theta_i \right\rangle$: ↑ vs. ↓
- For symmetric molecules: $\left\langle \sum_i \left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right)\right\rangle$: ↕ vs. ↔
- Nematic liquid crystal – the “director” is not known:

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

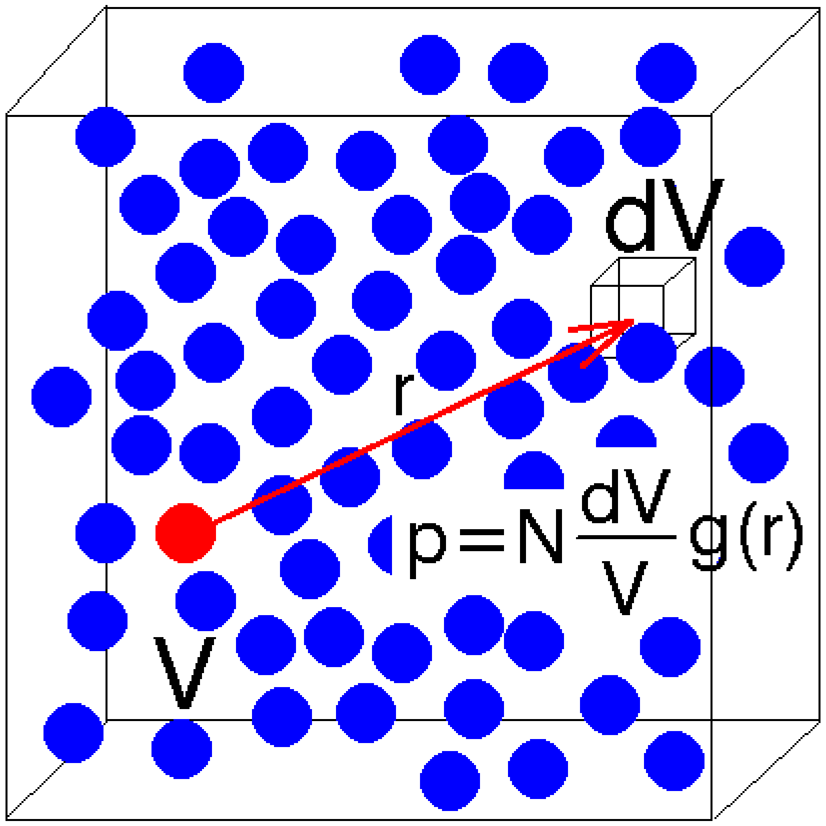


- Formulas detecting local order (e.g., tetrahedral around water molecules as Steinhardt’s parameters based on spherical harmonics), onset of crystallization can be detected . . .

Structure of fluids – correlation functions



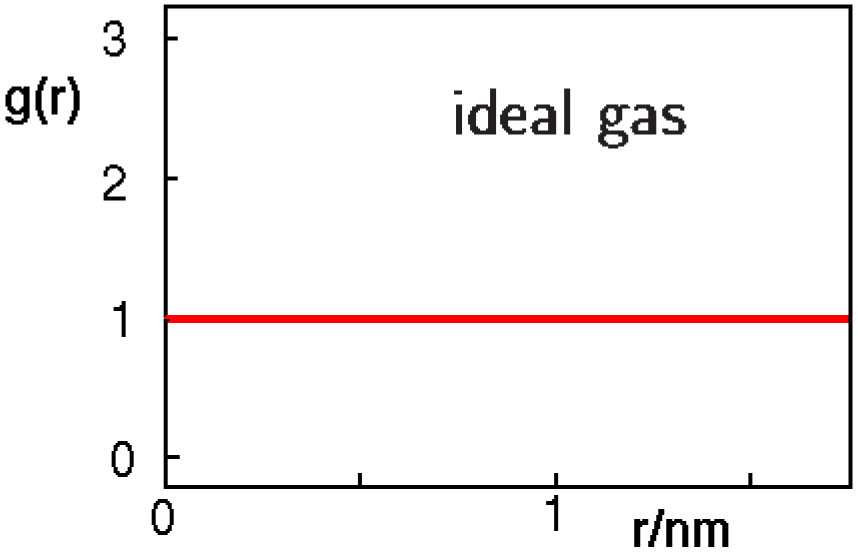
randomly distributed molecules
(ideal gas)

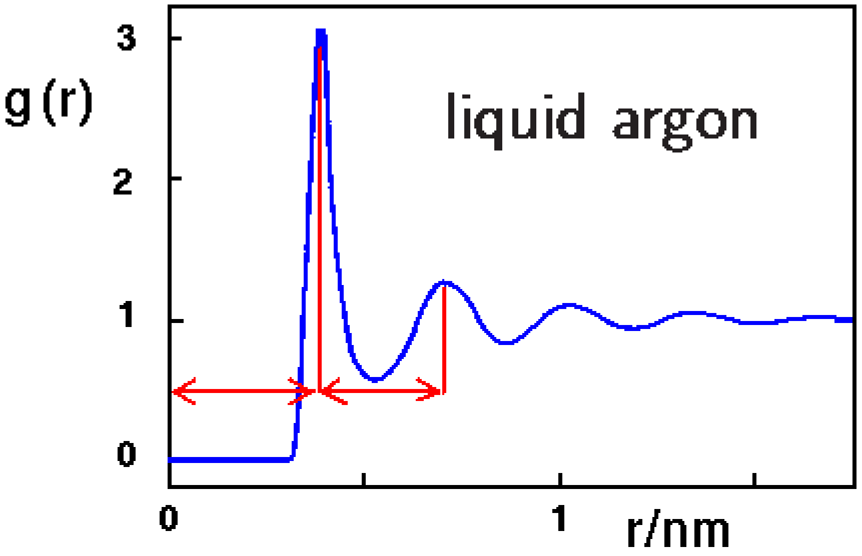


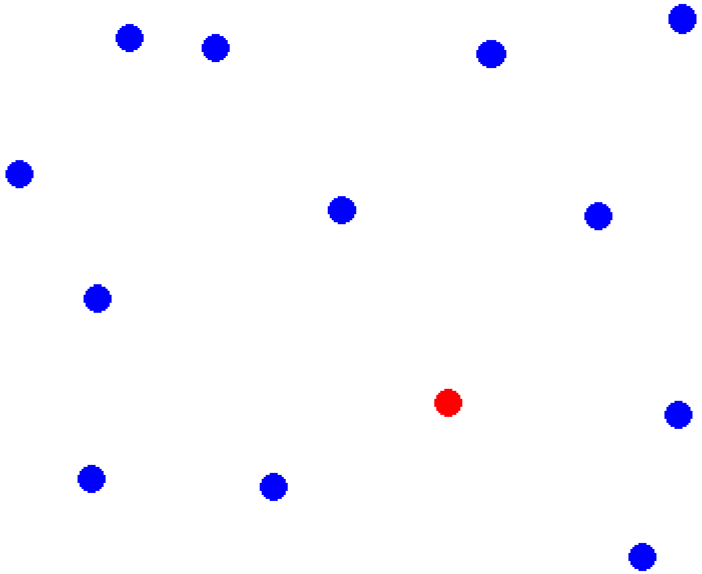
liquid

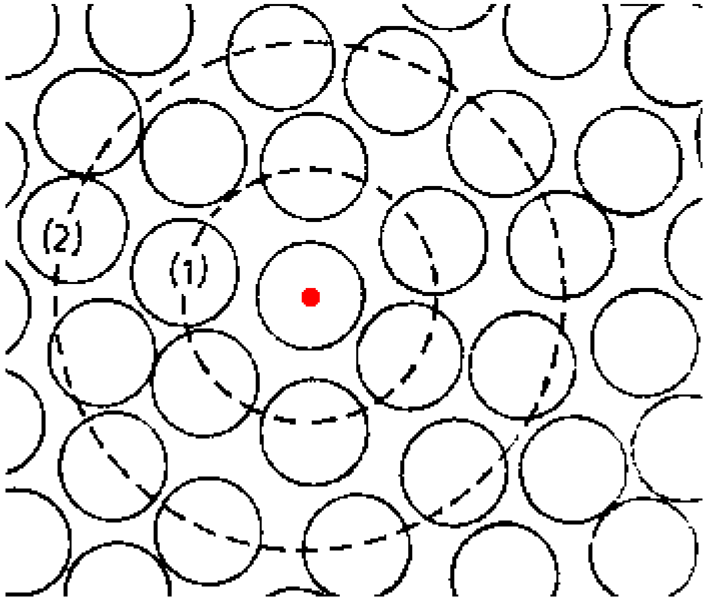
$g(r)$ = pair correlation function = radial distribution function = probability density of finding a particle r apart from another particle, normalized so that for randomly distributed particles (ideal gas) it is 1

Structure of fluids – correlation functions

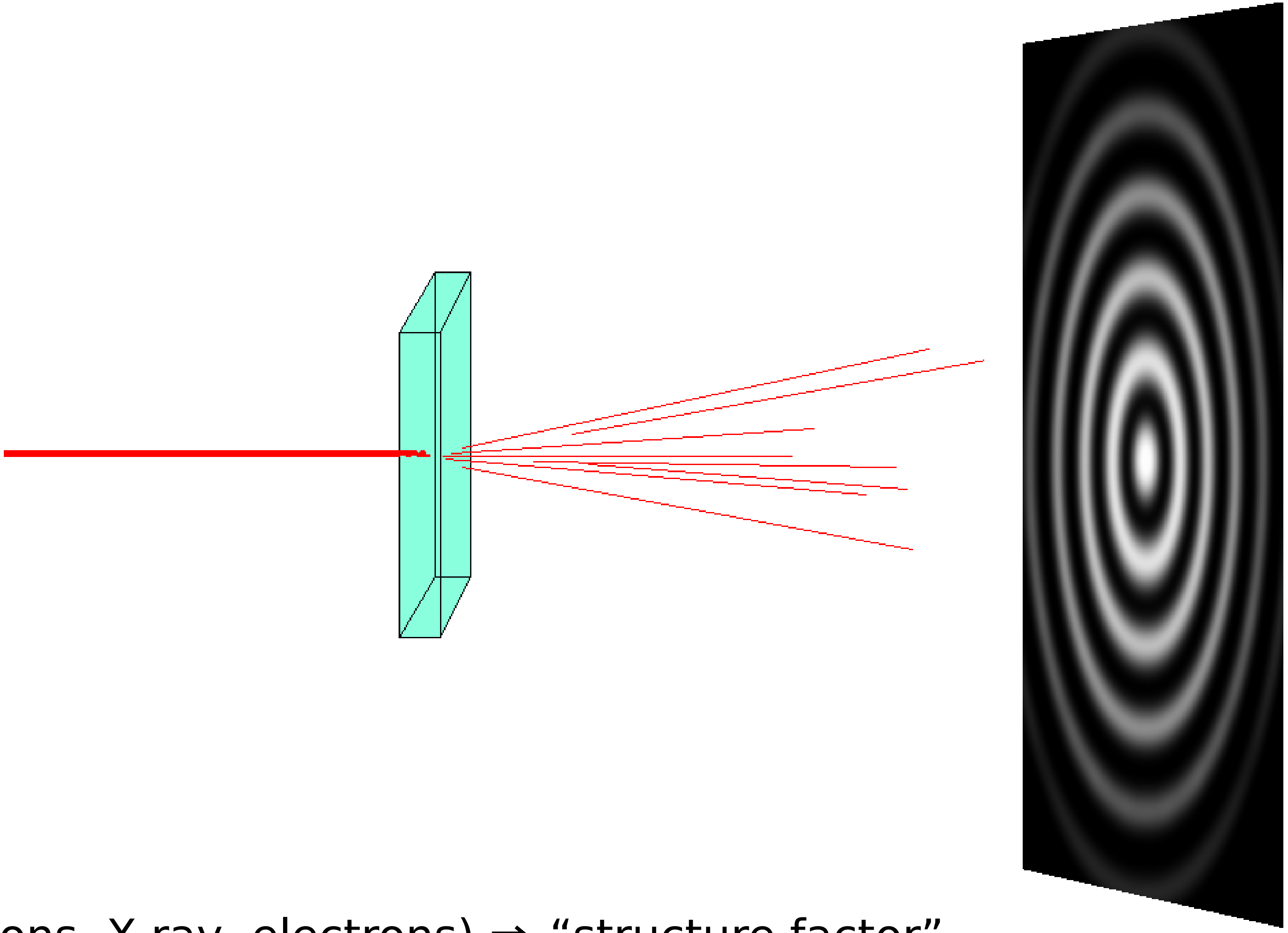






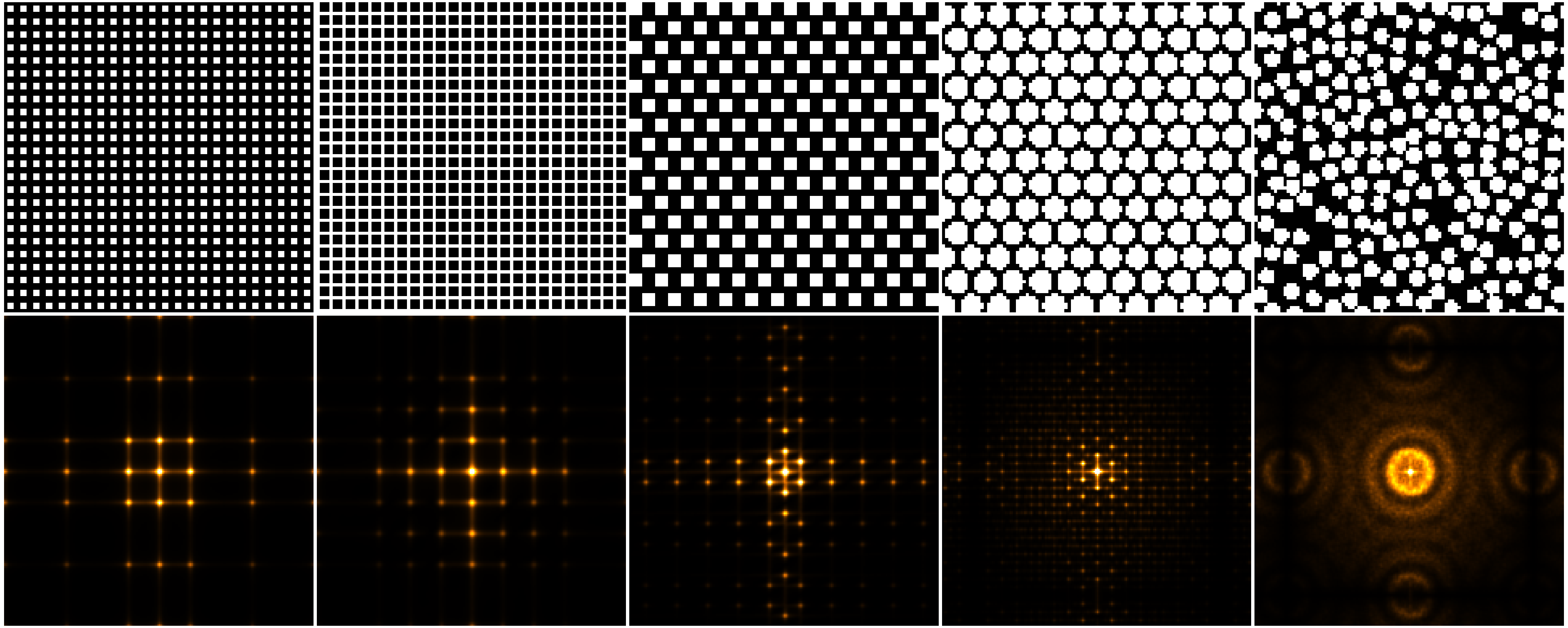


How to obtain structure – experiment

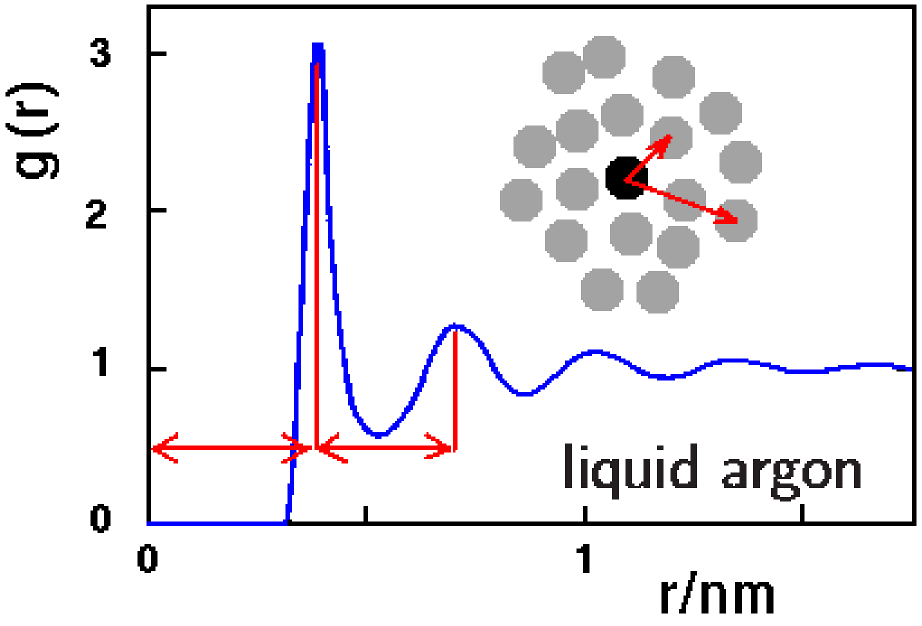


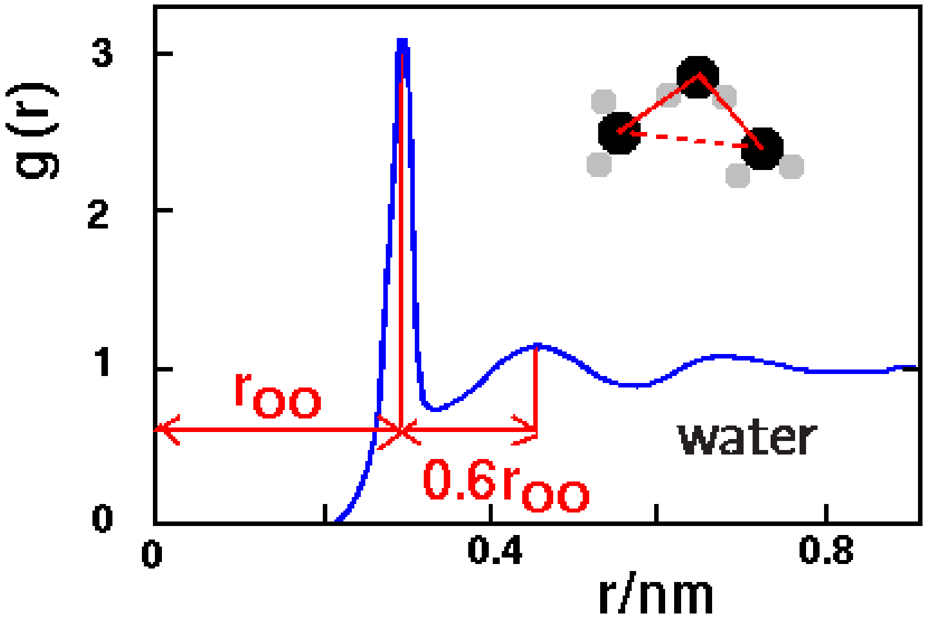
- Diffraction (neutrons, X-ray, electrons) ⇒ “structure factor”
- inverse Fourier transform ⇒ RDF

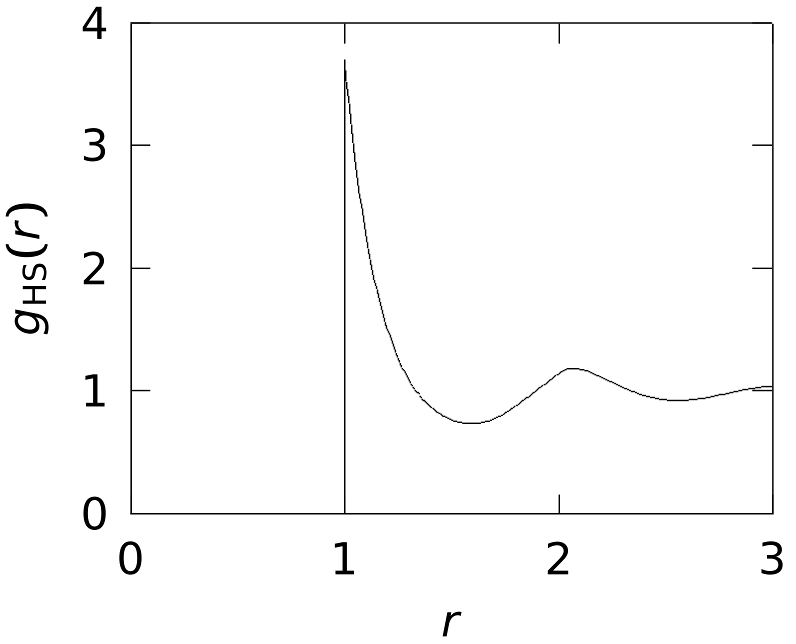
How to obtain structure



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.

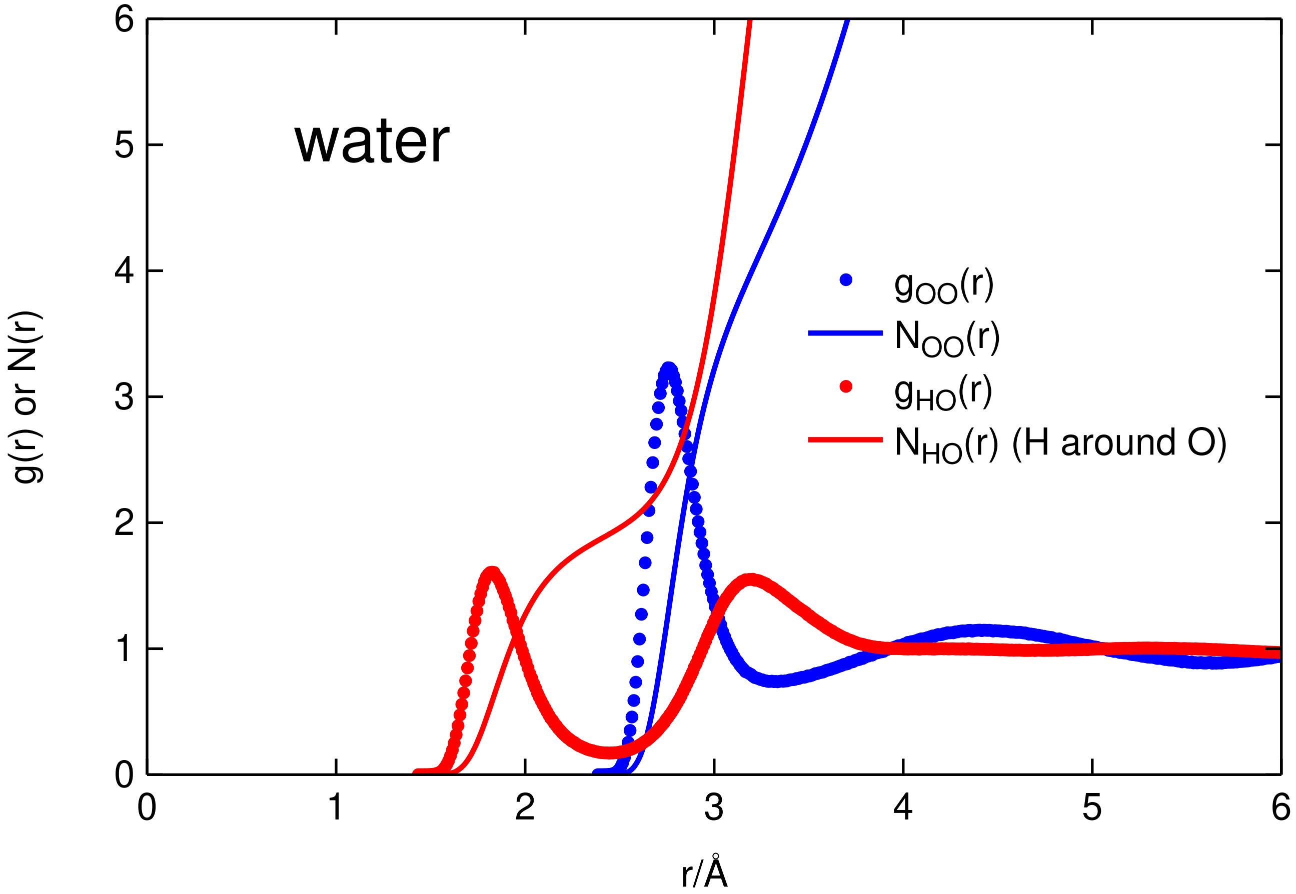
Running coordination number

$\rho = N/V$ = number density

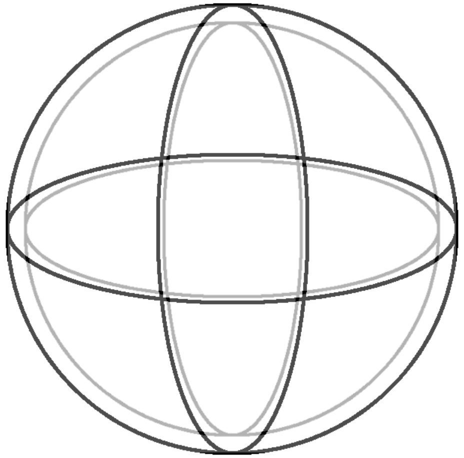
Also “cumulative radial distribution function”

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

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

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

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):

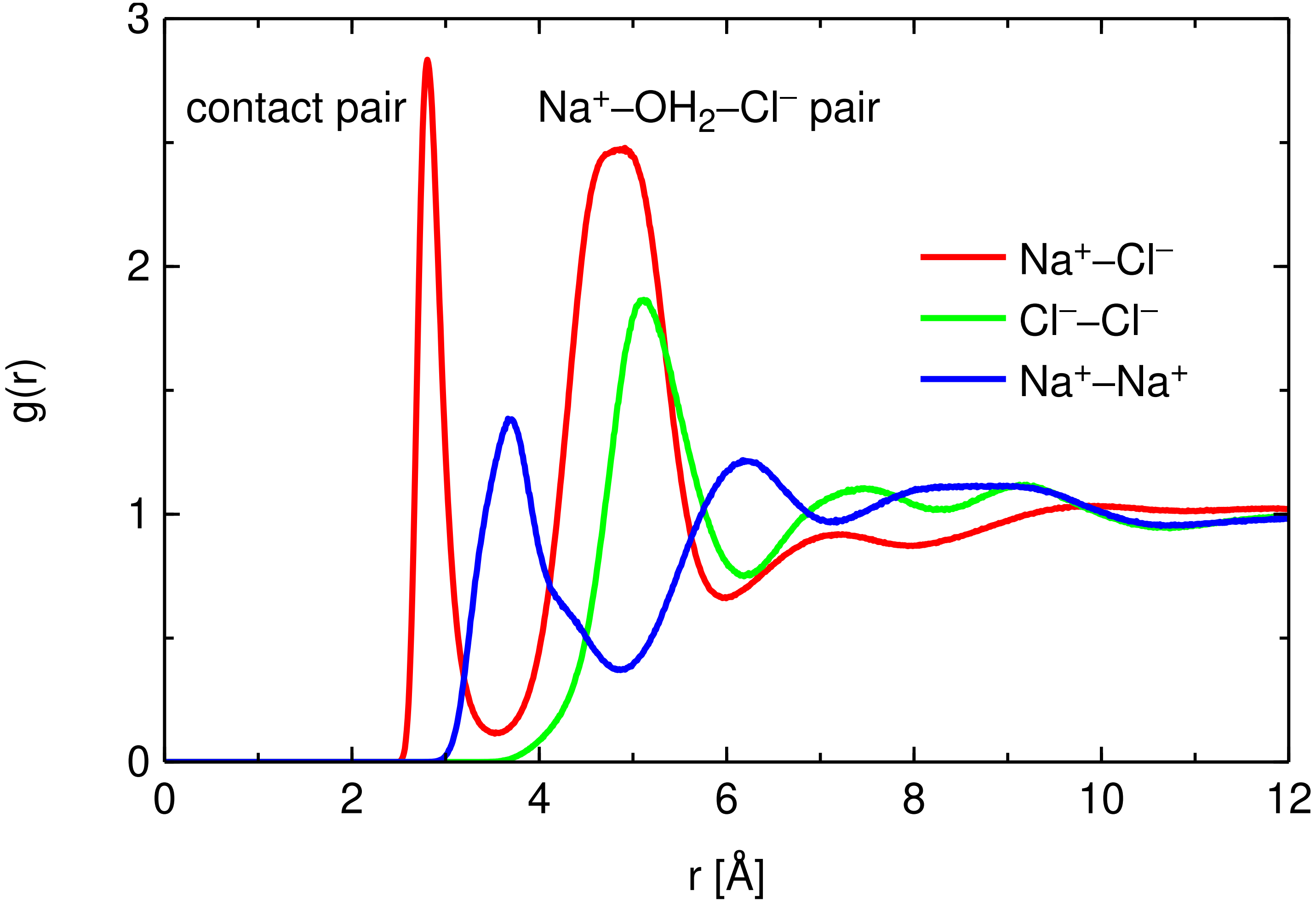
$$\mathcal{N}_i^{\text{id. gas}} = \frac{N}{2}\rho \Delta V_i$$

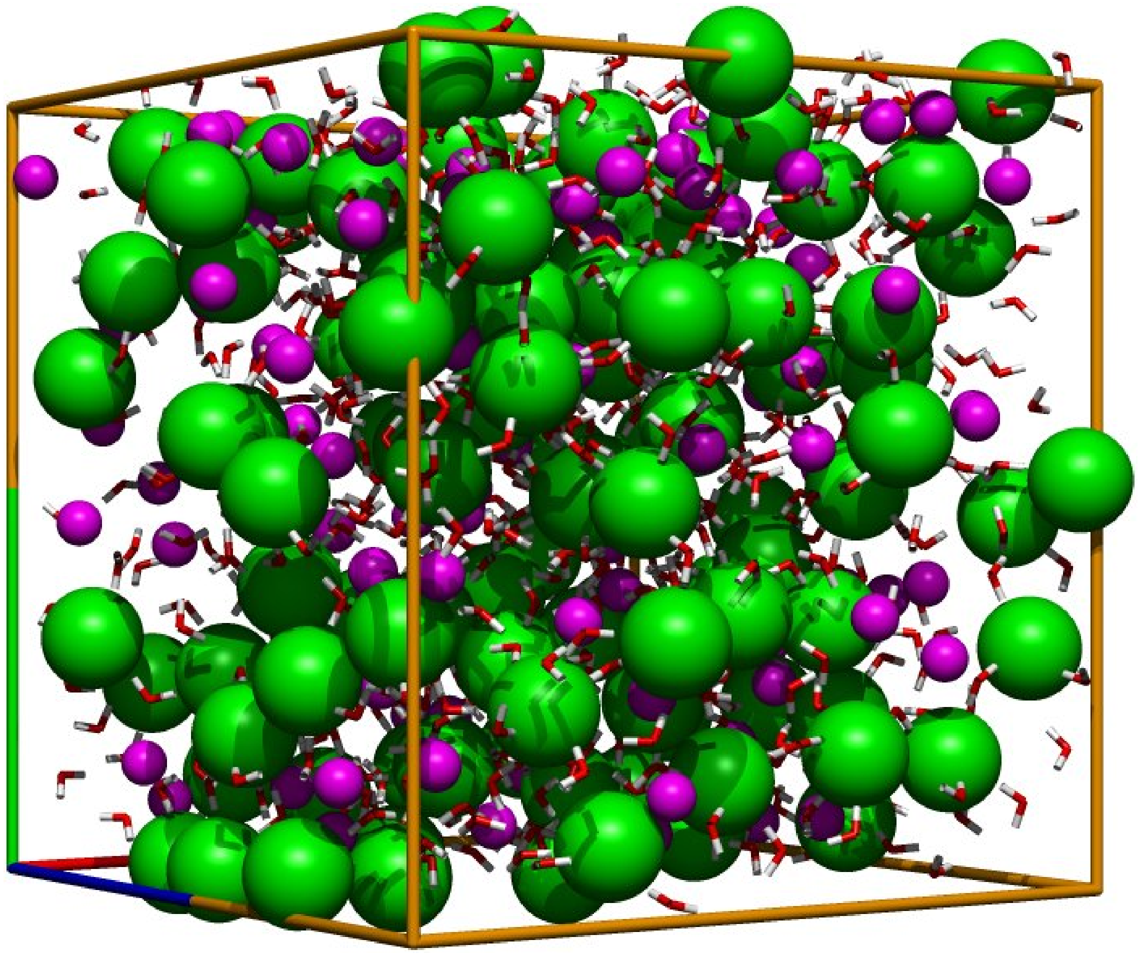
Radial distribution function:

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

Another example – brine

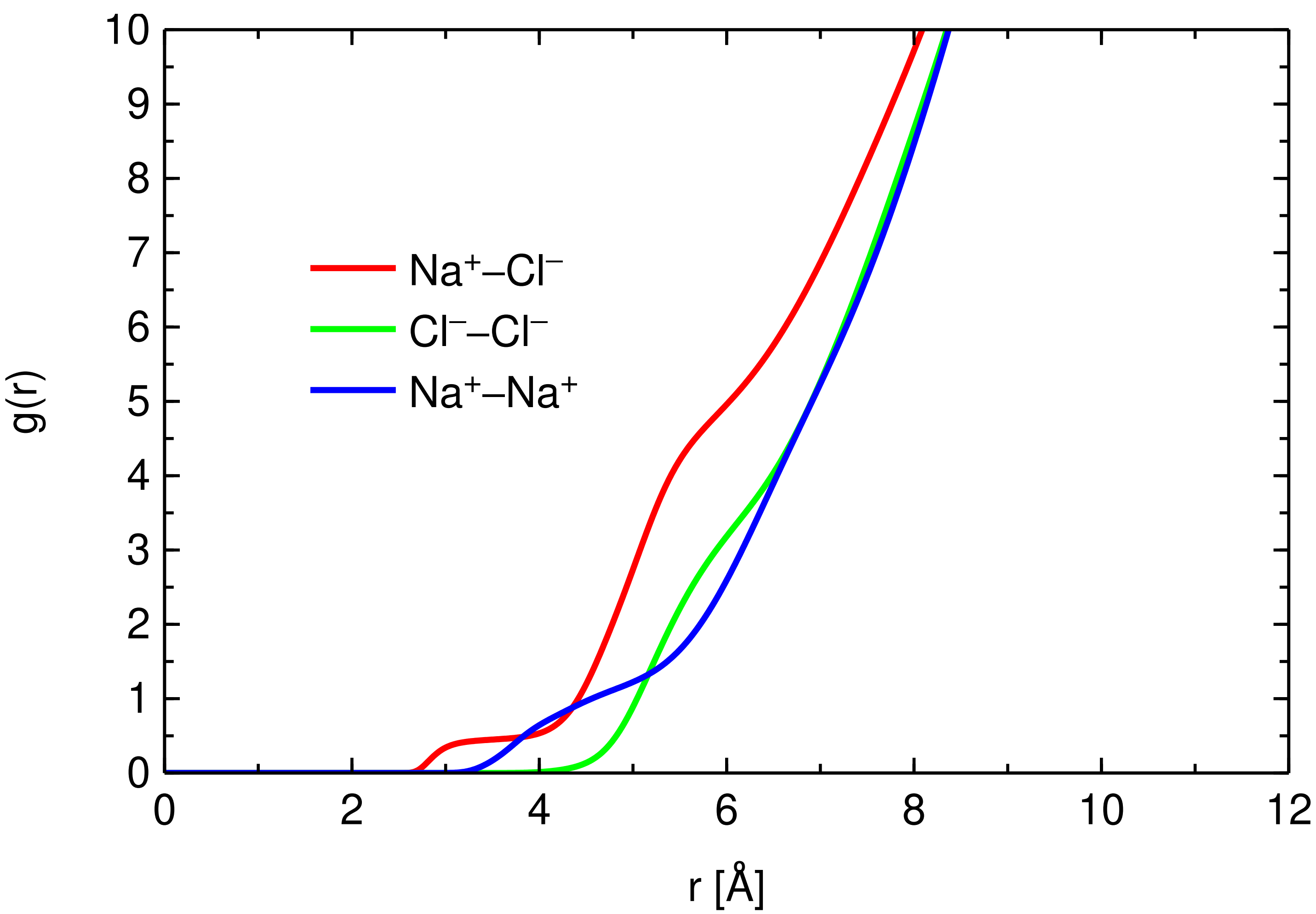
RDFs of supersaturated (10.5 mol/kg) solution of NaCl:

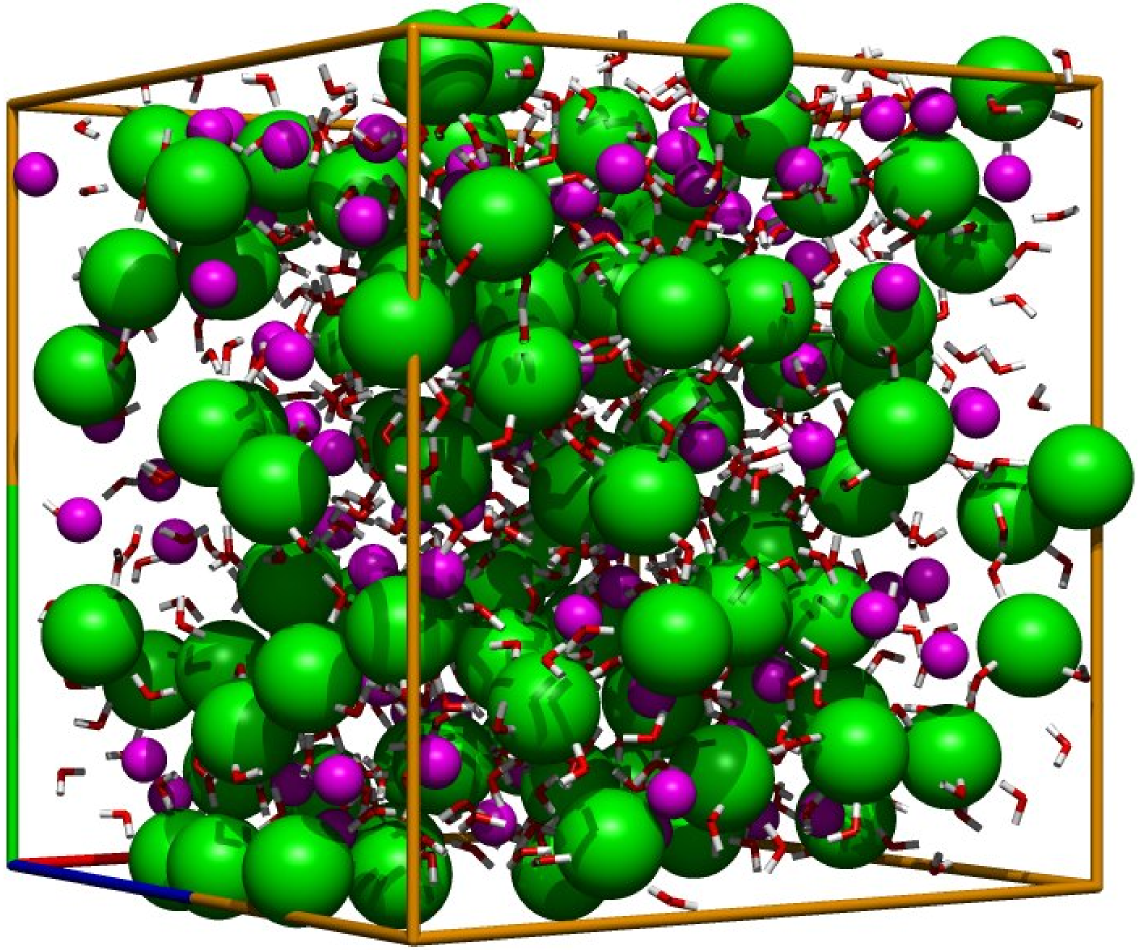




Another example – brine

CNs of supersaturated (10.5 mol/kg) solution of NaCl:





SIMOLANT – installation (Windows)

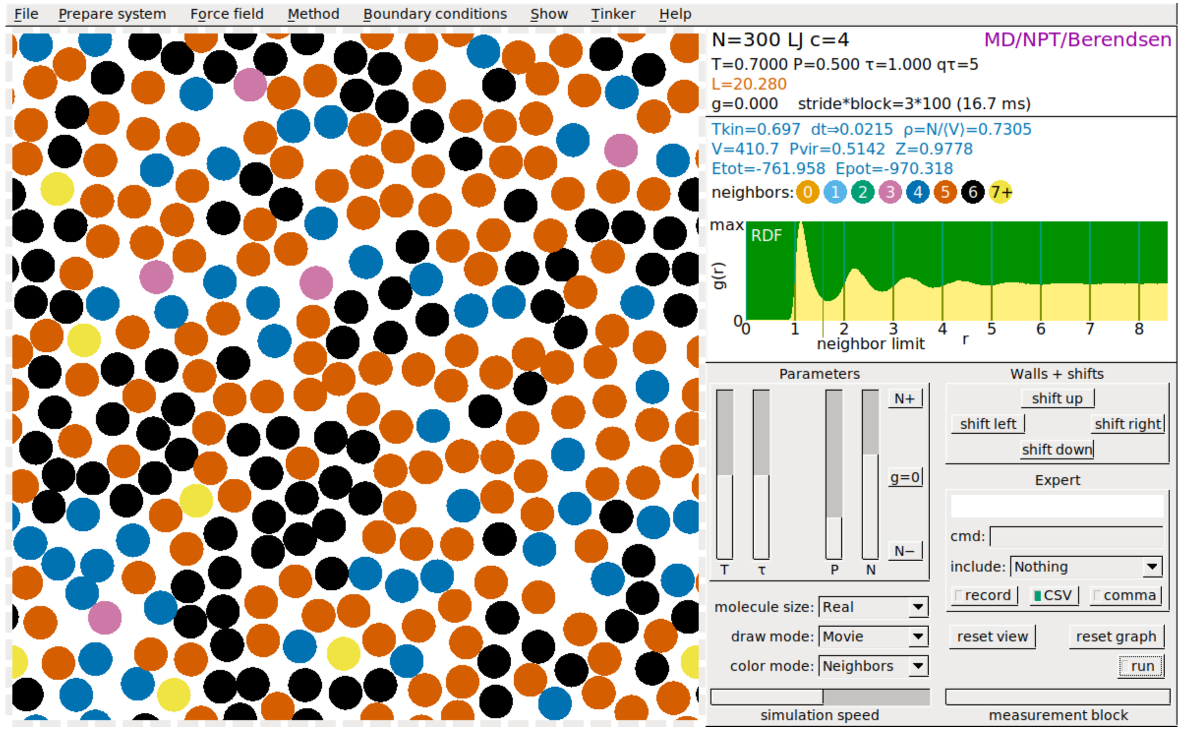
- http://old.vscht.cz/fch/software/simolant
  or Google simolant
- Download `simolant-win32.zip`
- **Create a folder** and unpack SIMOLANT there.
  Do not run directly from `simolant-win32.zip`!
- Run `simolant.exe`

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

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: Prepare system → Periodic liquid
- For smoother results, move slider “measurement block” to maximum
- Increase/decrease temperature a bit (slider “T”).
  Try a different pressure (slider “P”).
  NB: the RDF graph is scaled from 0 to maximum!
- Set the temperature to maximum ($T = 5$): only a small first peak should remain.
- Decrease temperature below 0.4 to crystallize.
- To obtain a nearly perfect crystal without defects, select Menu: Prepare system → Periodic crystal. Again, you may try to heat/cool. You should get:



N=300 LJ c=4 MD/NPT/Berendsen

T=0.7000 P=0.500 τ=1.000 qτ=5

L=20.280

g=0.000 stride*block=3*100 (16.7 ms)

Tkin=0.697 dt⇒0.0215 ρ=N/⟨V⟩=0.7305

V=410.7 Pvir=0.5142 Z=0.9778

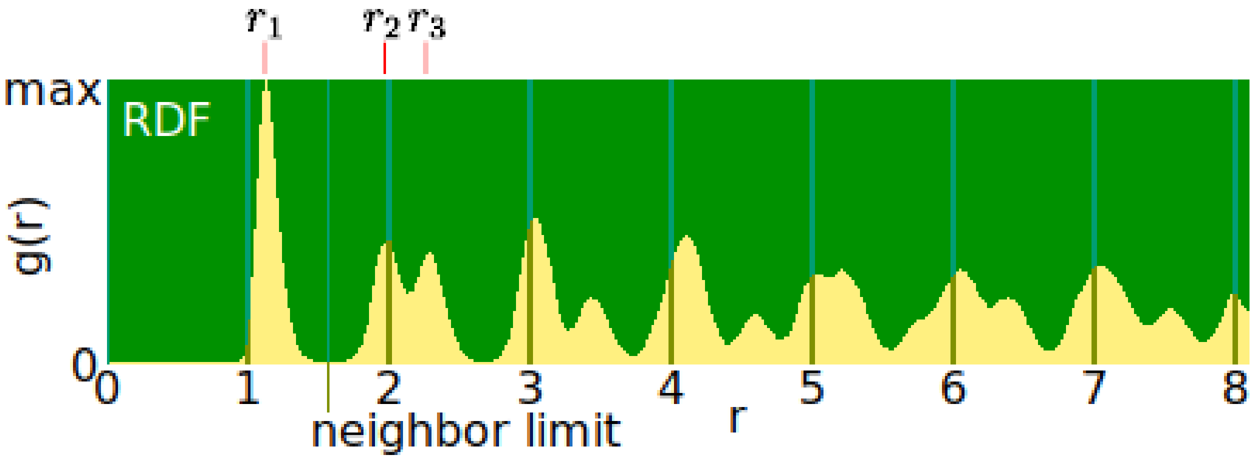
Etot=-761.958 Epot=-970.318

molecule size: Real

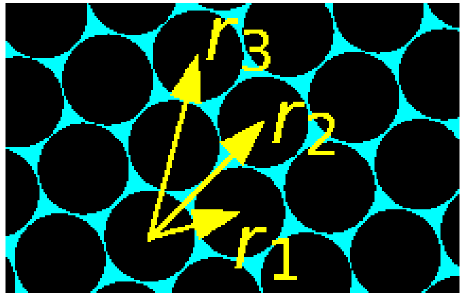
draw mode: Movie

color mode: Neighbors

include: Nothing



- 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 homogeneous and isotropic liquid:

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

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):

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

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):

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

Or (mixtures, in a region):

$$g(r_{12}) = \frac{\rho_2(\vec{r}_1, \vec{r}_2)}{\rho_1(\vec{r}_1)\, \rho_2(\vec{r}_2)},$$

where ρ_n is the n-particle distribution function, $\rho_1 = \rho$ in a homogeneous fluid.

Calculation of RDF in simulations – exact

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

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

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

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

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:

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

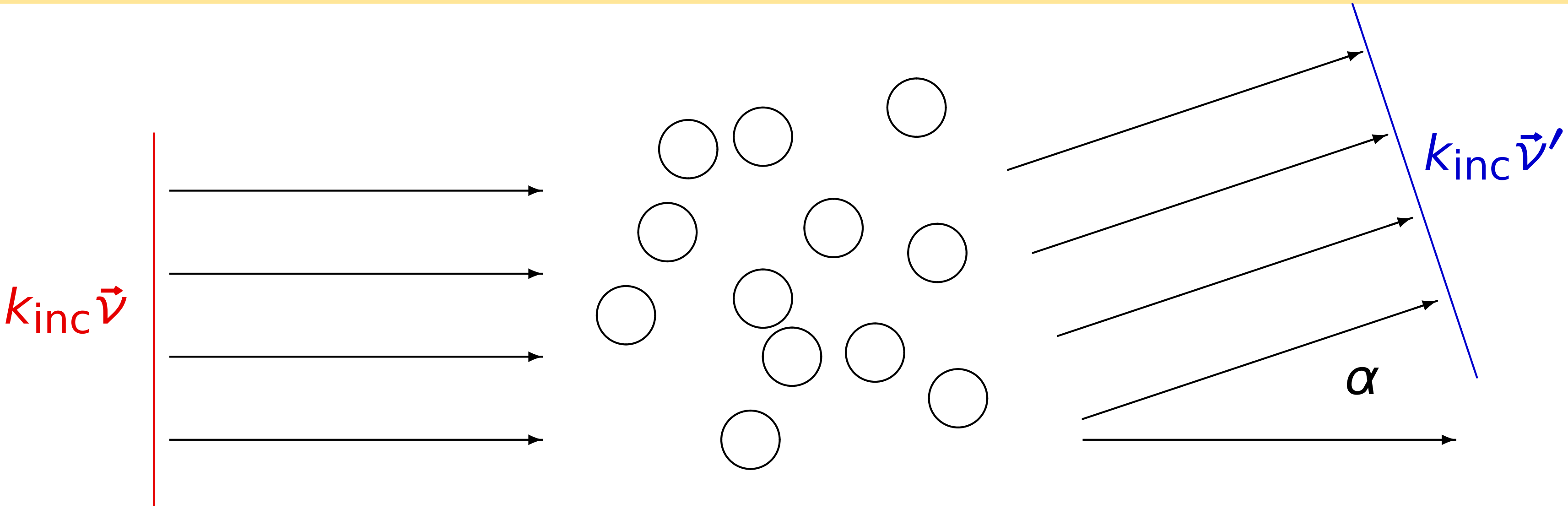
$$\langle U\rangle = \binom{N}{2}\frac{V}{Q_{\mathrm{NVT}}}\int \mathrm{e}^{-\beta U}4\pi r_{12}^2\mathrm{d}r_{12}u(r_{12})\mathrm{d}\vec{r}_3\ldots\mathrm{d}\vec{r}_N$$

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

Pressure:

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

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)

Definition $k=2\pi/\lambda$ is common in physics wheras $k=1/\lambda$ in crystallography; then, factor 2π is in the exponential: $\exp[2\pi i\vec{k}\cdot\vec{r}]$.

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

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:

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

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)

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

Structure factor and RDF

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

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

The integral diverges as $V \to \infty$ ⇒ 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:

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

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

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)

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

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:

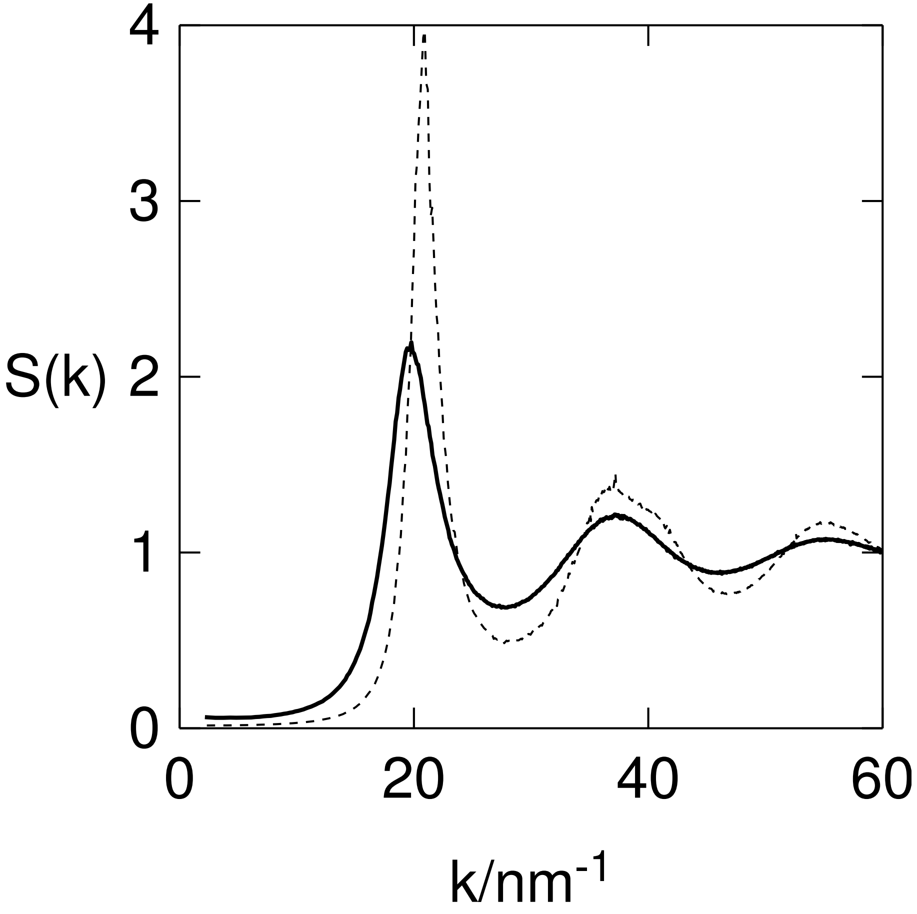
$$S(k) = \sum_{k=|\vec{k}|} S(\vec{k}) / \sum_{k=|\vec{k}|} 1$$

$S(k)$ 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.

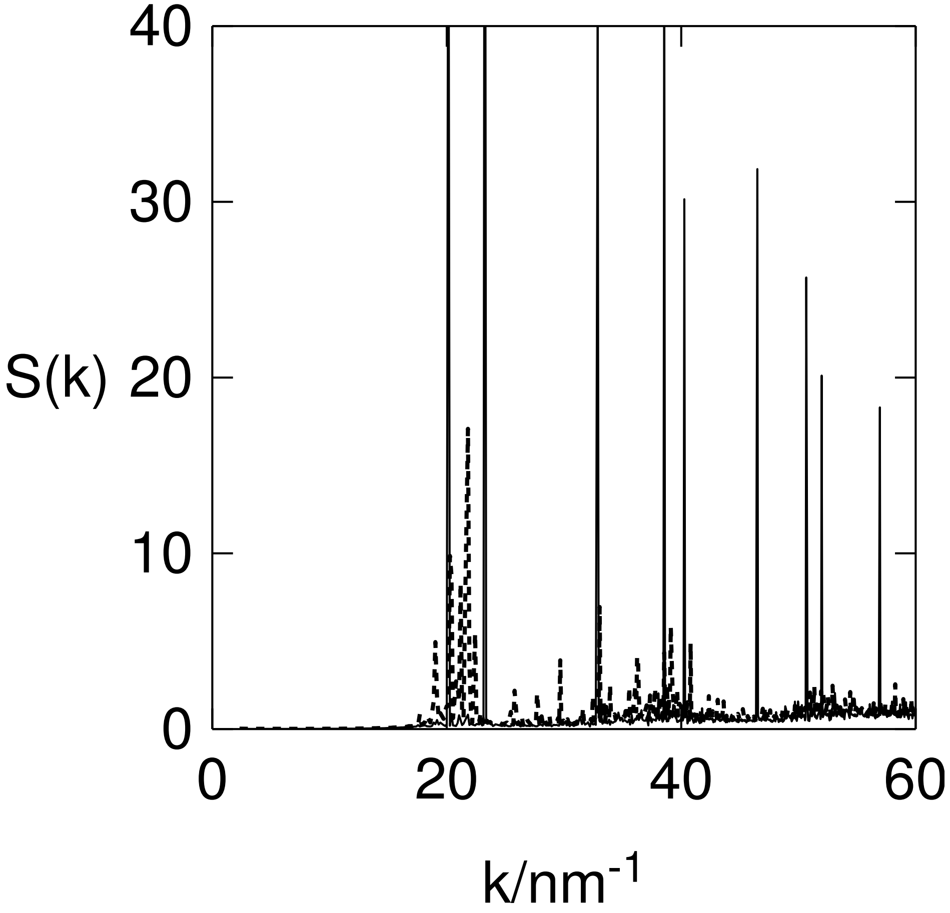
If one wishes, 3D $S(\vec{k})$ can be obtained by the inverse Fourier transform from RDF $g(\vec{r})$ and vice versa

- 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)

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

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

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

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

Exercise: structure factor of NaCl crystal/melt

Scattering lenghts [fm]: Na: 3.63, Cl: 9.577 (^{35}Cl: 11.65, ^{37}Cl: 3.08)

Tasks:

- Simulate a crystal at 1000 K
- Switch to NVT and generate a trajectory (about 100 configurations)
- Calculate the SF directly
- Compare with inverted RDF
- Melt and repeat for the liquid
- Try different isotopes

You need: `nacl.ble` `nacl.def` `nacl.cfg` `na.mol` `na.gol` `cl.mol` `cl.gol`

Make your folder, and install (to your folder) by:

```
guest@403-a324-01:~/VY$ mkdir YOU
guest@403-a324-01:~/VY$ cd YOU
guest@403-a324-01:~/VY$ unzip /home/jiri/nacl.zip
```

Inspect carefully `nacl.def`!

Exercise: structure factor of the NaCl crystal

A crystal is prepared in `nacl.def` **Start + equilibration**

- start simulation; all variables are default:

  ```
  guest@403-a324-01:~/VY$ cook nacl -s
  ```

  `init="start"` start from prepared configuration

  `;` end of data set + start of simulation

- after the run has finished:

  `key="cp"` show the convergence profile

  `key="show"` show the trajectory

  `;` another 100 steps if not equilibrated

- final run:

  `tau.P=0` use NVT now

  `init="start"` use the configuration, measurements + trajectory restarted

  `;` end of data set + start of simulation

  `key="rdf"` calculate + show RDF

  `key="cn"` show the coordination numbers

  `key="quit"` or ctrl-d = control returns to the command prompt

Exercise: structure factor of the crystal directly

The structure factor will be calculated from the trajectory, `nacl.plb`, recorded in previously.

- data: optionally change b_i at the end of table `Lennard-Jones` in `nacl.ble`
- How long is the trajectory?

```
guest@403-a324-01:~/VY$ plbinfo nacl.plb
```

- Calculate the structure factor (`-m1` = reads `nacl.plb`)

```
guest@403-a324-01:~/VY$ cook nacl -m1 -s
```

  `reread.from=1 reread.to=101` read `nacl.plb` from .. to

  `tau.P=0` NVT (do not change the box)

  `el.kappa=15/2/pi ;` max. k-vector

- The result is in `nacl.sfr`. To show:

```
guest@403-a324-01:~/VY$ plot nacl.sfr
```

Exercise: structure factor of the NaCl crystal

Now the same by the Fourier transform of the RDF

Calculate the RDF first:

```
guest@403-a324-01:~/VY$ rdfg nacl -g -p
```

Fourier transform for a mixture with given b_i:

```
guest@403-a324-01:~/VY$
                  cat nacl.∗.g | sfourier 100 30 216 NA:3.63 CL:9.577 >| nacl.sfg
```

Comparison:

```
guest@403-a324-01:~/VY$ plot nacl.sfr nacl.sfg
```

`nacl.sfr` = direct result

`nacl.sfg` = RDF-inverted result

Exercise: structure factor of the NaCl melt

We will melt the sample, equilibrate, and simulate the melt.

- Melting:

  ```
  guest@403-a324-01:~/VY$ cook nacl -s
  ```

  `T=5000` a lot at start, to melt the crystal
  `tau.P=0` but NVT, so that it does not evaporate
  `no=50 ;` start 50 steps

- Cooling the melt

  `T=1400 ;` temperature of the melt and cooling in NVT

- Equilibrating of the melt sample at given temperature, pressure

  `bulkmodulus=2e9` approx. bulk modulus of the liquid for NPT [in Pa]
  `tau.P=1` time constant of the barostat
  `no=100;` running at selected temperature, pressure in NPT
  `key="cp"` to have a look whether the system has equilibrated
  `;` repeat until equilibrated

- Final run

  `tau.P=0` NVT again to calculate RDF + write a trajectory
  `init="start" ;`

- To be followed by the same algorithm as in the case of crystal. . .