Structural quantities

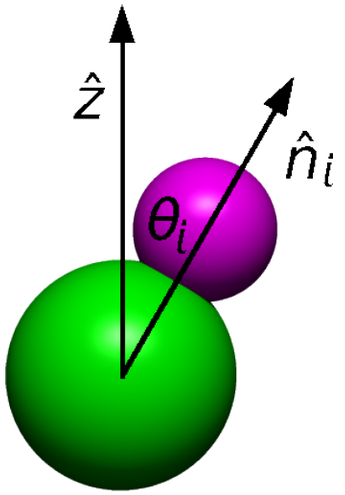
Correlation functions

- 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

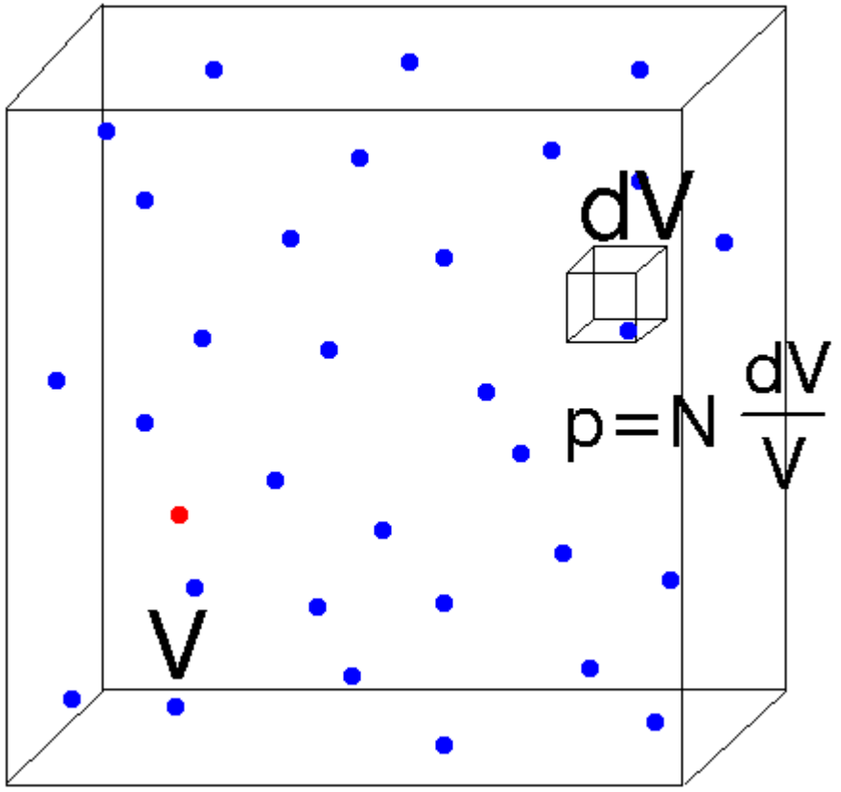
- Ordering in the z-direction: $\left\langle \sum_i \cos\theta_i \right\rangle$: ↑ vs. ↓
- For symmetric molecules: $\left\langle \sum_i \left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2} \right) \right\rangle$: ↕ vs. ↔
- Nematic liquid crystal – the “director” is not known:

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

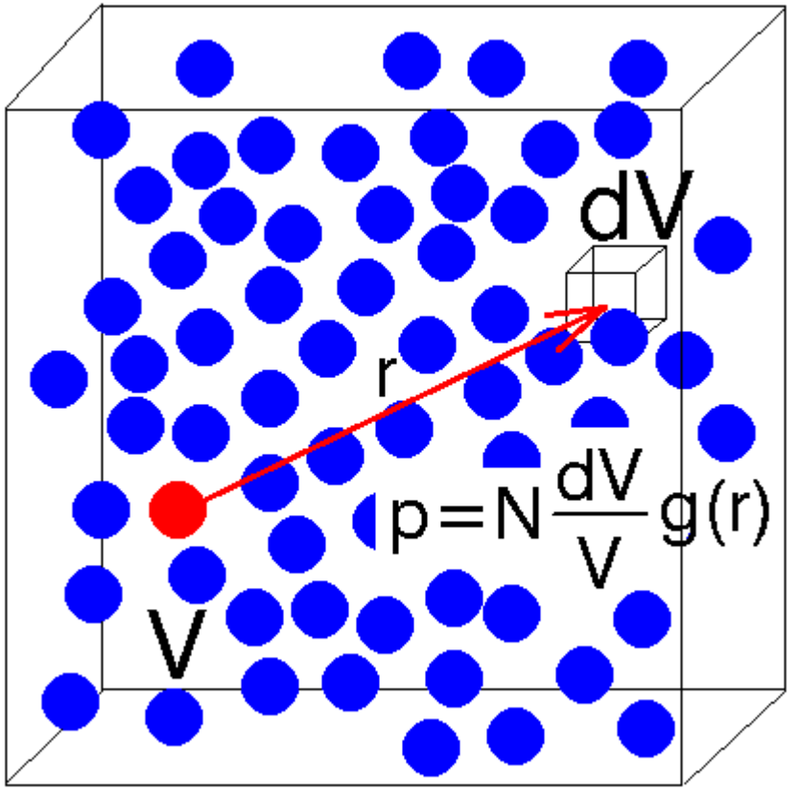


- Formulas detecting local order (e.g., tetrahedral around water molecules as Steinhardt’s parameters based on spherical harmonics), onset of crystallization can be detected . . .

Structure of fluids – correlation functions



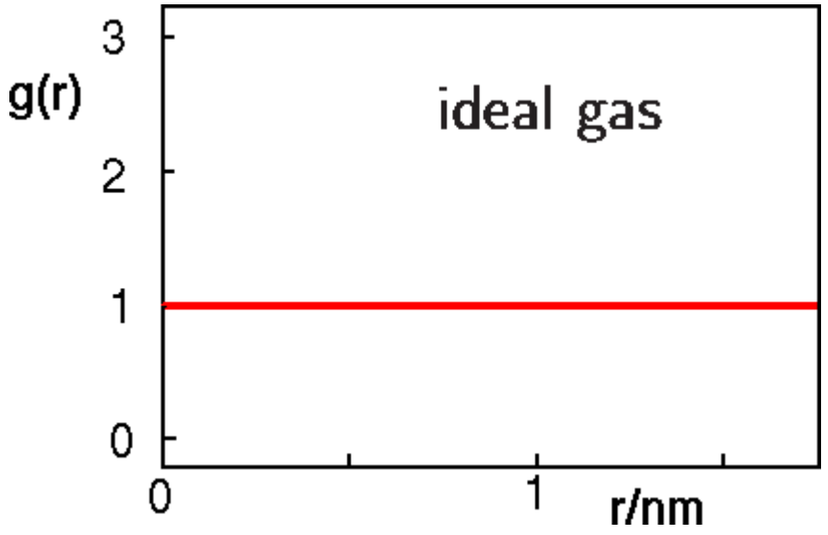
randomly distributed molecules
(ideal gas)

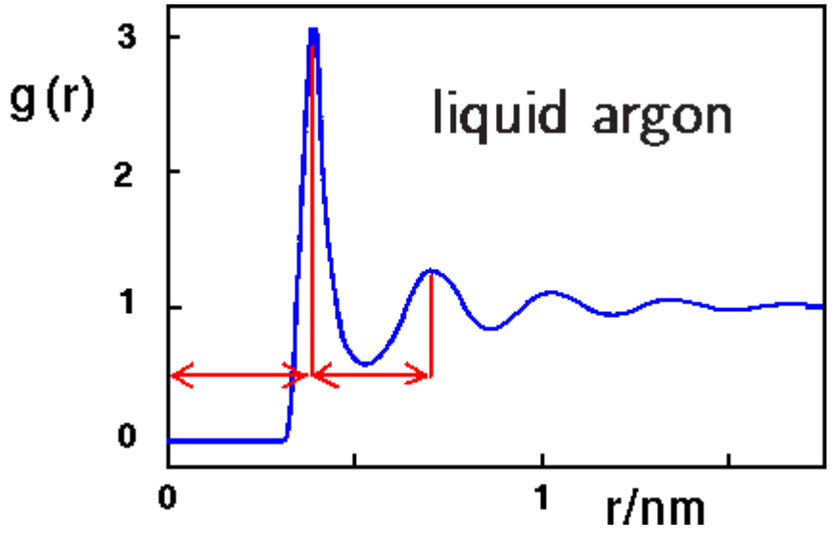


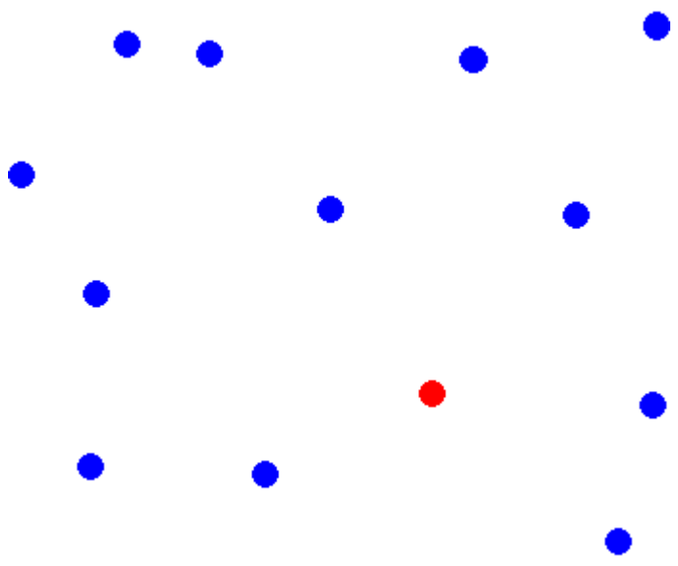
liquid

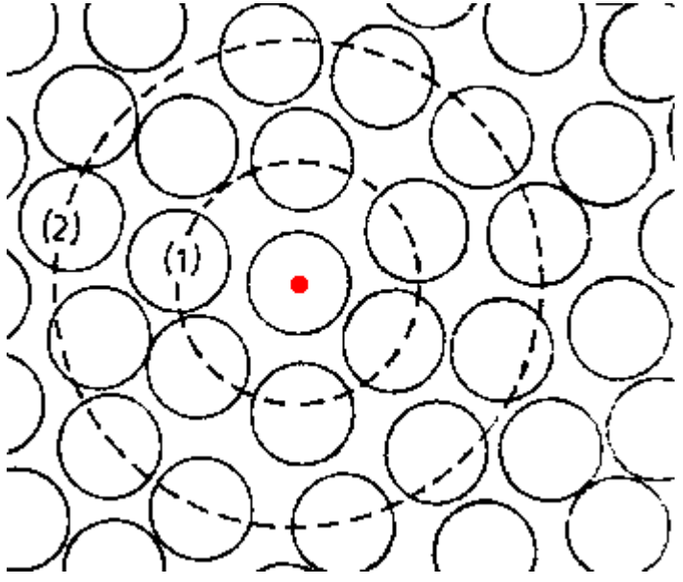
$g(r)$ = pair correlation function = radial distribution function = probability density of finding a particle r apart from another particle, normalized so that for randomly distributed particles (ideal gas) it is 1

Structure of fluids – correlation functions

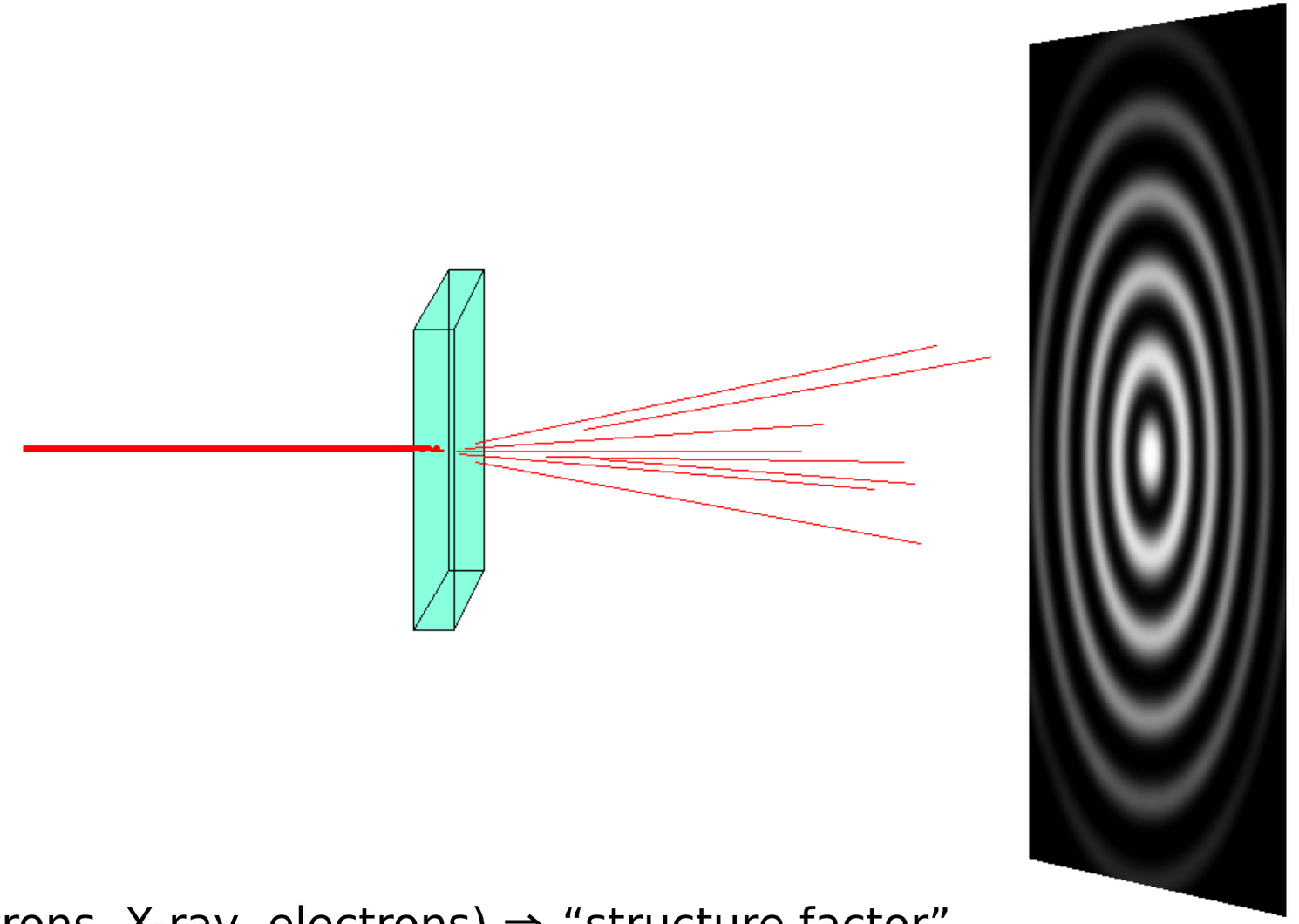






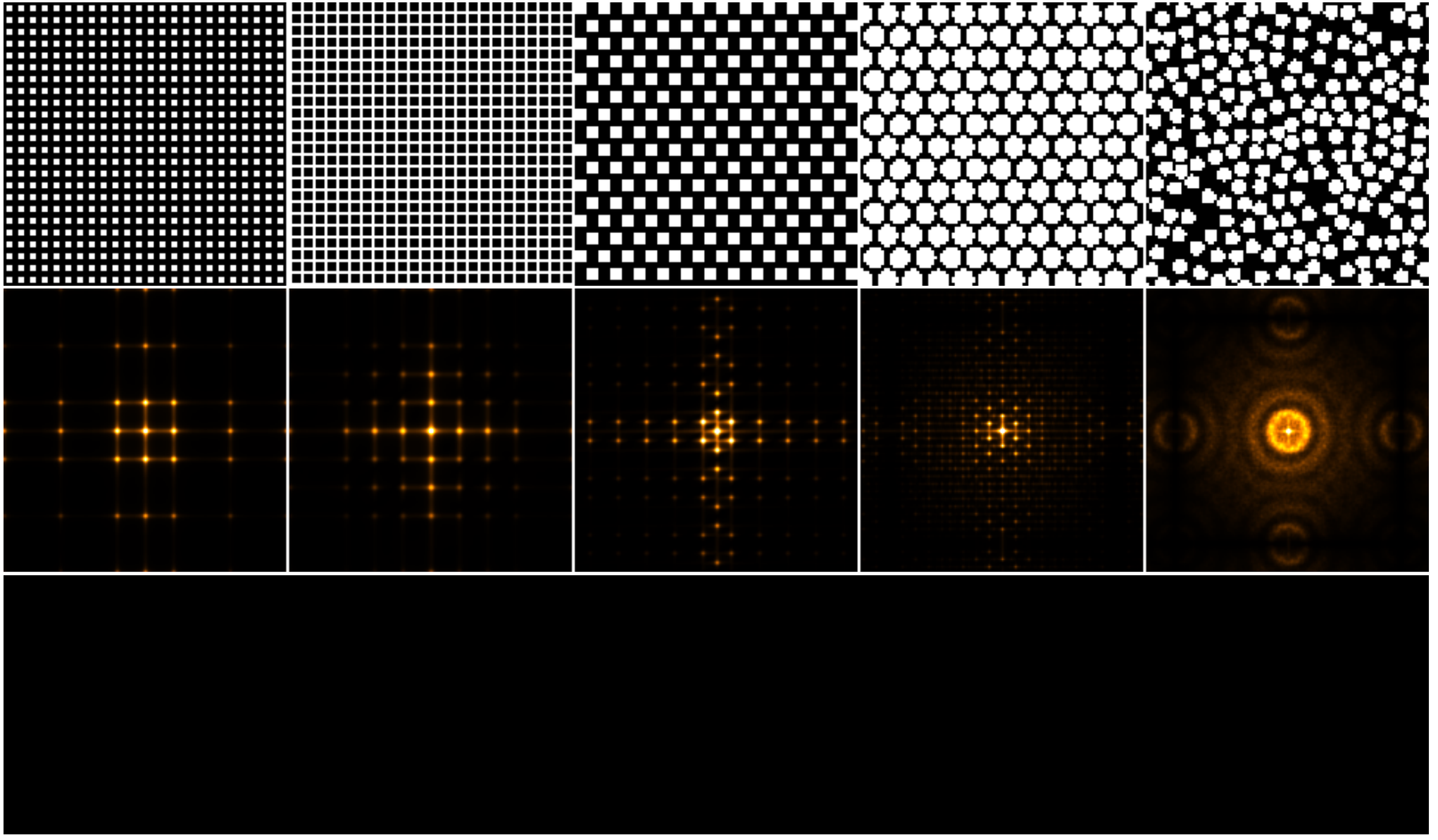


How to obtain structure – experiment

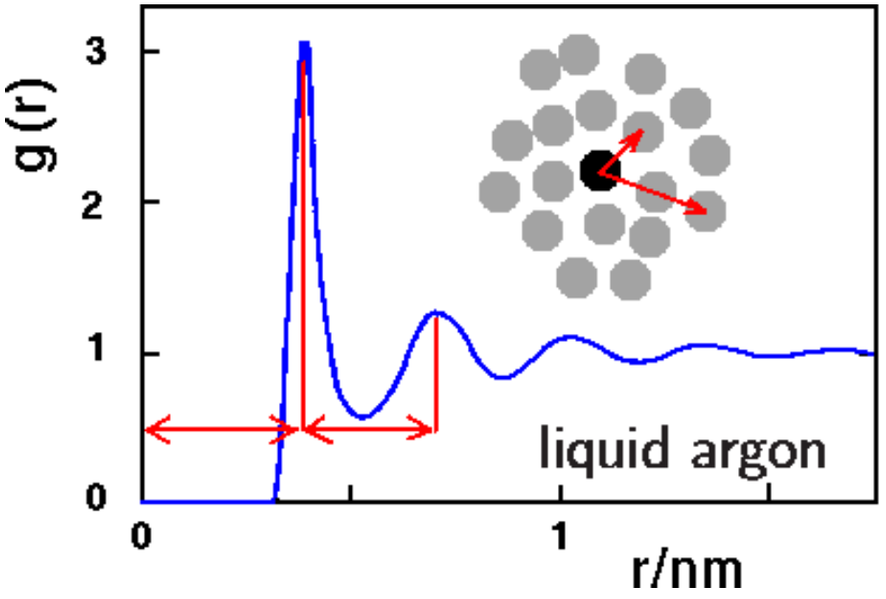


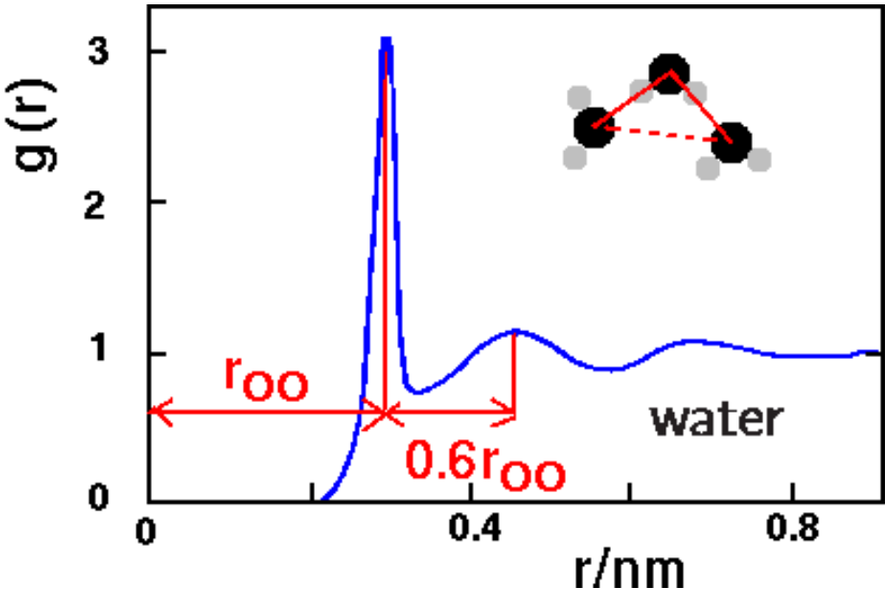
- Diffraction (neutrons, X-ray, electrons) ⇒ “structure factor”
- inverse Fourier transform ⇒ RDF

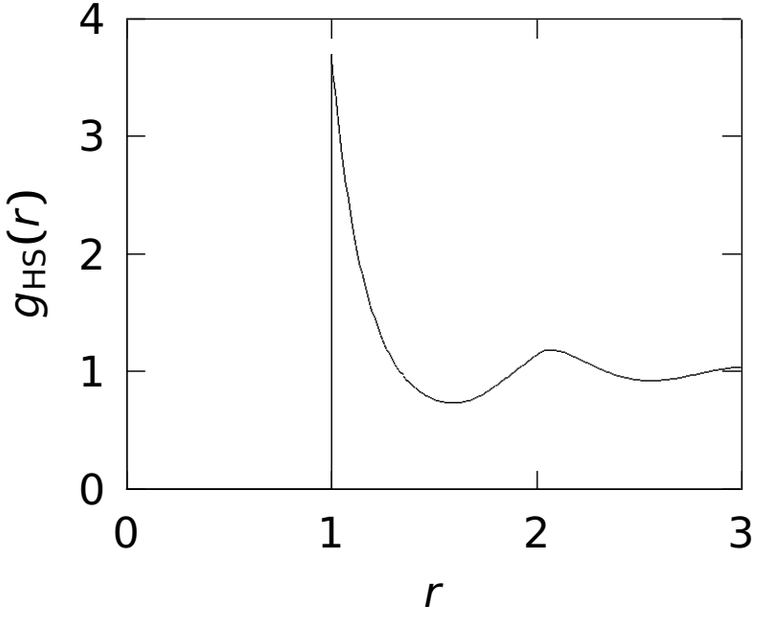
How to obtain structure



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.

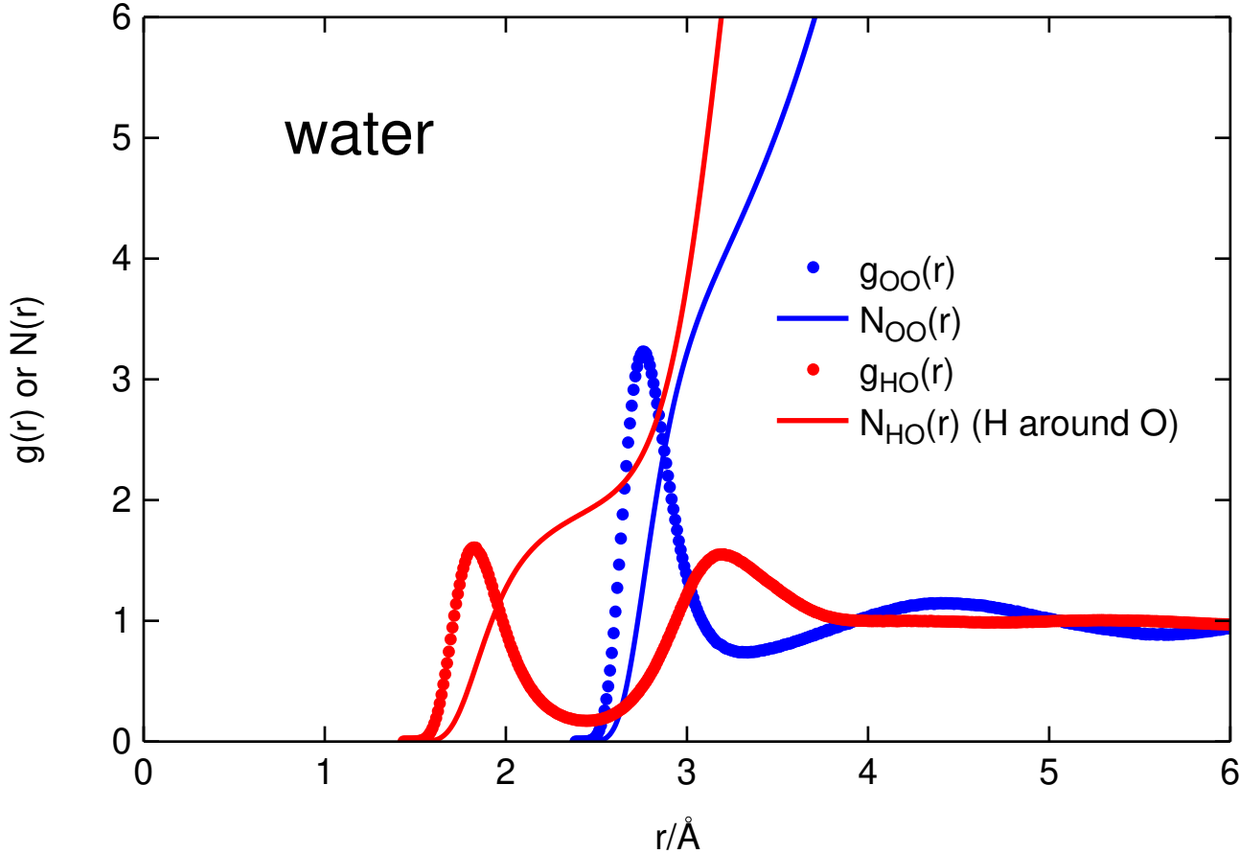
Running coordination number

Also “cumulative radial distribution function”

$\rho = N/V$ = number density

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

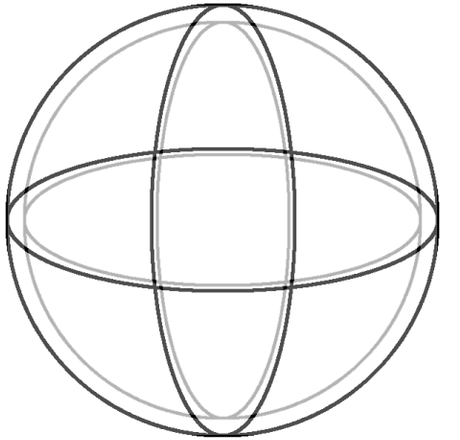
For r_{min} = first minimum on the RDF curve, $N(r_{\mathrm{min}})$ = “coordination number” = averaged number of molecules in the first shell



RDF from simulations – simple

Histogram of the number of particle pairs, h_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, $\boldsymbol{\rho} = N/V$):

$$\boldsymbol{\rho}\Delta V_i$$

Sum over all particles (1/2 to count each pair just once):

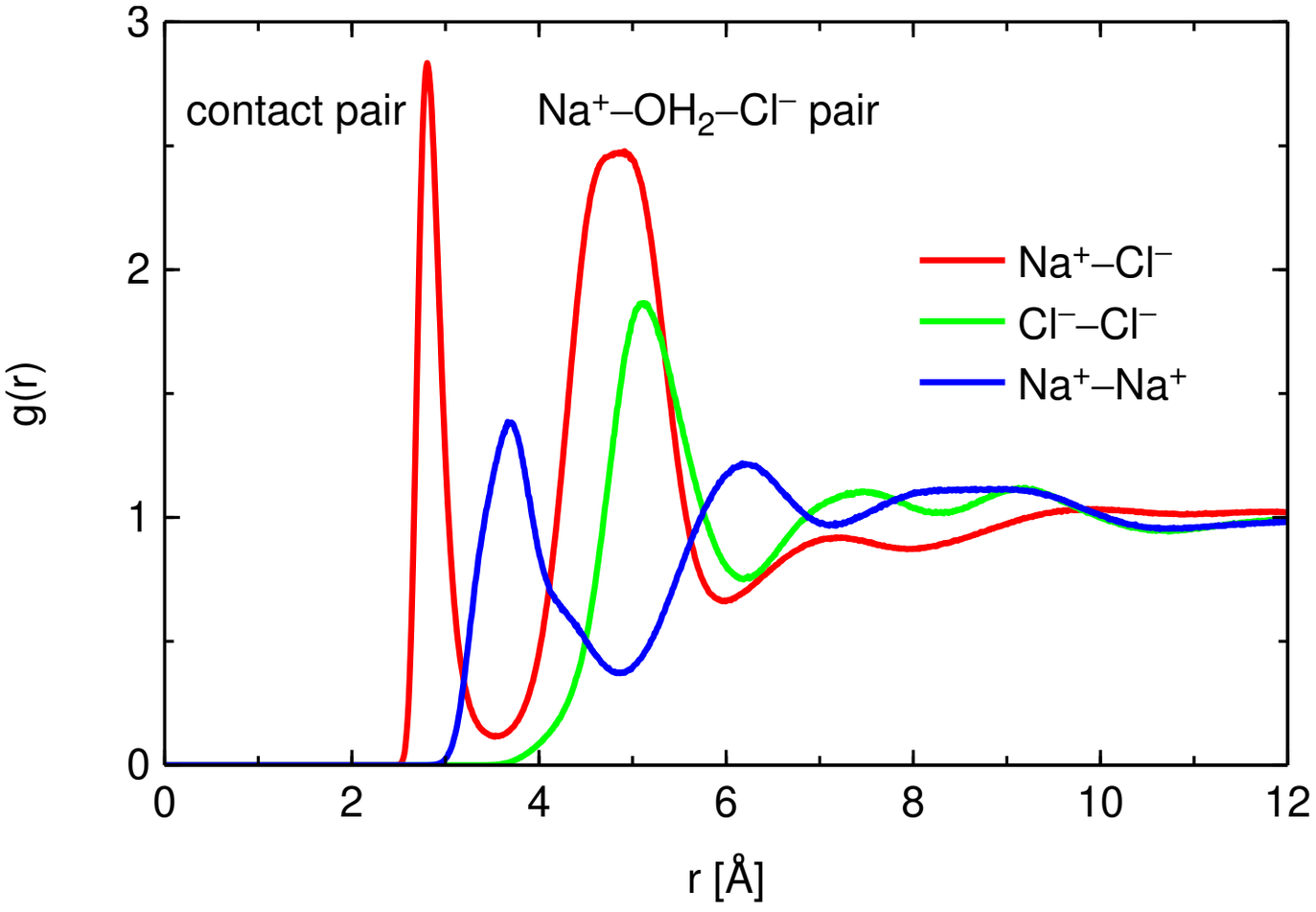
$$h_i^{\text{id. gas}} = \frac{N}{2}\boldsymbol{\rho}\Delta V_i$$

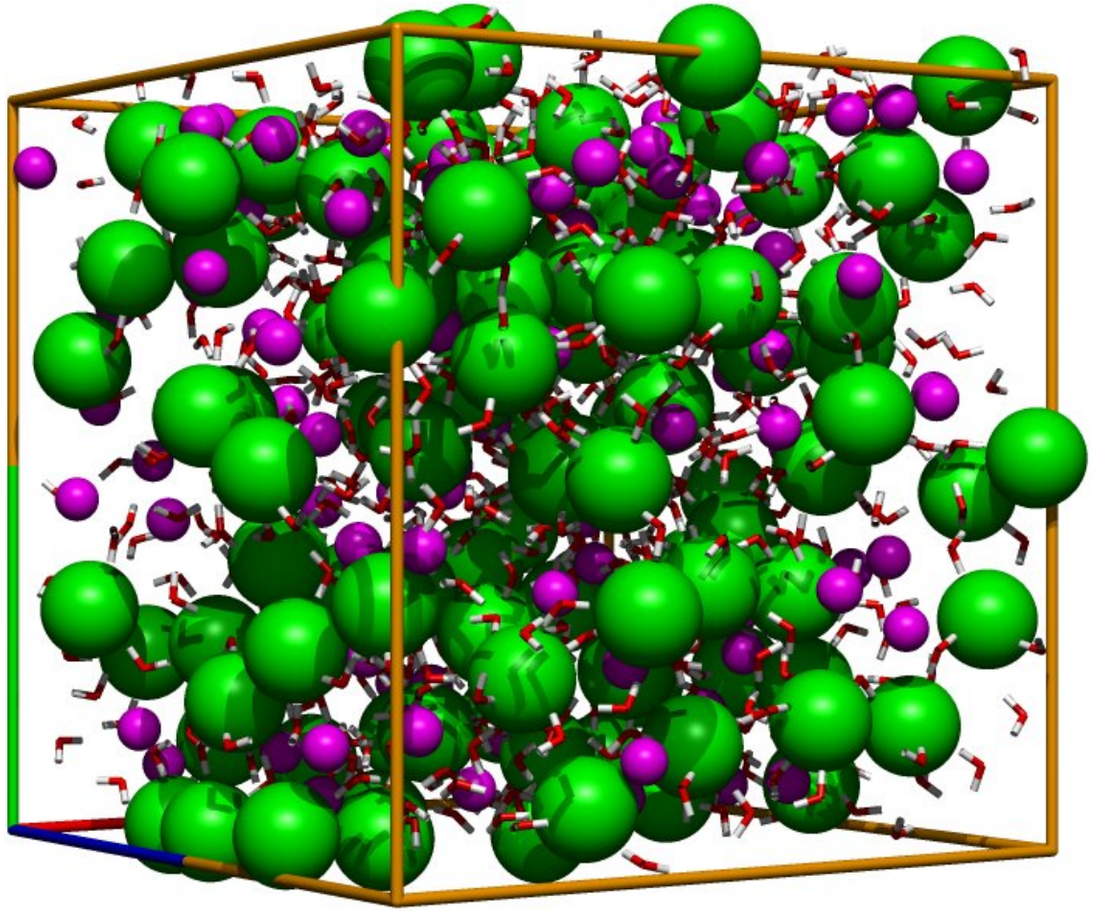
Radial distribution function:

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

Another example – brine

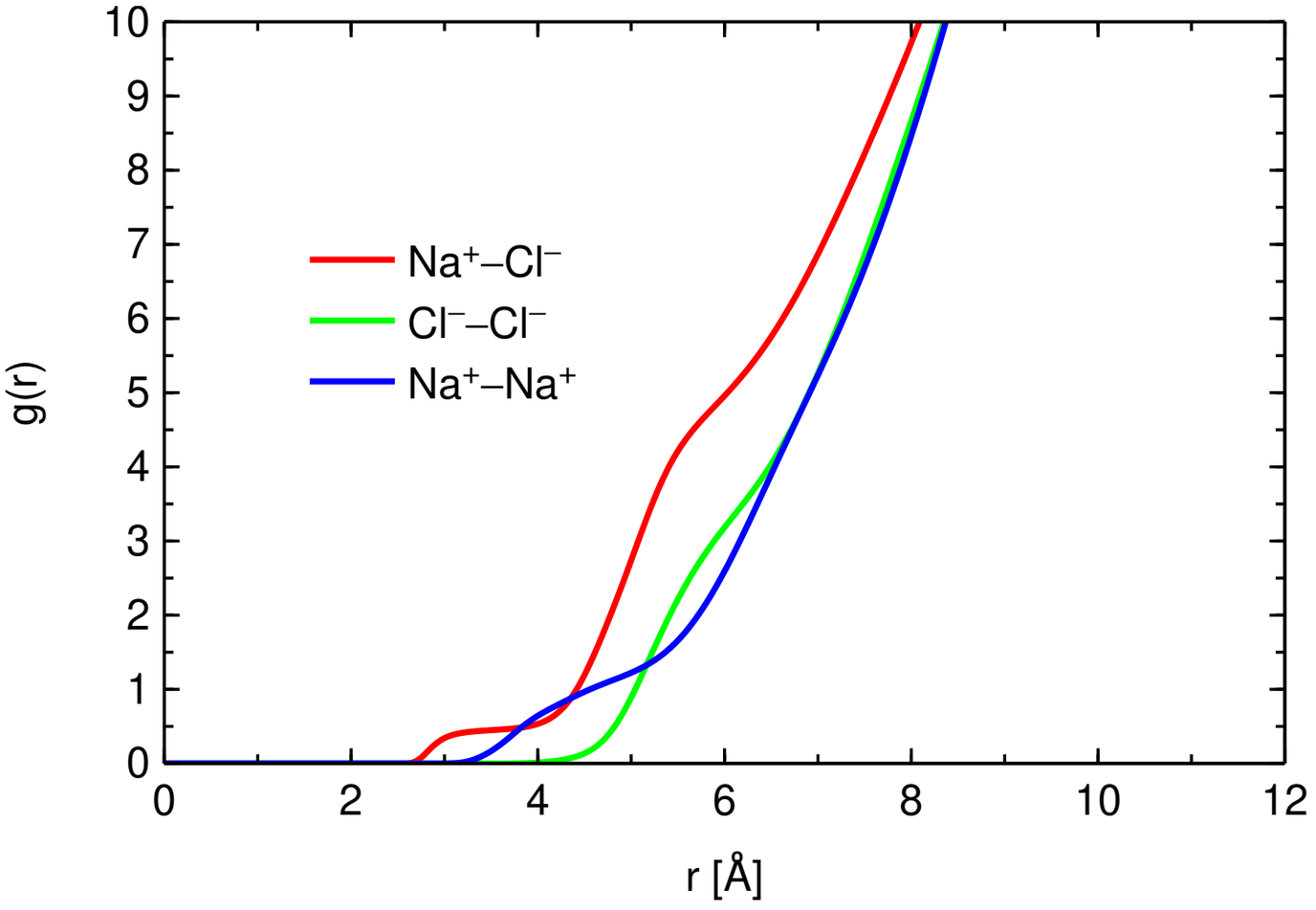
RDFs of supersaturated (10.5 mol/kg) solution of NaCl:

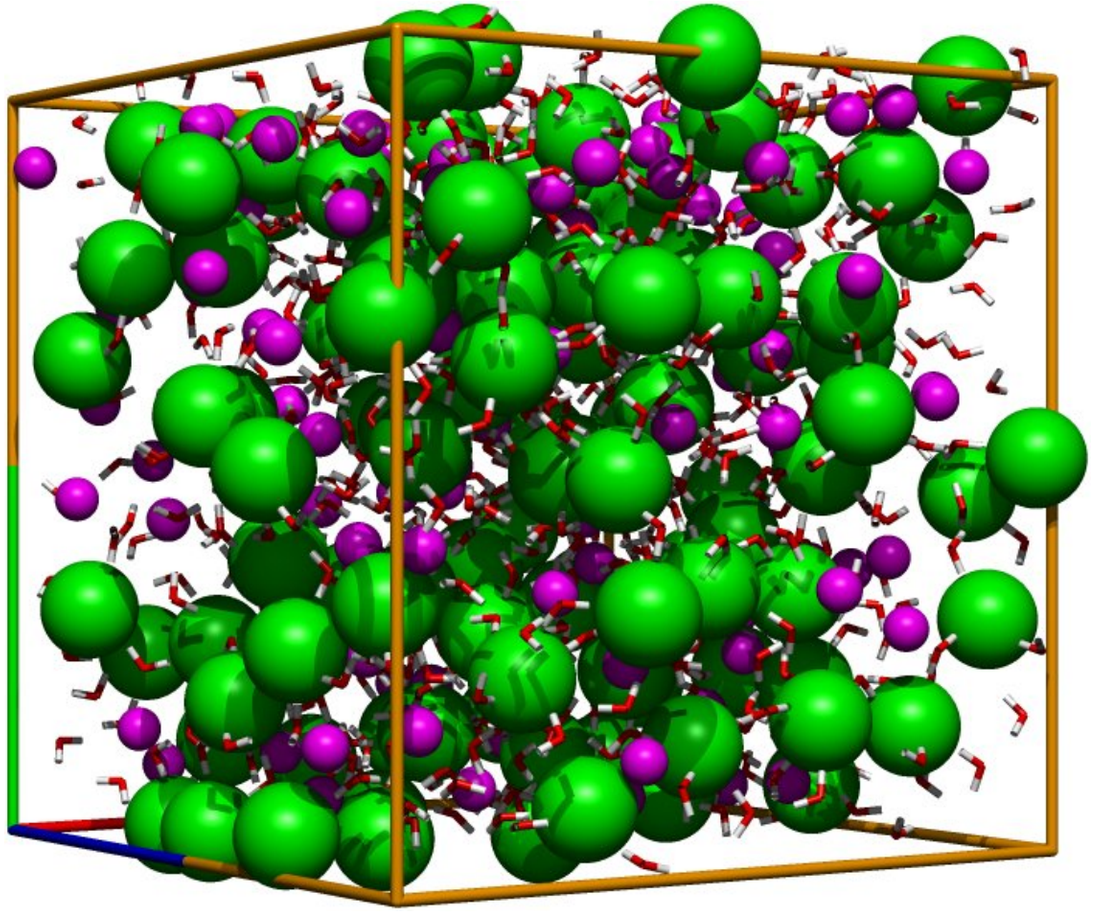




Another example – brine

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





SIMOLANT – installation (Windows)

How to install SIMOLANT (Windows):

- Google 🔍 simolant or links:
  - https://github.com/kolafaj/SIMOLANT
    → executables
  - http://old.vscht.cz/fch/software/simolant
- Download `simolant-win.zip`
- Create a folder and unpack `simolant-win.zip` into it
  Do not run directly from
  "folder" `simolant-win.zip`
  - help would not work
  - you would not find the created files
- Run `simolant.exe`

Hints:

- The calculated data are exported to protocols `simolant.txt` and `simolant.csv` with decimal dot, the CSV separator is comma.
  If you like decimal comma (e.g., for localized excel) and CSV separator semicolon, select ▮comma in panel "Measure" (so that it gets green: ▮comma).[a]
- If you restart SIMOLANT, the old versions of `simolant.txt` and `simolant.csv` are overwritten by the new files. To avoid this, you may change the base name `simolant` in Menu: File → Protocol name..

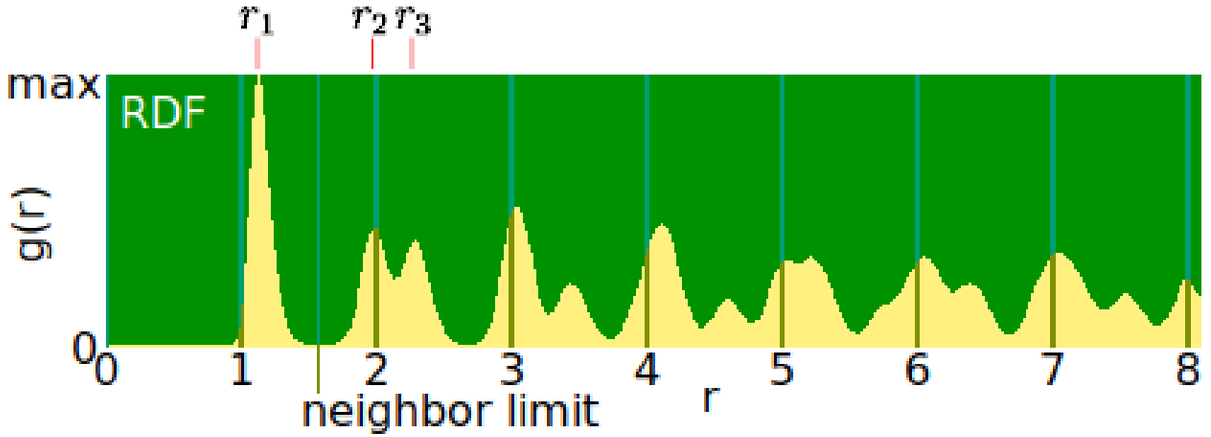
[a] SIMOLANT does not detect localization and never will.

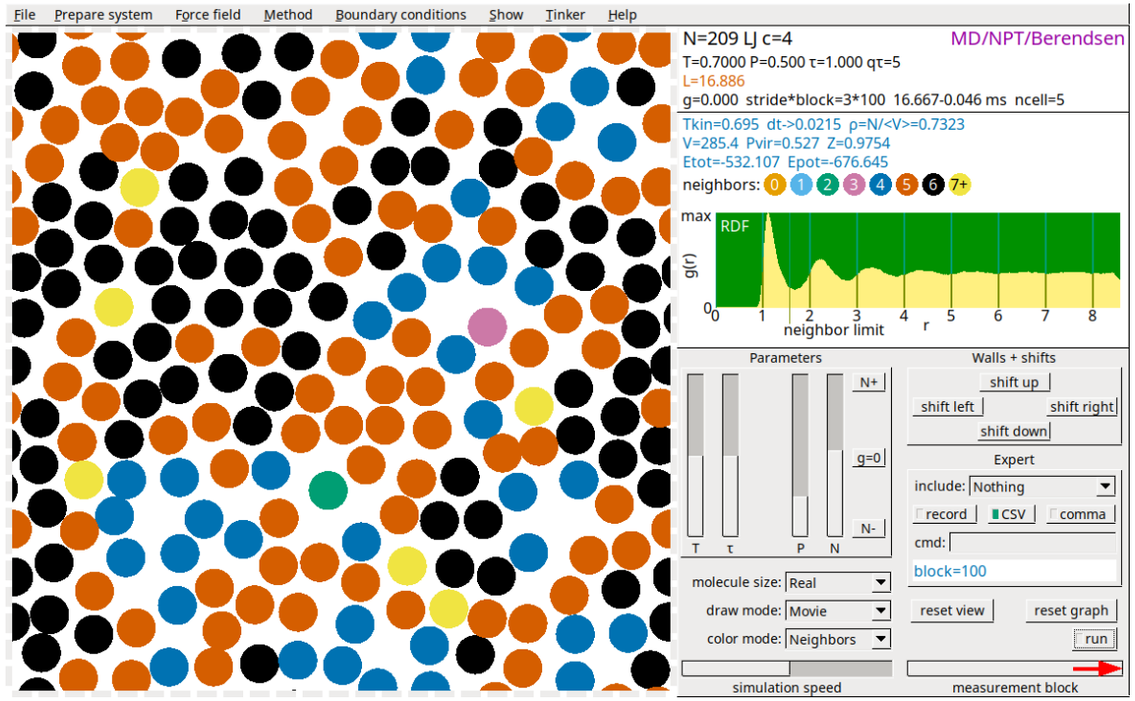
SIMOLANT: Observe RDF yourself

- Menu: Prepare system → Periodic liquid

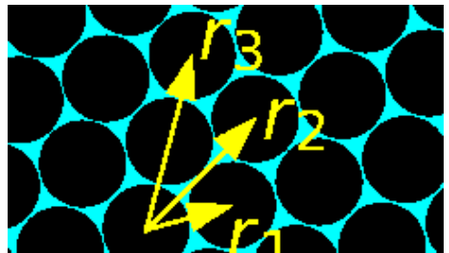
The RDF graph is scaled from 0 to maximum.

- For smoother results, move slider “measurement block” to maximum (esp. for gas).
- Increase/decrease temperature a bit (slider “T”). You may change pressure, too (slider “P”).
- 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:





- 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:

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

Equivalently: $g(\vec{r}) = \left(1 - \frac{1}{N}\right) V \langle \delta(\vec{r}_{12} - \vec{r}) \rangle$

For a mixture: $g_{ij}(\vec{r}) = V \langle \delta(\vec{r}_{12} - \vec{r}) \rangle$

Normalization and thermodynamic limit (fluid): $\lim_{N\to\infty, r\to\infty} g(r) = 1$

↑

Using n-particle distribution functions:

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

where $\rho_1 = \rho$ in a homogeneous fluid.

# of particles around one chosen particle in NVT "over whole system" (imagine periodic b.c.):

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

Ideal gas: $g(\vec{r}) = 1 - \frac{1}{N}$

Extension (short-range potentials): $\lim_{r\to\infty} g(r) = 1 - \frac{\kappa_T}{N\kappa_T^{\text{id. gas}}} + \mathcal{O}(1/N^2)$, where κ_T = compressibility

Calculation of RDF in simulations – exact

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

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

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

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

The formula again:

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

Correlation function and thermodynamics

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

Residual internal energy:

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

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

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

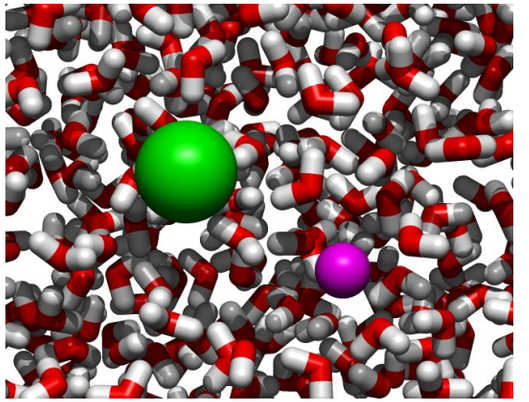
Pressure:

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

Case study: RDF and PMF in infinite dilution. 1. Direct simulation

The potential of mean force (PMF) between two particles (ions) in a solution is

$$U_{\mathrm{PMF}}(r) = -RT \ln g(r).$$

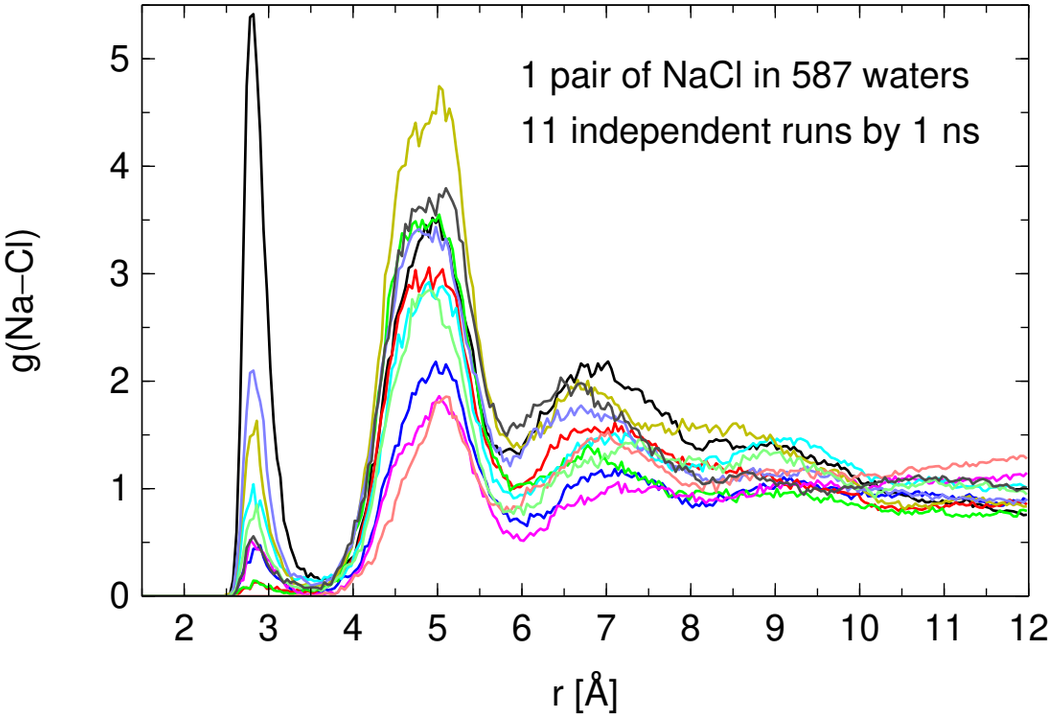


Calculating $g(r)$ or $U_{\mathrm{PMF}}(r)$ in **infinite dilution** is demanding:

- poor statistics (only 1 pair of ions),
- possible barrier between contact and water-separated ion pairs.

Example: NaCl in water

- Force field: Joung–Cheatham NaCl + SPC/E water
- 1 pair of Na^+Cl^- in 587 water molecules (box 26 Å^3)
- $T = 300\,\mathrm{K}$, $\rho = 1002.5\,\mathrm{kg\,m^{-3}}$
- mass repartitioning: equalization factor 0.8, $h = 2\,\mathrm{fs}$
- 1 measurement every 10 fs
- RDF range $c = 12\,\text{Å}$



RDF+PMF. 2. Why is it so inaccurate?

Barrier crossing:

- $g_{\min} \approx 0.1 \Rightarrow 10\times$ typical time (in water $\approx 1\,\mathrm{ps}$) needed,
- it is not so bad, but worsens the time scale caused by diffusion

Diffusion:

- Experimental molar conductivities [$\mathrm{S\,m^2\,mol^{-1}}$]: $\lambda_\oplus = 0.00501, \lambda_\ominus = 0.00763$
- Approximate mutual conductivity (not so important): $\lambda = \sqrt{\lambda_\oplus^2 + \lambda_\ominus^2}$
- (Mutual) diffusion coefficient: $D = \lambda RT/F^2 = 2.4 \cdot 10^{-9}\,\mathrm{m^2\,s^{-1}}$
- Distance to travel: $d = c/2$ ($c = \mathrm{cutoff} = 12\,\text{Å}$)
- Typical diffusion time (1D approx.): $t = d^2/2/D = 70\,\mathrm{ps}$

Both phenomena together cause poor convergence in time scale $t \times 10 \sim 1\,\mathrm{ns}$

RDF+PMF. 3. Metadynamics $h(r) = 1$

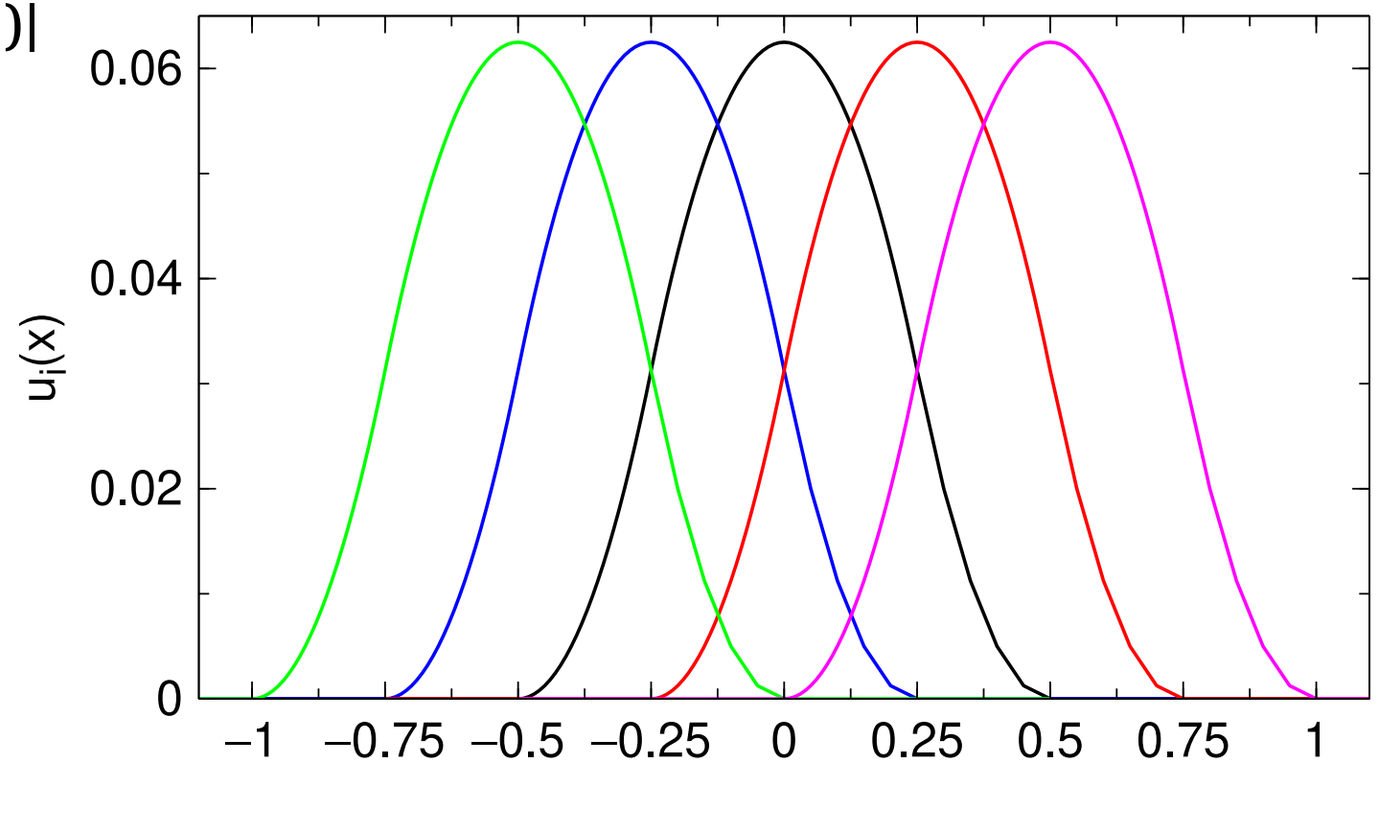
Generalized coordinate: $r = |\vec{r}(\mathrm{Na}^+) - \vec{r}(\mathrm{Cl}^-)|$

The bias potential is

$$U_{\mathrm{bias}}(r) = \frac{1}{2d^2} \sum_{i=0}^{n_{\max}} A_i u(r - id),$$

where $d = 0.25\,\text{Å}$ and

$$u(x) = \begin{cases} 0 & \text{for } x < -2d, \\ (2d + x)^2/2 & \text{for } x \in [-2d, -d], \\ d^2 - x^2/2 & \text{for } x \in [-d, +d], \\ (2d - x)^2/2 & \text{for } x \in [+d, +2d], \\ 0 & \text{for } x > +2d \end{cases}$$

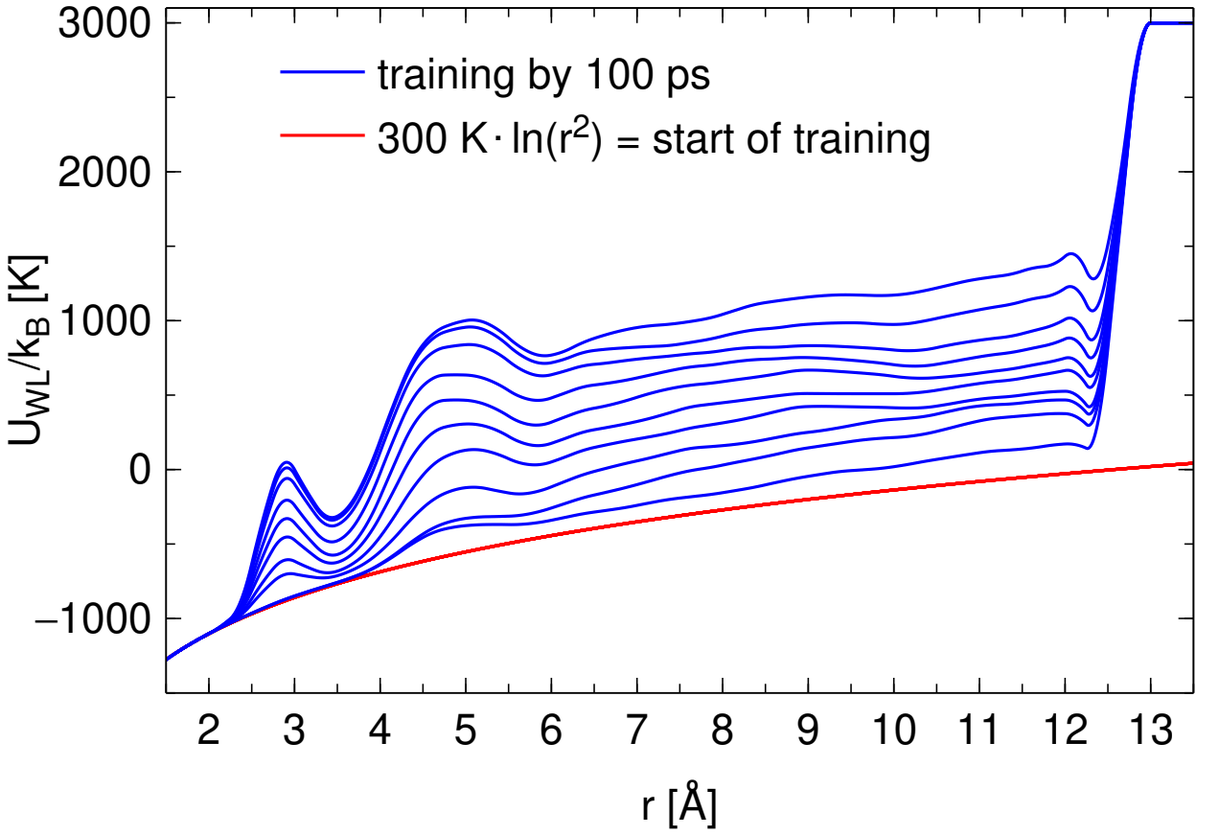


Wang–Landau update: $A_i \mathrel{+}= (d - x) \cdot \dfrac{\omega}{h(r)}, \quad A_{i+1} \mathrel{+}= x \dfrac{\omega}{h(r)}, \quad i = r/d$ (1)

- Starting from a basin $U = 0$ inside wall $A_{n_{\max}} = 3000\,\mathrm{K}$
- ω selected so that the basin fills to 40% of $A_{n_{\max}}$
- Simple version: $h(r) = 1$ (the density of Cartesian points will be included later)
- Opposite possibility: $h(r) = 4\pi r^2$ (see below)

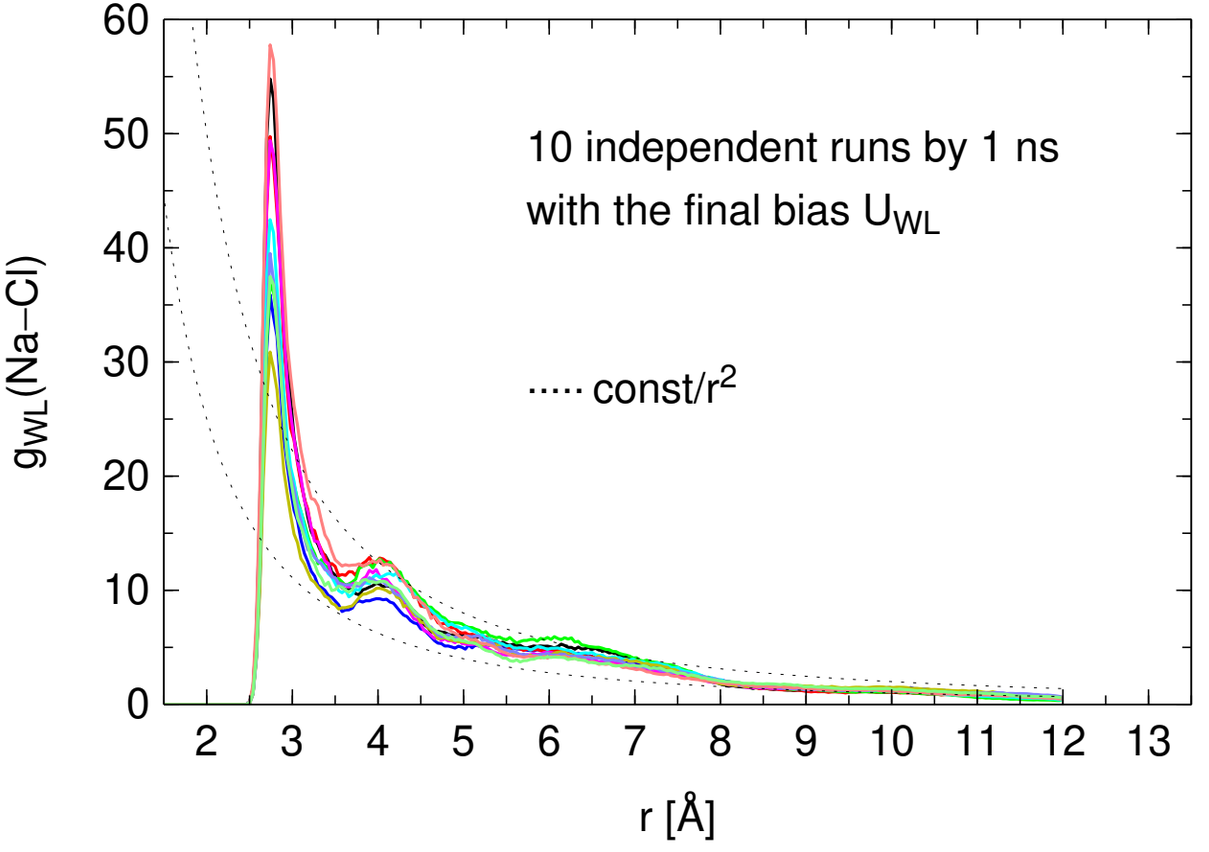
RDF+PMF. 4. Metadynamics $h(r) = 1$ raw results

Training $U_{WL} \approx U_{PMF} + \text{const}$, total time = 1 ns



- The convergence is slow.
- Does not matter, faster runs with bias will follow.

Raw radial distribution function with the bias



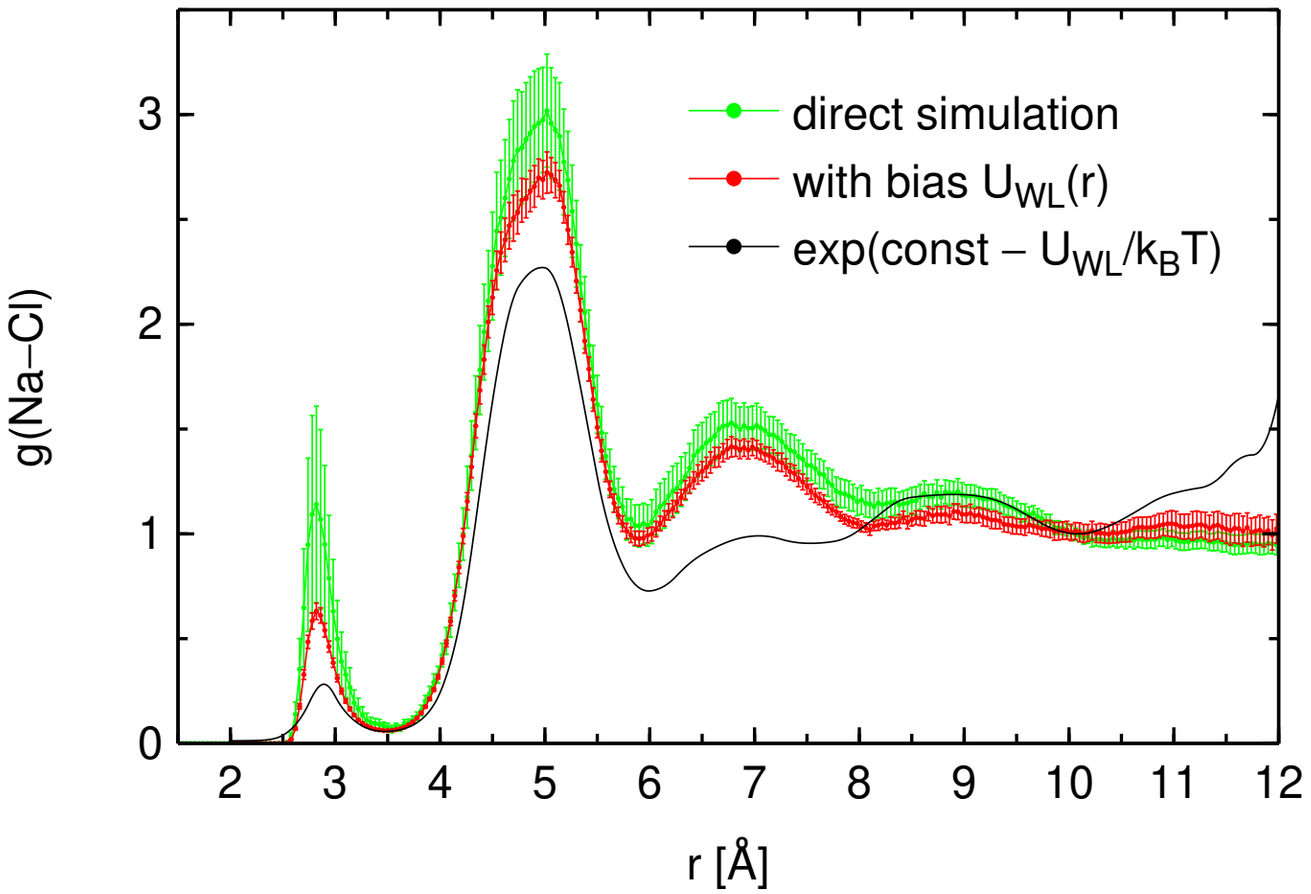
- The difference from const/r^2 is due to discretization, peaks appear for large dU_{PMF}/dr.
- Finer grid would be problematic close to cation–anion contact.

RDF+PMF. 5. Metadynamics $h(r) = 1$ final results

- — 10 independent $g(r)$'s with the bias, multiplied by $\exp(-U_{WL}/k_BT)$ and shifted to $g(10\,\text{Å}) = 1$
- — direct simulation
- RDF grid 0.04 Å, standard errors from 11 or 10 blocks
- Both methods are based on 11 ns trajectories (comparable times)

Summary:

- Wang–Landau is more accurate at short separations.
- For long r, the accuracy is comparable.
- Sampled uniformly: half samples $r < c/2$, half samples $r > c/2$.
- Short separations are oversampled!

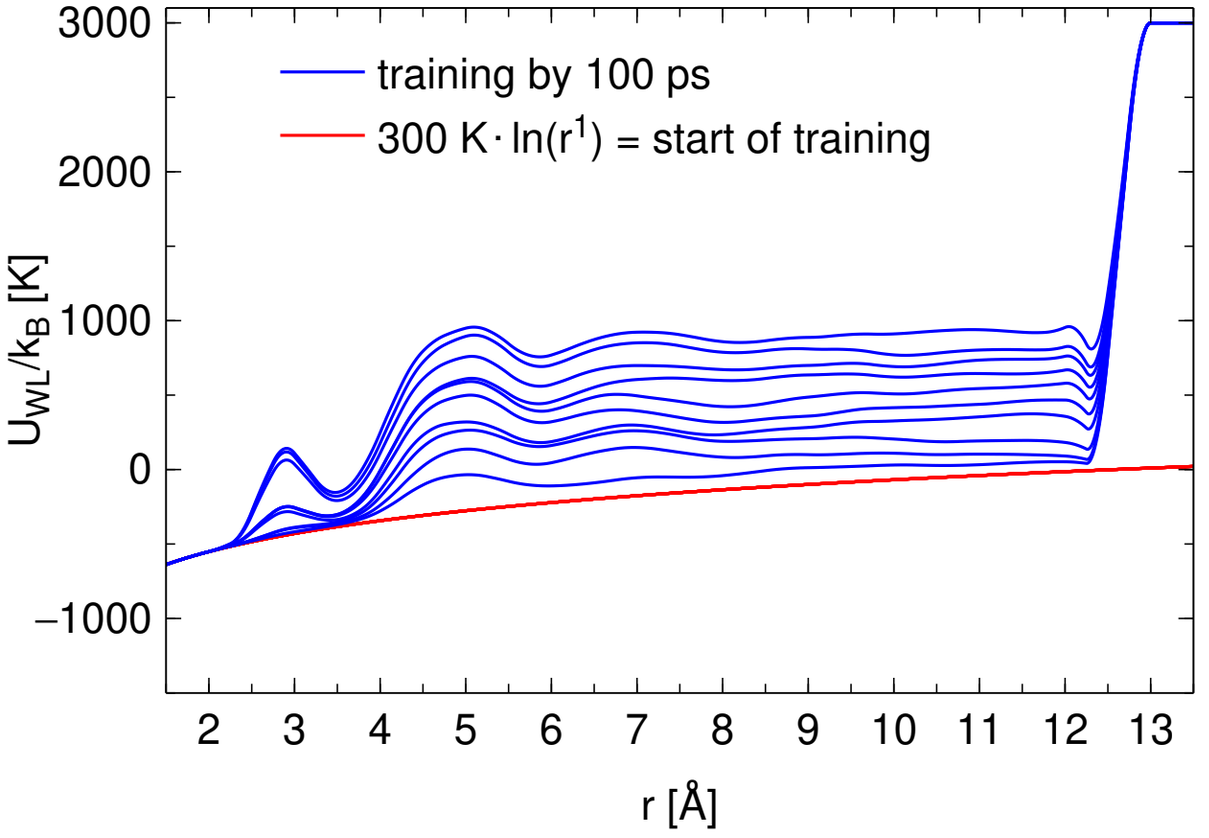


Can we do it better?

- Yes, let's try pre-bias $h(r) = r$ in (1)!
- $h(r) = r^2$ (correct Cartesian volume element) would oversample long separations

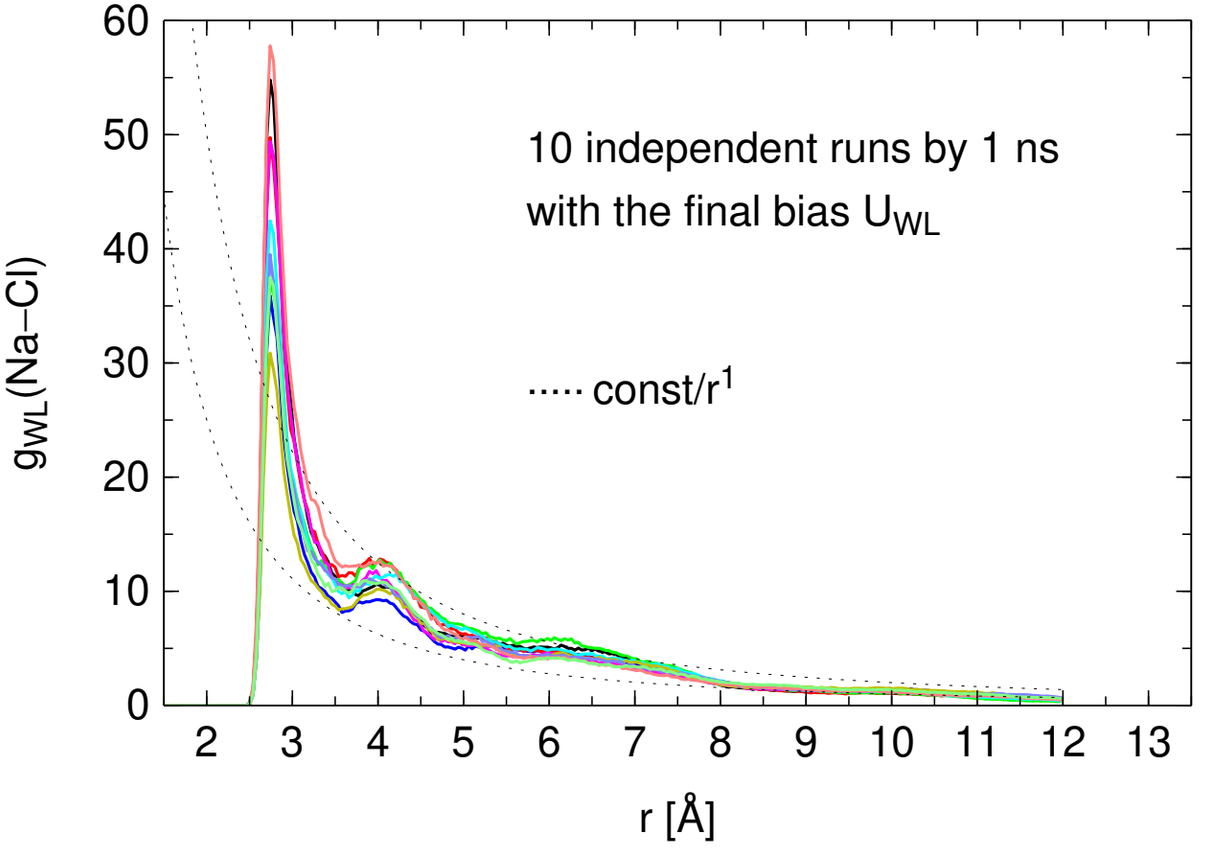
RDF+PMF. 6. Metadynamics $h(r) = r$ raw results

Training $U_{WL} \approx U_{PMF} + \text{const}$, total time = 1 ns



- The convergence is slow at short separations.

Raw radial distribution function with the bias



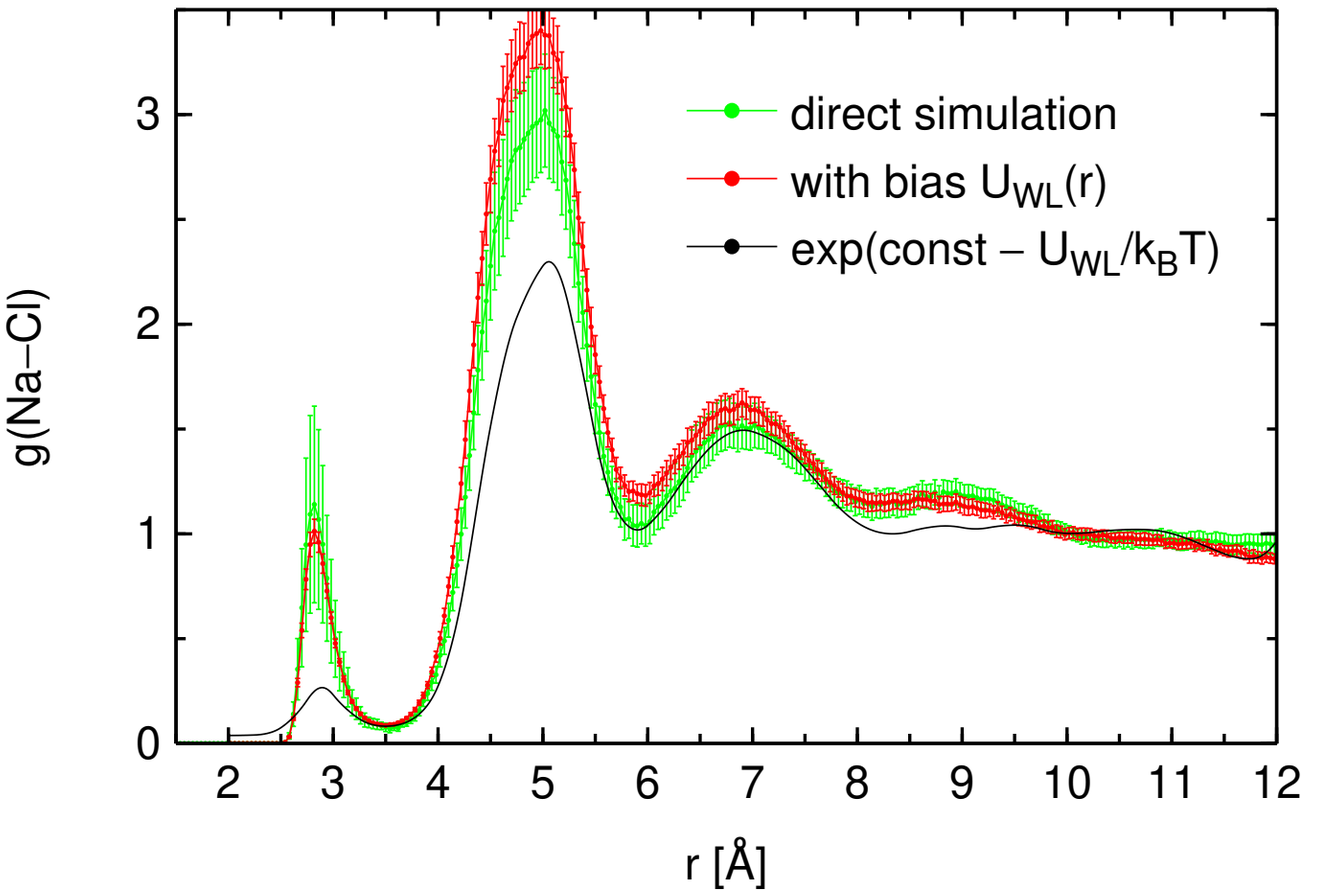
- The difference from const/r^2 is due to discretization, peaks appear for large dU_{PMF}/dr.
- Finer grid would be problematic close to cation–anion contact.

RDF+PMF. 7. Metadynamics $h(r) = r$ final results

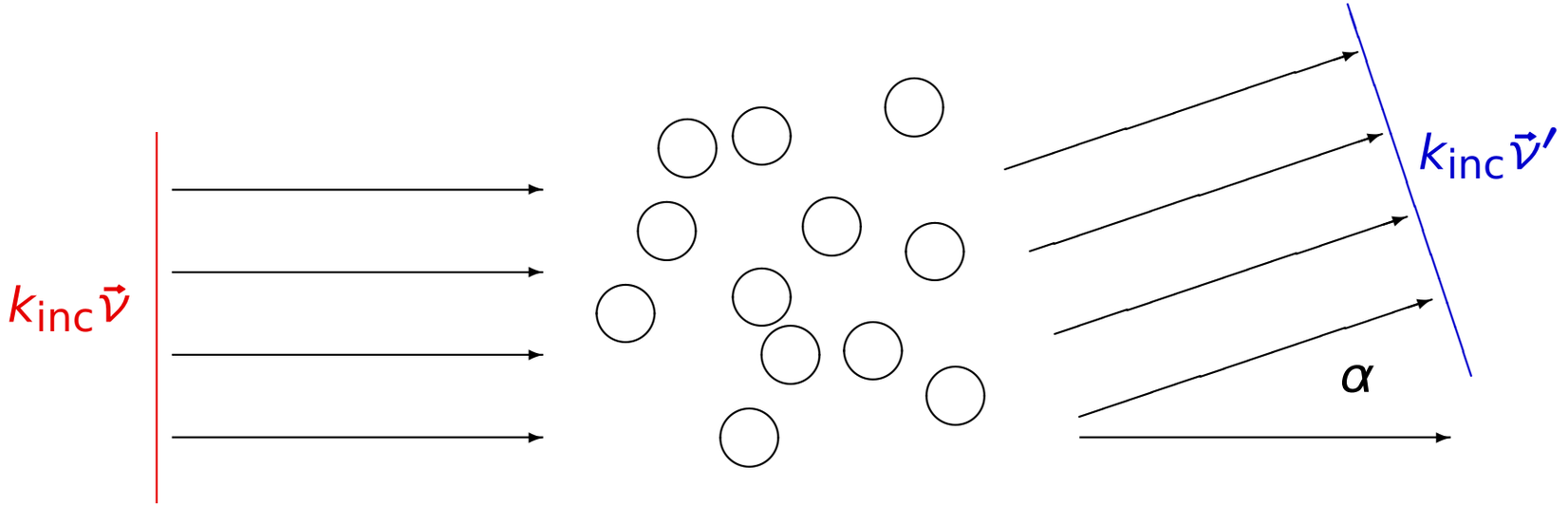
- — 10 independent $g(r)$'s with the bias, multiplied by $\exp(-U_{WL}/k_BT)$ and shifted to $g(10\,\text{Å}) = 1$
- — direct simulation
- RDF grid 0.04 Å, standard errors from 11 or 10 blocks
- both methods are based on 11 ns trajectories (comparable times)

Summary:

- Accuracy is spread more uniformly over distances.



Structure factor



- Weak (the same wave scatters only once)
- 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. $\vec{\nu}\cdot\vec{r}=\text{const}$) via atom r_j to the detector ($\vec{\nu}'\cdot\vec{r}=\text{const}$) is $\vec{\nu}\cdot\vec{r}_j-\vec{\nu}'\cdot\vec{r}_j+\text{const}$
- Wave vector $\vec{k}_{\text{inc}}=k_{\text{inc}}\vec{\nu}$, $k_{\text{inc}}=2\pi/\lambda$
- Formally the incident wave is (except phase):

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

$$\exp[i(k_{\text{inc}}\vec{\nu}-k_{\text{inc}}\vec{\nu}')\cdot\vec{r}_j]=\exp[i\vec{k}\cdot\vec{r}_j],\quad\text{where}\quad\vec{k}=k_{\text{inc}}\vec{\nu}-k_{\text{inc}}\vec{\nu}',\quad k=|\vec{k}|=2\sin(\alpha/2)k_{\text{inc}}\approx\alpha k_{\text{inc}}$$

Structure factor

Waves scattered by all atoms interfere:

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

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)

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

Structure factor and RDF

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

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

The integral diverges as $V \to \infty \Rightarrow$ 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 $\exp(-\alpha k^2)$, $\lim_{\alpha\to 0}$)

$$
S(\vec{k}) = 1 + \boldsymbol{\rho} \int_V [g(\vec{r}) - 1]\cos(\vec{k}\cdot\vec{r})\mathrm{d}\vec{r} \overset{V\to\infty}{=} 1 + \boldsymbol{\rho} \int [g(\vec{r}) - 1]\cos(\vec{k}\cdot\vec{r})\mathrm{d}\vec{r}
$$

Structure factor and RDF

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

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

and the 3D inverse Fourier transform is

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

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

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

The $k \to 0$ limit:

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

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

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)

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

In the same way we can evaluate the inverse Fourier transform:

$$\boldsymbol{\rho}[g(r) - 1] = \frac{1}{8\pi^3} \int [S(\vec{k}) - 1] \cos(\vec{k} \cdot \vec{r}) \, \mathrm{d}\vec{k} = \frac{1}{2\pi^2 r} \int_0^\infty \sin(kr)[S(k) - 1] \, k \mathrm{d}k$$

$$r[g(r) - 1] \leftrightarrow k[S(k) - 1] \quad (\text{sine transform})$$

$S(k)$ 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:

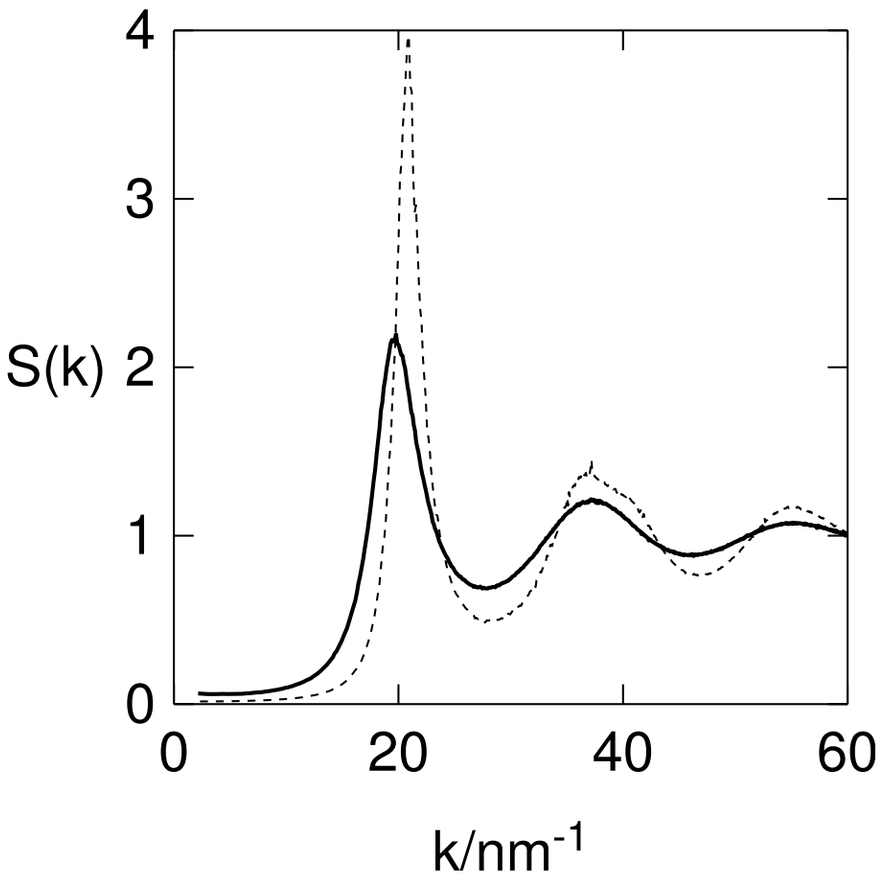
$$S(k) = \sum_{k=|\vec{k}|} S(\vec{k}) / \sum_{k=|\vec{k}|} 1$$

$S(k)$ 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.

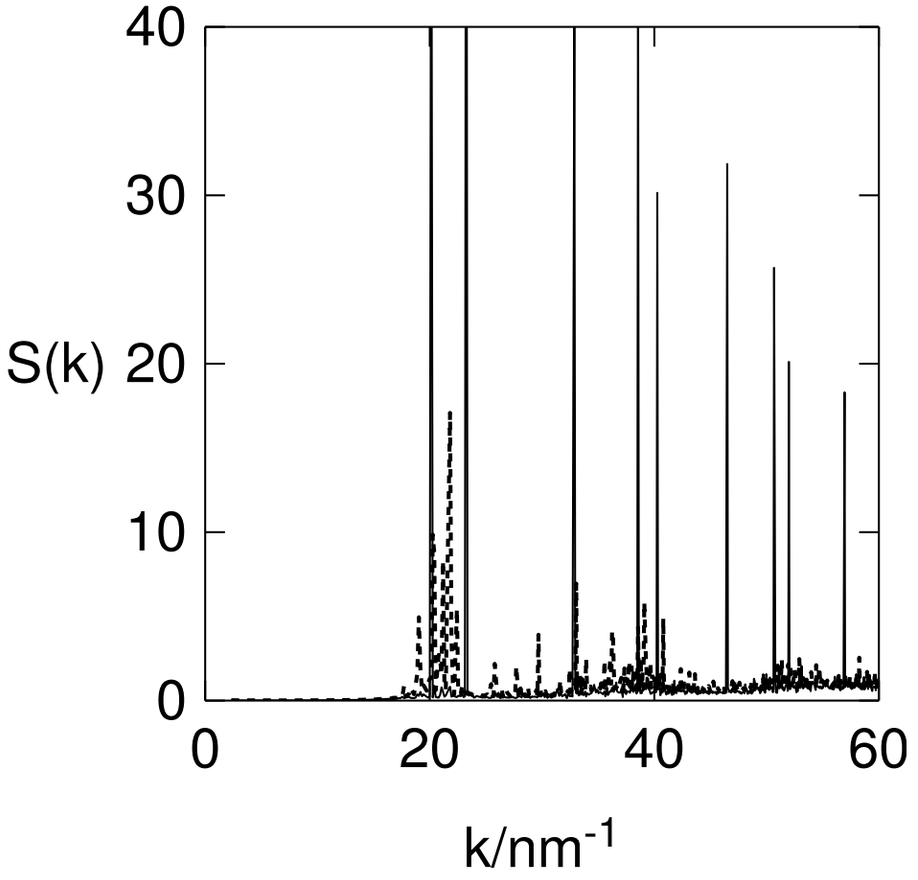
Alternatively, 3D $S(\vec{k})$ can be obtained by the inverse Fourier transform from RDF $g(\vec{r})$ and vice versa.

- 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 for point scattering (nuclear scattering of neutrons), in general integration over the scatterer density (form factor)

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

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

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

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