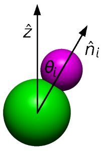
Structural quantities

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

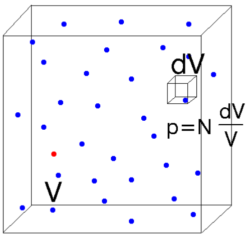


- Ordering in the z-direction: $\langle \sum_i \cos\theta_i \rangle$: ↑ vs. ↓
- For symmetric molecules: $\left\langle \sum_i \left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right)\right\rangle$: ↕ vs. ↔
- Nematic liquid crystal – the “director” is not known:

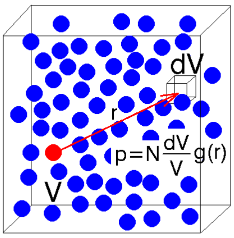
$$Q_{\alpha\beta} = \left\langle \sum_i \left(\frac{3}{2}\hat{n}_{\alpha,i}\hat{n}_{\beta,i} - \frac{1}{2}\delta_{\alpha\beta}\right)\right\rangle, \quad \text{eigenvector of the max. eigenvalue = director}$$

- 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



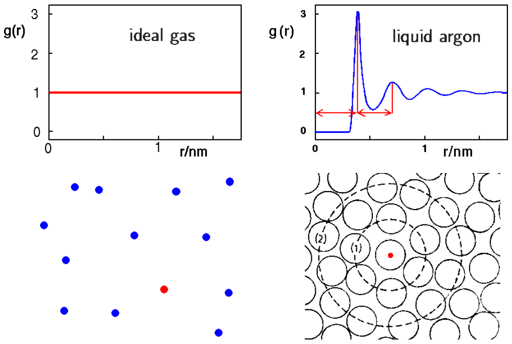
randomly distributed molecules
(ideal gas)



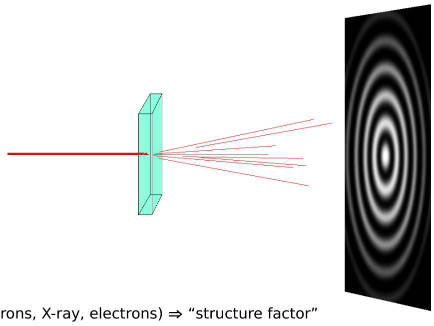
liquid

$g(r)$ = 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

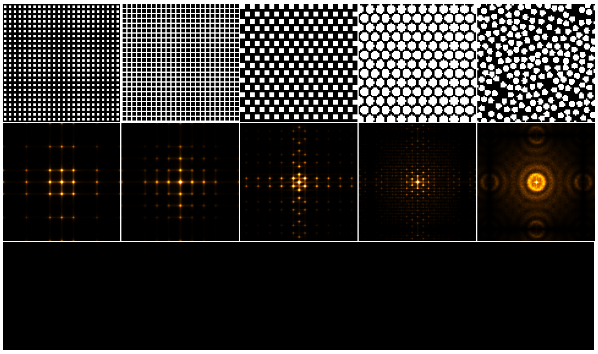


How to obtain structure – experiment

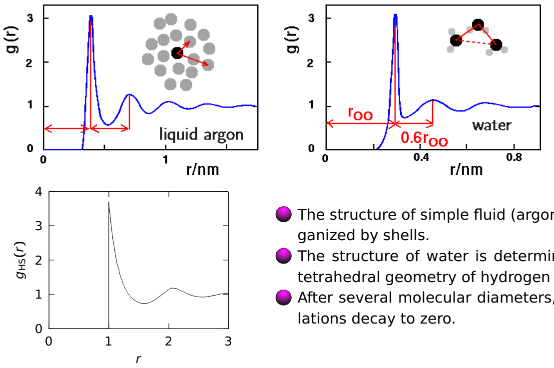


- Diffraction (neutrons, X-ray, electrons) ⇒ “structure factor”
- inverse Fourier transform ⇒ RDF

How to obtain structure



Argon, hard spheres, water



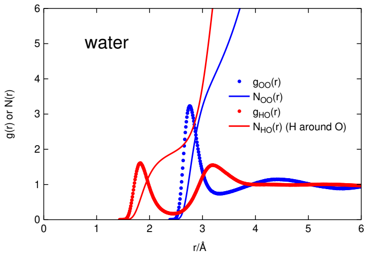
- The structure of simple fluid (argon, HS) is organized by shells.
- The structure of water is determined by the tetrahedral geometry of hydrogen bonds.
- After several molecular diameters, the correlations decay to zero.

Running coordination number

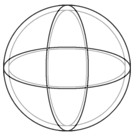
Also “cumulative radial distribution function” $\rho = N/V$ = number density

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

For $r_{\min}$ = first minimum on the RDF curve, $N(r_{\min})$ = “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):

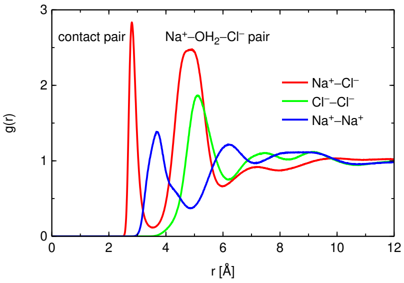
$$\mathcal{N}_i^{\text{id. gas}} = \frac{N}{2}\rho\Delta V_i$$

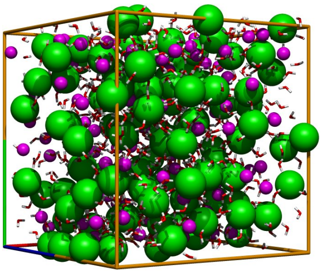
Radial distribution function:

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

Another example – brine

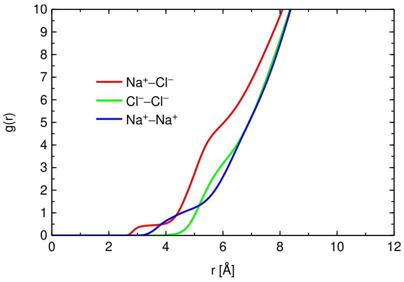
RDFs of supersaturated (10.5 mol/kg) solution of NaCl:

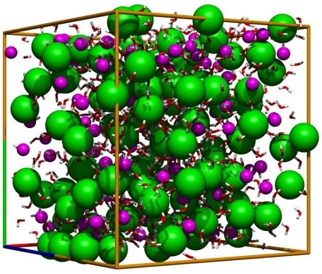




Another example – brine

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..

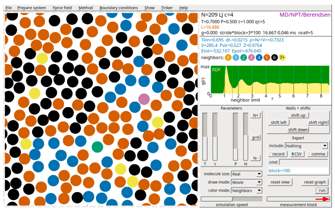
SIMOLANT: Observe RDF yourself

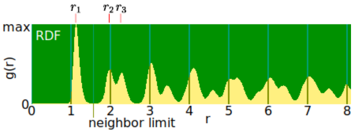
`simolant -l10 -N209 -Pblock=100`

- Menu: Prepare system → Periodic liquid

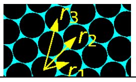
The RDF graph is scaled from 0 to maximum.

- 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:

$$g(r) \equiv g(r_{12}) \overset{\text{isotr.}}{=} g(\vec r_{12}) \overset{\text{homog.}}{=} g(\vec r_1, \vec r_2) = \frac{N(N-1)}{\rho^2 Q_{\text{NVT}}} \int \dots \int \exp[-\beta U(\vec r_1, \vec r_2, \dots, \vec r_N)]\, \mathrm{d}\vec r_3 \dots \mathrm{d}\vec r_N$$

↑
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.

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): $\lim\limits_{N\to\infty, r\to\infty} g(r) = 1$

# 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): $\lim\limits_{r\to\infty} g(r) = 1 - \dfrac{\kappa_T}{N\kappa_T^{\text{id. gas}}} + \mathcal{O}(1/N^2)$, where κ_T = compressibility

Calculation of RDF in simulations – exact

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

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

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

$$\begin{aligned}
\langle \mathcal{N}_i \rangle &= \frac{1}{Q_{\text{NVT}}} \sum_{j<k} \int_{r_{jk} \in \mathcal{I}_i} \exp[-\beta U(\vec r^N)] \mathrm{d}\vec r^N \\
&= \frac{1}{Q_{\text{NVT}}} \binom{N}{2} V \int_{r_{12} \in \mathcal{I}_i} \left\{ \int \exp[-\beta U(\vec r^N)] \mathrm{d}\vec r_3 \dots \mathrm{d}\vec r_N \right\} \mathrm{d}\vec r_{12} \\
&= \frac{N}{2} \rho \int_{\mathcal{I}_i} g(r) \mathrm{d}\vec r \\
&\approx \frac{N^2}{2V} g(r_i) \Delta V_i
\end{aligned}$$

The formula again:

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

Correlation function and thermodynamics

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

Residual internal energy:

$$\langle U \rangle = \frac{1}{Q_{\text{NVT}}} \int \sum_{i<j} u_{ij}(r_{ij}) \mathrm{e}^{-\beta U} \mathrm{d}\vec r_1 \dots \mathrm{d}\vec r_N$$

$$\langle U \rangle = \binom{N}{2} \frac{V}{Q_{\text{NVT}}} \int \mathrm{e}^{-\beta U} 4\pi r_{12}^2 \mathrm{d}r_{12} u(r_{12}) \mathrm{d}\vec r_3 \dots \mathrm{d}\vec r_N$$

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

Pressure:

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

RDF and PMF in infinite dilution. 1. Direct simulation

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

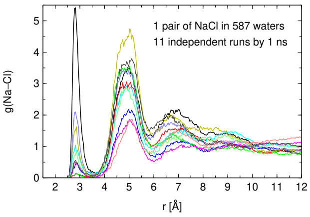
$$U_{\text{PMF}} = -RT \ln g(r).$$

Calculating $g(r)$ and U_{PMF} 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)
- $T = 300\,\text{K}$, $\rho = 1002.5\,\text{kg}\,\text{m}^{-3}$
- mass repartitioning: equalization factor 0.8, $h = 2\,\text{fs}$
- 1 measurement every 10 fs
- RDF range $c = 12\,\text{Å}$



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

Barrier crossing:

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

Diffusion:

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

Both phenomena together cause poor convergence in time scale $t \times 10$

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

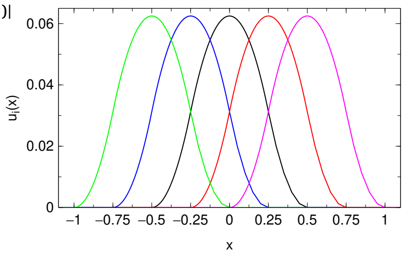
Generalized coordinate: $r = |\vec r(\text{Na}^+) - \vec r(\text{Cl}^-)|$

The bias potential is

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

where $d = 0.25\,\text{Å}$ and

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

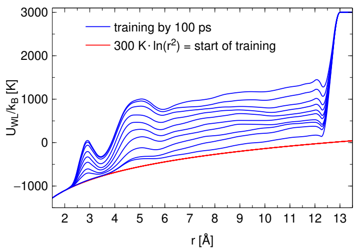


Wang–Landau update: $$A_i \mathrel{+}= (d-x)\cdot\frac{\omega}{h(r)}, \quad A_{i+1} \mathrel{+}= x\frac{\omega}{h(r)}, \quad i = r/d \tag{1}$$

- Starting from a basin $U = 0$ inside wall $A_{n_{\max}} = 3000\,\text{K}$
- 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)

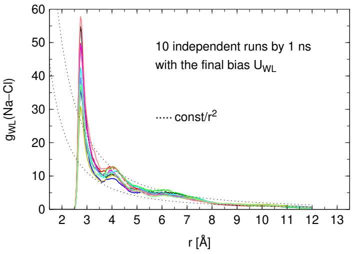
RDF and PMF. 4. Metadynamics $h(r) = 1$ raw results

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



- The convergence is slow.

Raw radial distribution function with the bias



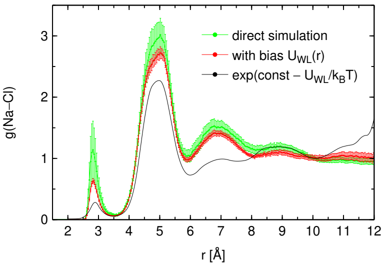
- The difference from const/r^2 is due to discretization, peaks appear for large $\mathrm{d}U_{\text{PMF}}/\mathrm{d}r$.
- Finer grid would be problematic close to cation–anion contact.

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

- ▬ 10 independent $g(r)$'s with the bias, multiplied by $\exp(-U_{\text{WL}}/k_{\text{B}}T)$ 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.
- Short separations are oversampled!

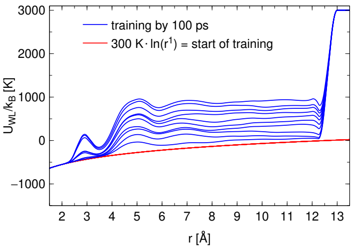


Can we do it better?

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

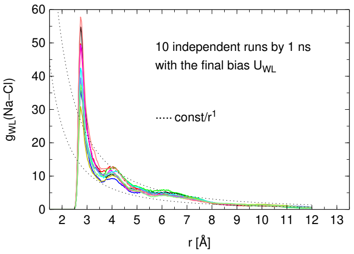
RDF and PMF. 6. Metadynamics $h(r) = r$ raw results

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



- The convergence is slow at short separations.

Raw radial distribution function with the bias



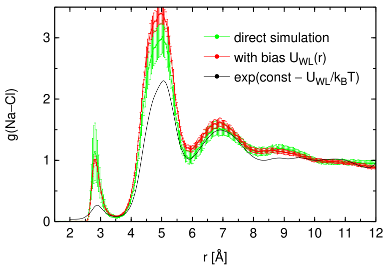
- The difference from const/r^2 is due to discretization, peaks appear for large $\mathrm{d}U_{\mathrm{PMF}}/\mathrm{d}r$.
- Finer grid would be problematic close to cation–anion contact.

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

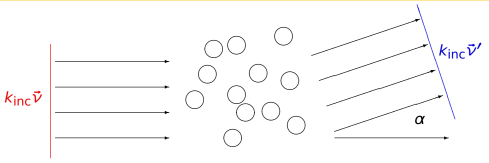
- 🟥 10 independent $g(r)$'s with the bias, multiplied by $\exp(-U_{\mathrm{WL}}/k_{\mathrm{B}}T)$ and shifted to $g(10\,\text{Å}) = 1$
- 🟩 direct simulation
- RDF grid 0.04 Å, standard errors from 11 or 10 blocks
- both methods are based on 11 ns trajectories (comparable times)

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. $\vec{\nu}\cdot\vec{r} = \mathrm{const}$) 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 (except phase):

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

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

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)

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

Structure factor and RDF

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

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

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

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

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:

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

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:

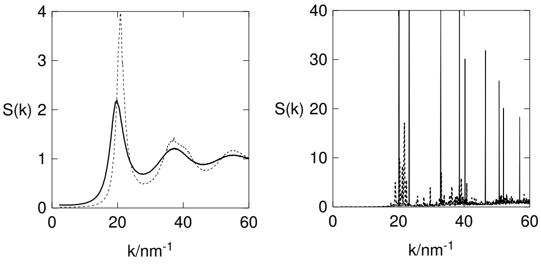
$$S(k) = \sum_{k=|\vec{k}|} S(\vec{k}) / \sum_{k=|\vec{k}|} 1$$

$S(k)$ 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.

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 ($\sum_I N_I b_I = \sum_j b_j$)

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:~ $ mkdir YOU
guest@403-a324-01:~ $ cd YOU
guest@403-a324-01:~ $ 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:~ $ 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:~ $ plbinfo nacl.plb
  ```
- Calculate the structure factor (`-m1` = reads `nacl.plb`)
  ```
  guest@403-a324-01:~ $ 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:~ $ 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:~ $ rdfg nacl -g -p
```

Fourier transform for a mixture with given b_i:

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

Comparison:

```
guest@403-a324-01:~ $ 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:~ $ 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. . .