Modelling F(Q) for liquids and glasses with

Empirical Potential Structure Refinement

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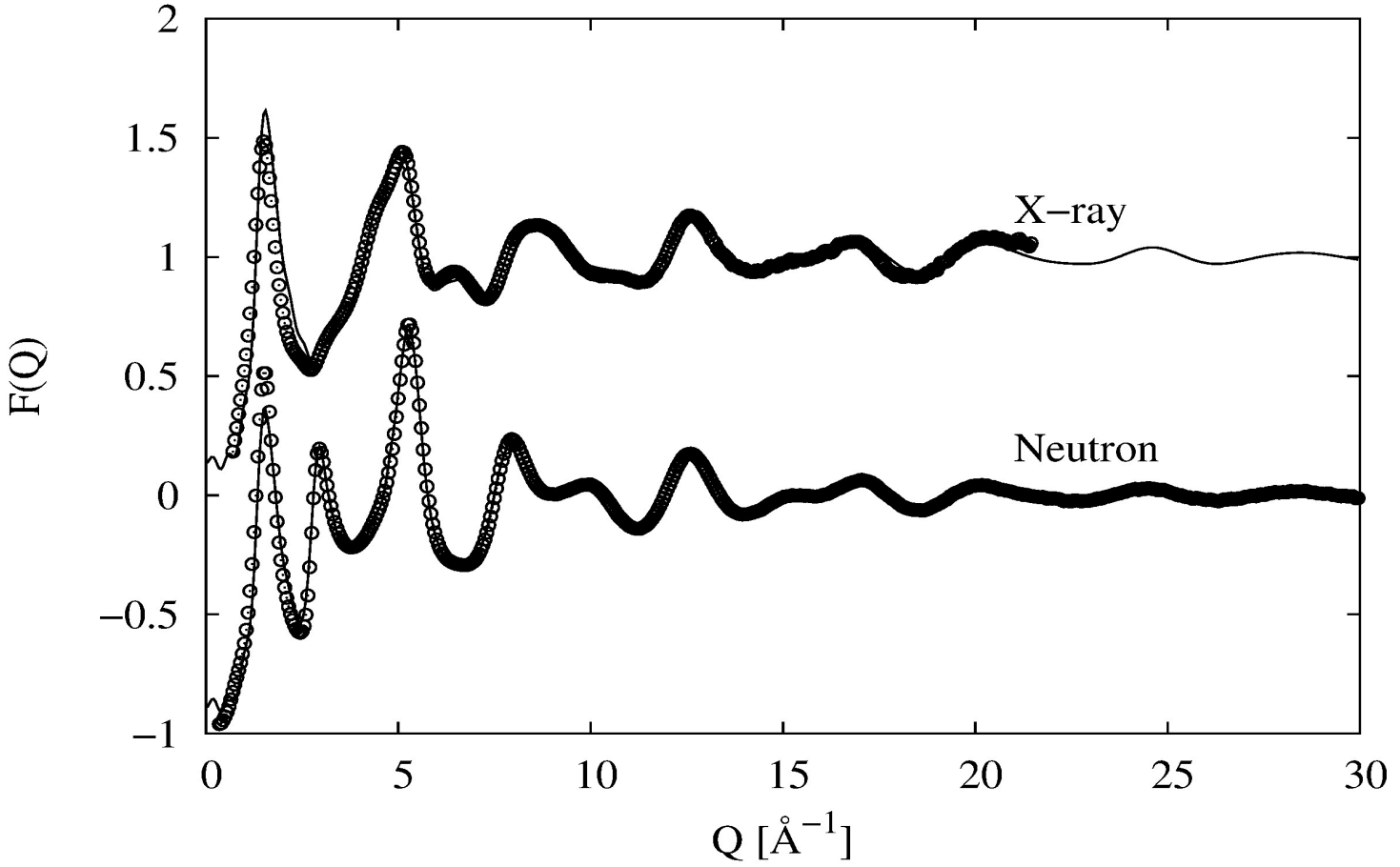
Neutron & X-ray diffraction data from amorphous SiO_2:



- But what does it mean?

The disordered materials structure factor:

The partial structure factors, $H_{\alpha\beta}(Q)$

The site-site radial distribution functions, $g_{\alpha\beta}(r)$

$$F(Q) = \sum_{\alpha,\beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_\alpha c_\beta b_\alpha b_\beta \left\{ 4\pi\rho \int r^2 \left(g_{\alpha\beta}(r) - 1 \right) \frac{\sin Qr}{Qr} dr \right\}$$

Atomic fraction of component "α"

The atom scattering factor or "form factor"

Introduce Empirical Potential Structure Refinement, EPSR

- Where appropriate, use harmonic constraints to define molecules.
- Use an existing "**Reference**" potential for the material in question taken from the literature (or generate your own if one does not exist).
- Perform a standard computer simulation.
- Use the diffraction data to perturb this reference potential, so that the simulated structure factor looks like the measured data. This is the "**Empirical**" potential

EPSR on SiO_2 – the reference potential

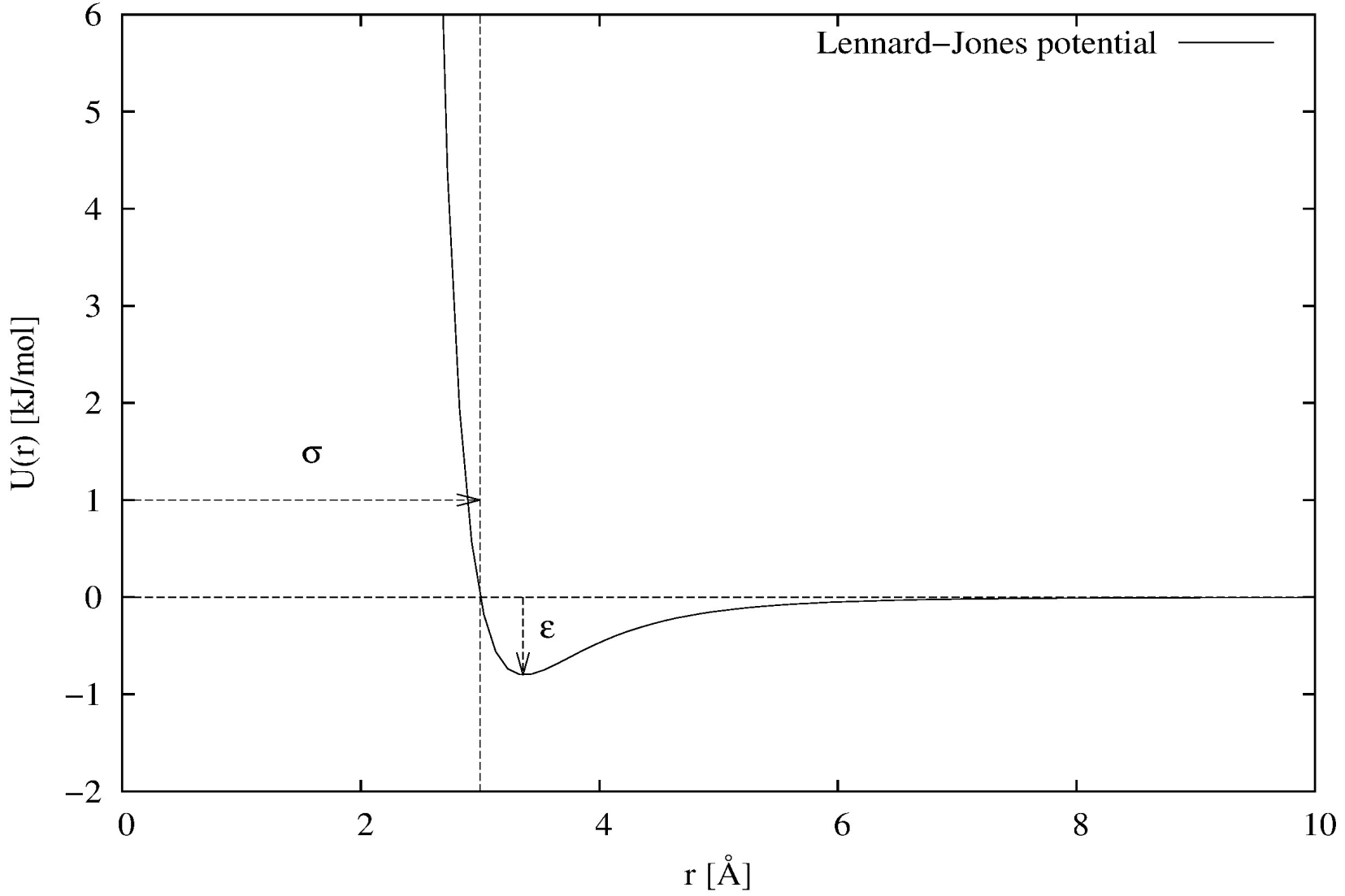
- What to use for a potential?
- Use Lennard-Jones + Coulomb + repulsive term:

$$U_{\alpha\beta}^{(ref)}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right] + \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r} + C_{\alpha\beta}\exp\left(\frac{1}{w_{\alpha\beta}}\left(r_{\alpha\beta} - r\right)\right)$$

where $\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_\alpha + \sigma_\beta)$

$$\epsilon_{\alpha\beta} = \sqrt{\epsilon_\alpha \epsilon_\beta}$$

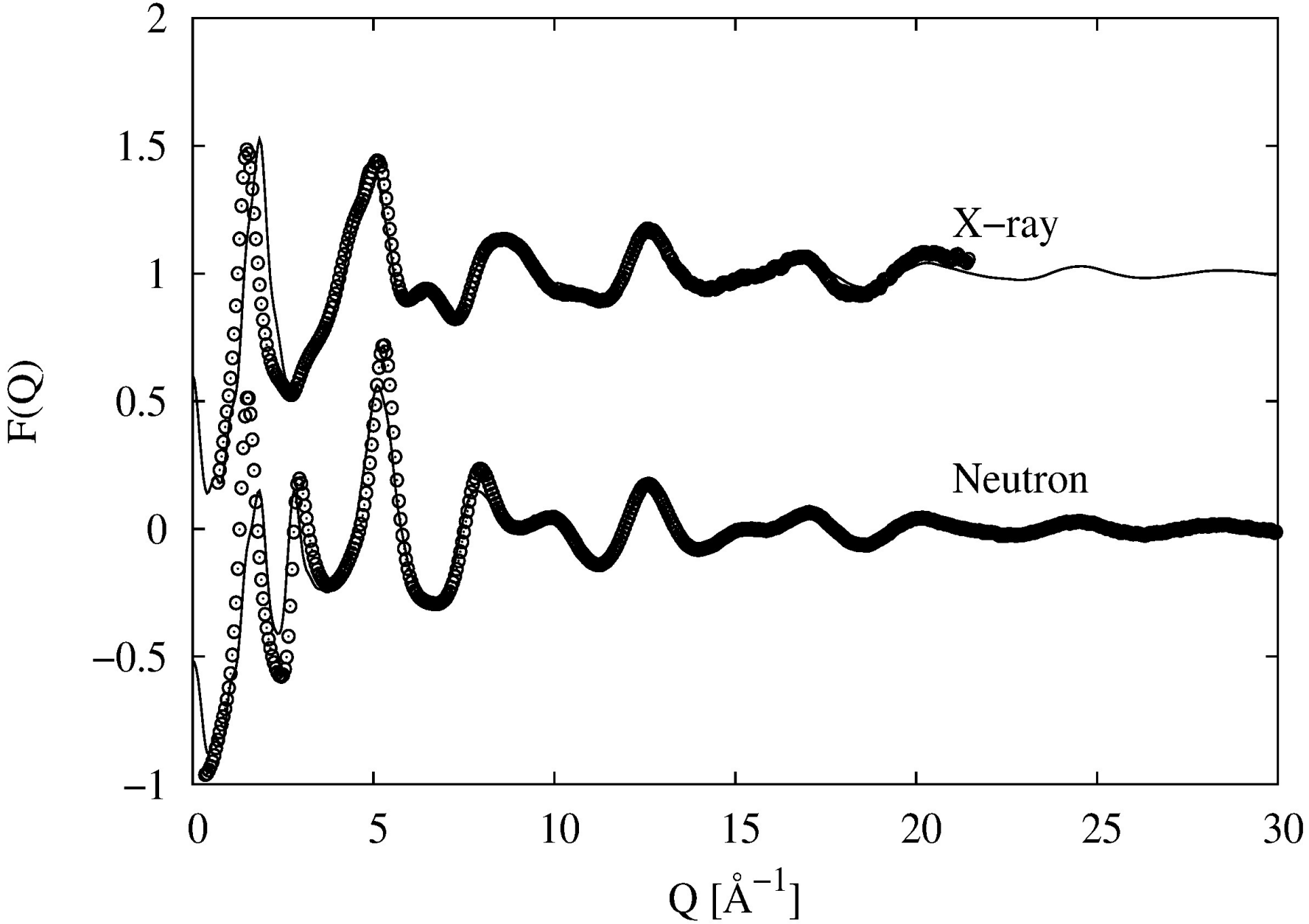
Sketch of the Lennard-Jones potential used in EPSR



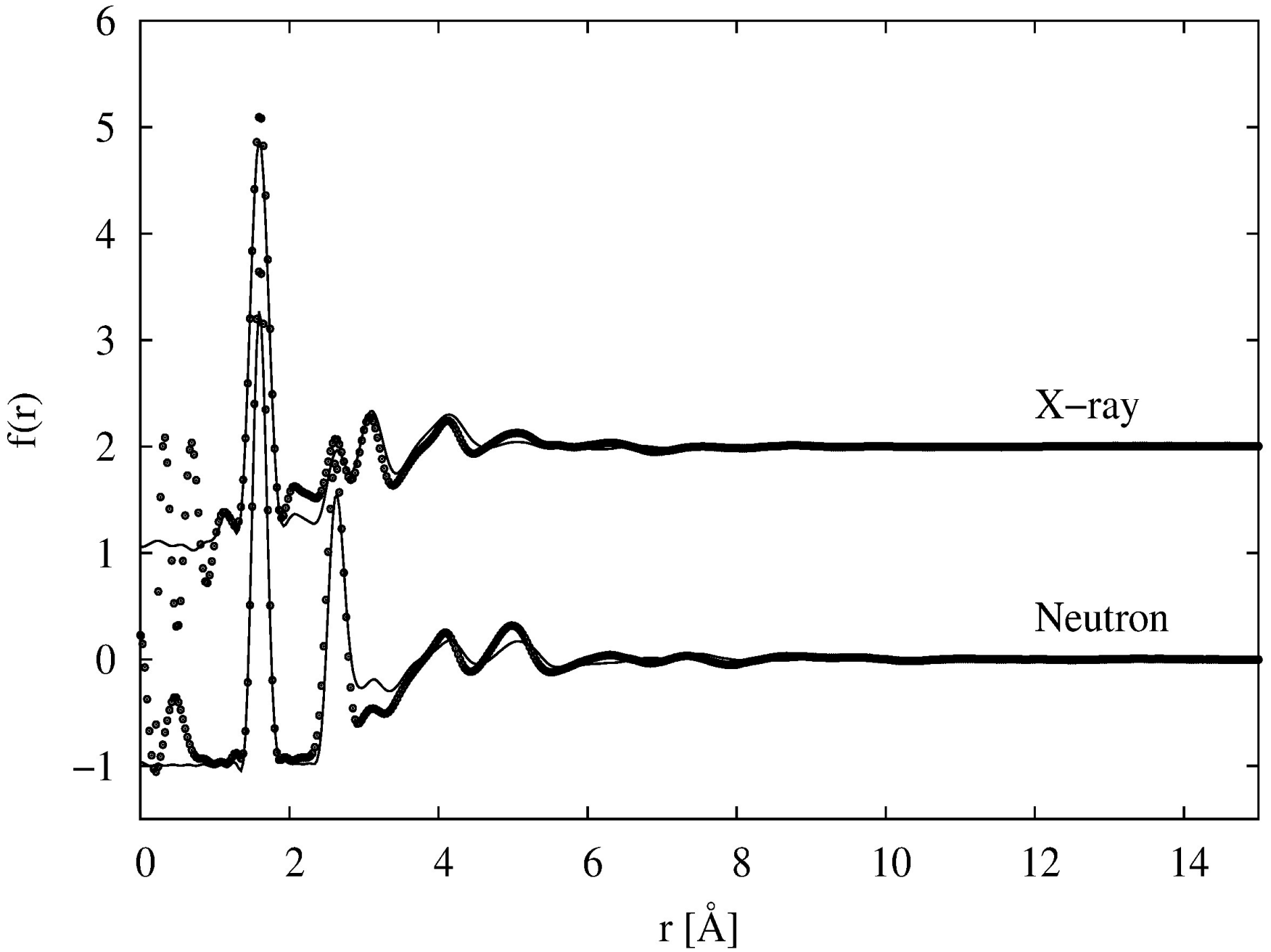
Reference potential for SiO_2:

Atom	ε [kJ/mole]	σ [Å]	q [e]
Si	0.80	0.90	+4
O	0.65	3.63	-2
r_{SiSi}	-	2.5	-
r_{SiO}	-	-	-
r_{OO}	-	-	-

SiO_2 with reference potential:



SiO_2 with reference potential:



Introducing the data - 1

$$F(Q) = \sum_{\alpha,\beta \geq \alpha} \left(2 - \delta_{\alpha\beta}\right) c_\alpha c_\beta b_\alpha b_\beta H_{\alpha\beta}(Q)$$

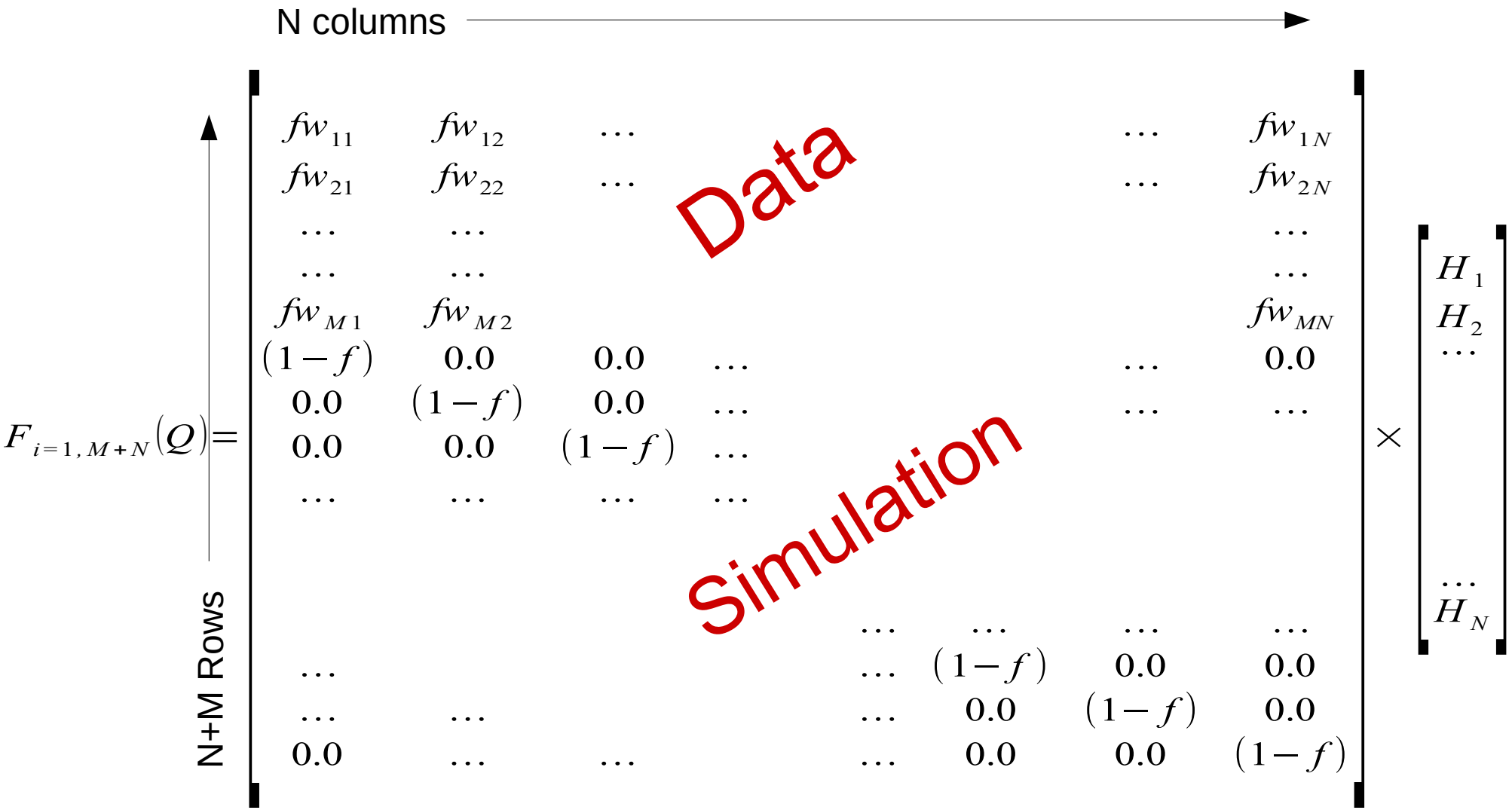
- M measured datasets, N partial structure factors: (Usually $M < N$)
- Setup scattering weights matrix, w_{ij}
- Setup modified weights matrix: w'_{ij}
  - Assign a "feedback" factor f for the data:

$$w'_{ij} = f w_{ij}, \qquad 1 \leq i \leq M, \quad f < 1$$

  - and $(1 - f)$ for the simulation:

$$w'_{ij} = (1 - f)\delta_{(i-M),j}, \quad M < i \leq M + N$$

EPSR modified weights matrix



Introducing the data - 2

- Form inversion of w'_{ij} :-

$$w'^{-1}_{ji},\ \ 1 \le j \le N,\ \ 1 \le i \le M+N$$

- Use w'^{-1}_{ji} to form perturbation to the site-site interatomic potential:

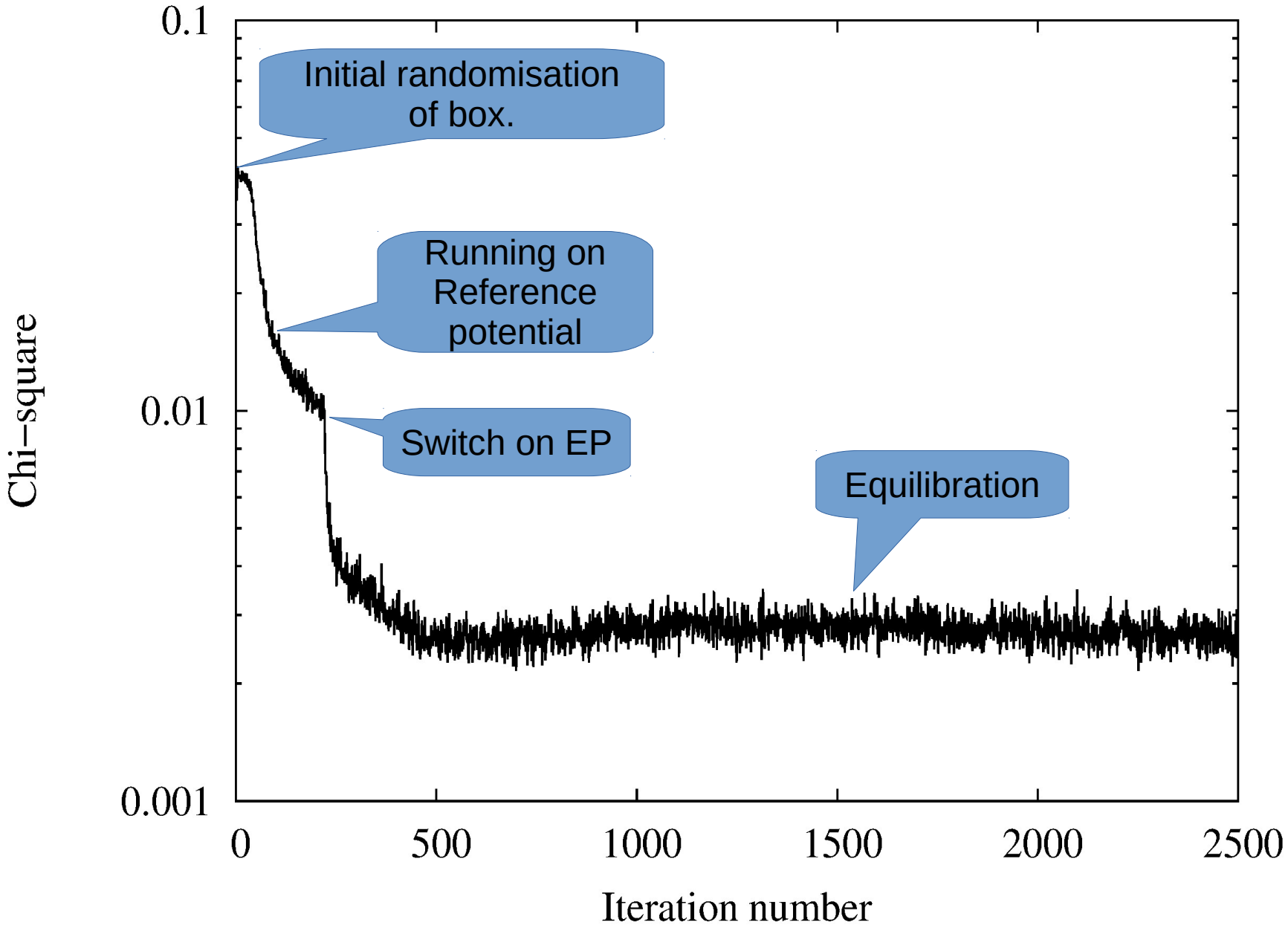
$$\Delta U_j(r) = \text{Fourier Transform of} \left\{ \sum_{i=1,M} w'^{-1}_{ji} \left(D_i(Q) - F_i(Q) \right) \right\}, \quad j = 1, N$$

- Accept or reject moves based on

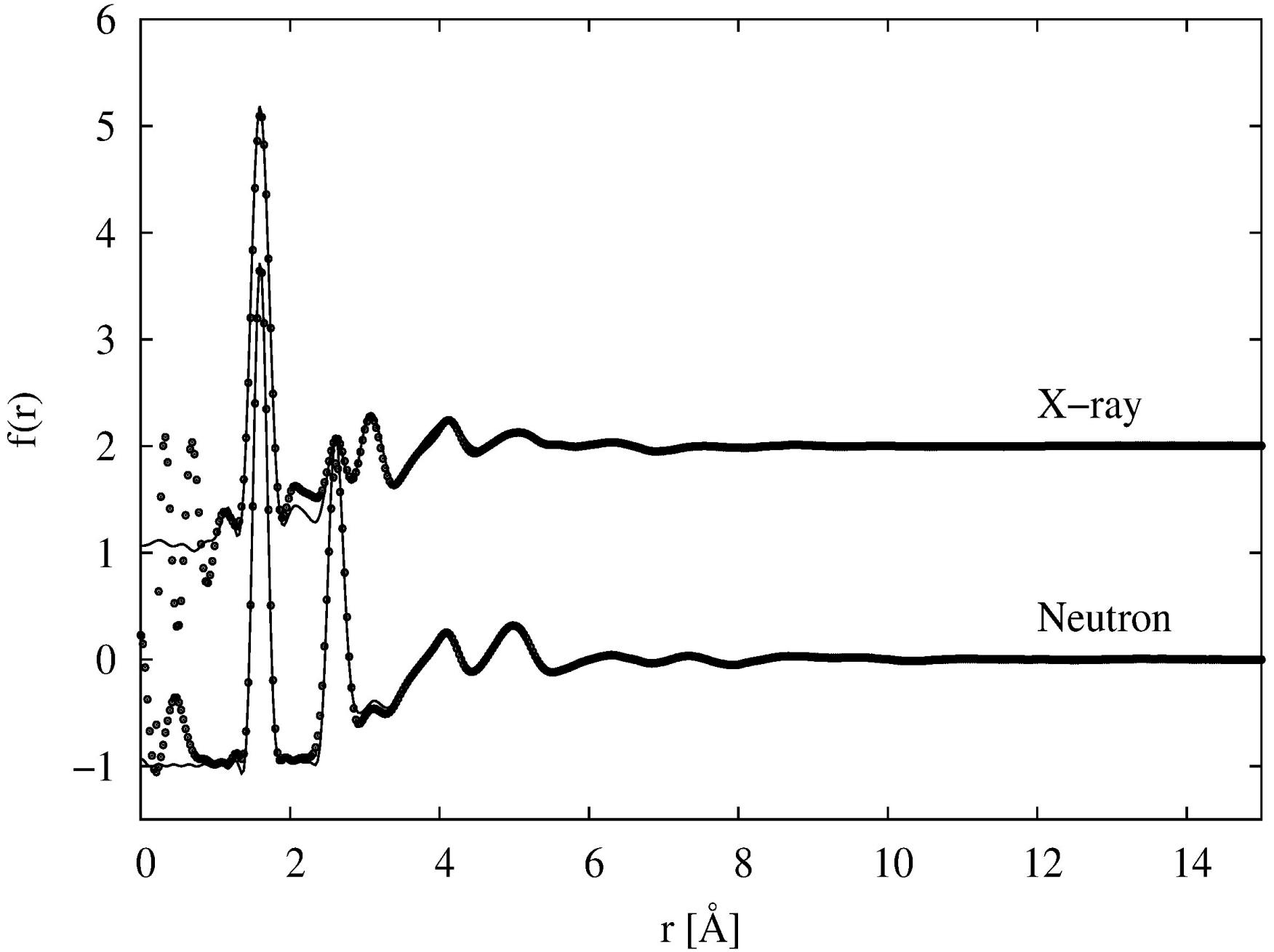
$$\Delta U = \Delta U^{(ref)} + \Delta U^{(ep)}$$

- Iterate many times, accumulating the perturbations until a fit is achieved.

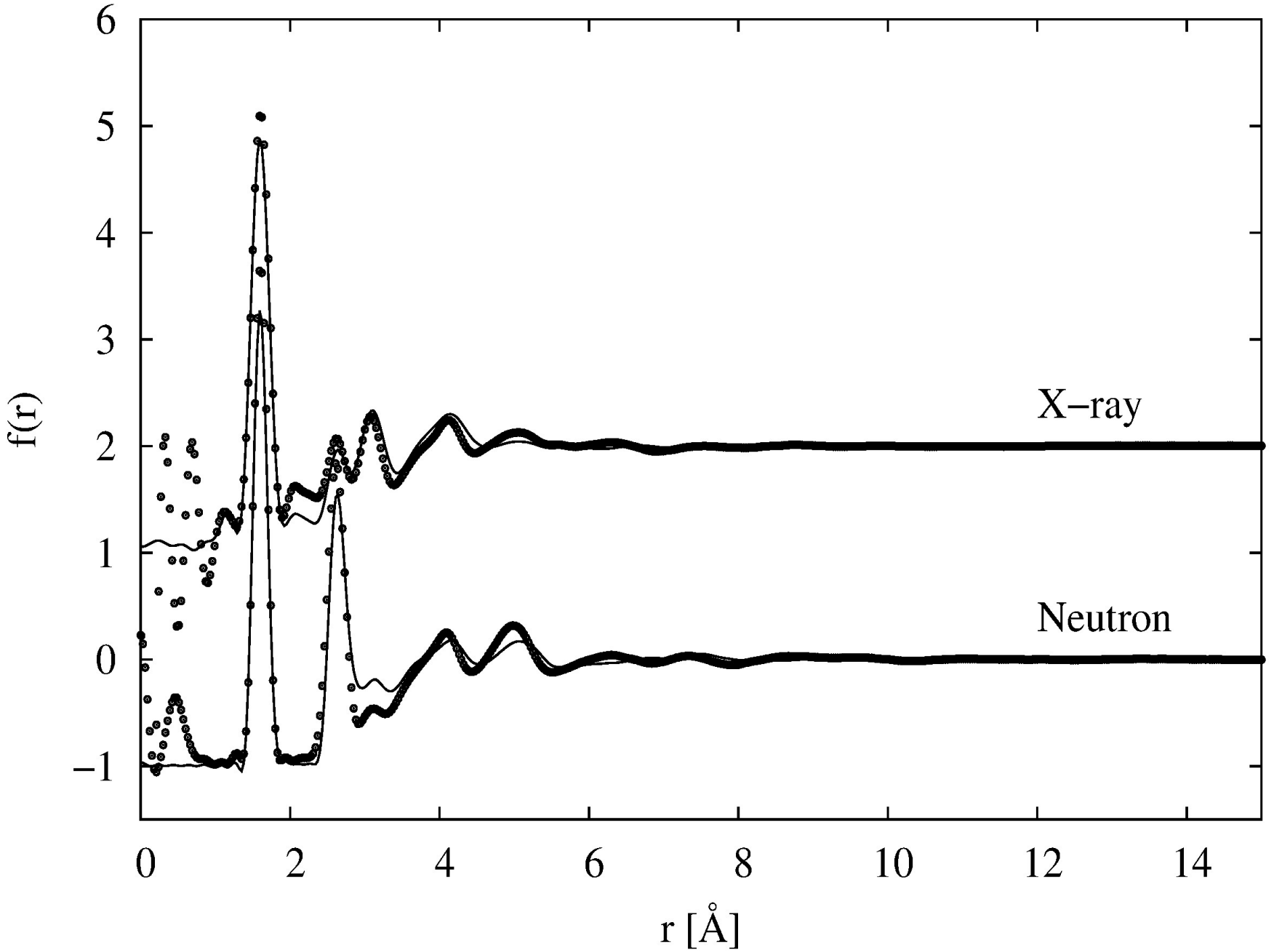
Switch on the empirical potential:



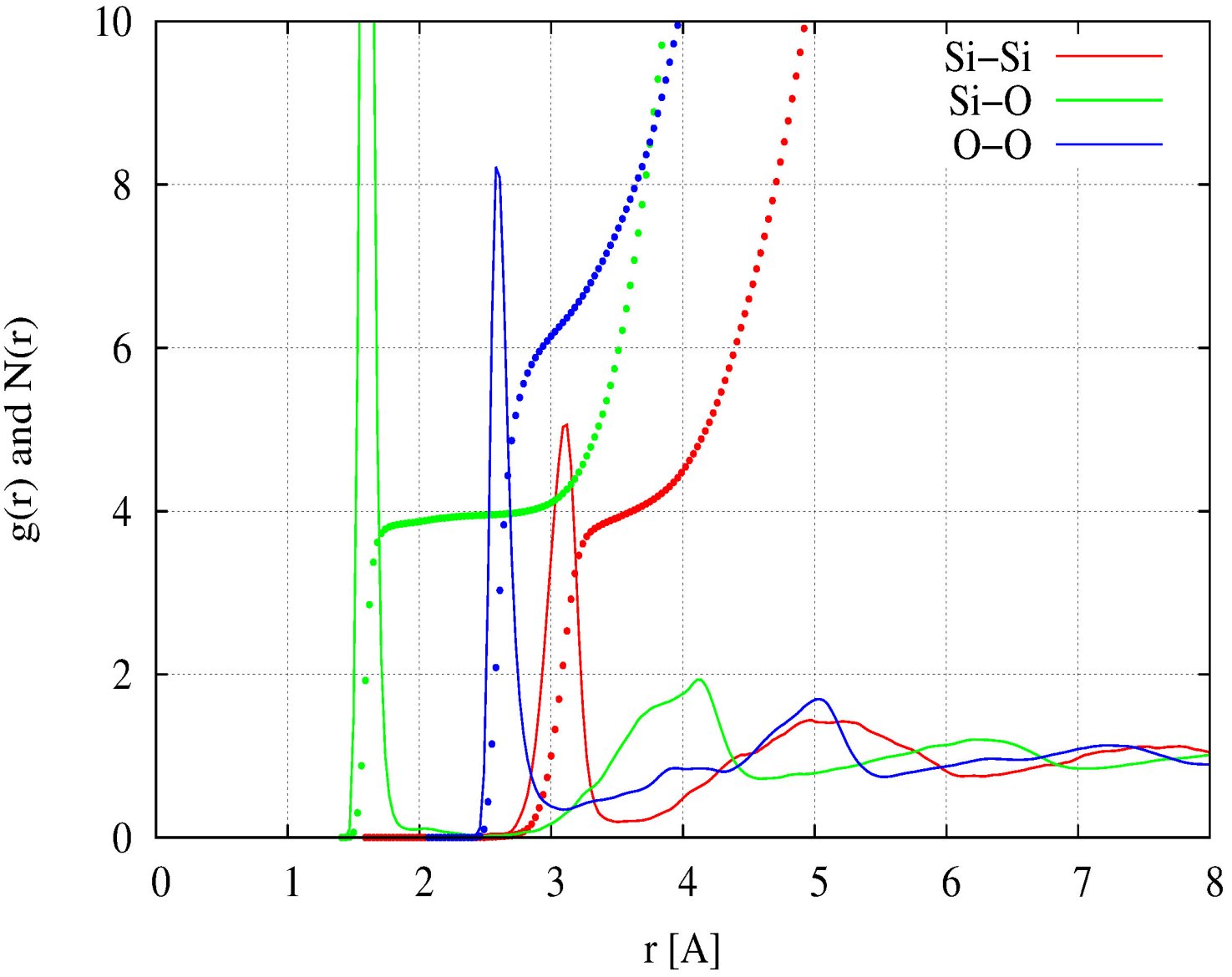
SiO_2 – final f(r):



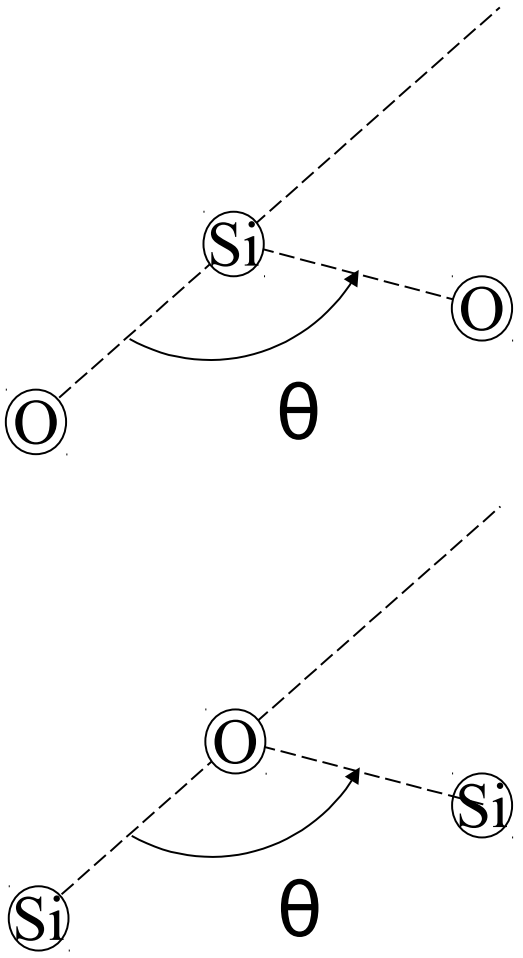
SiO_2 – initial f(r)

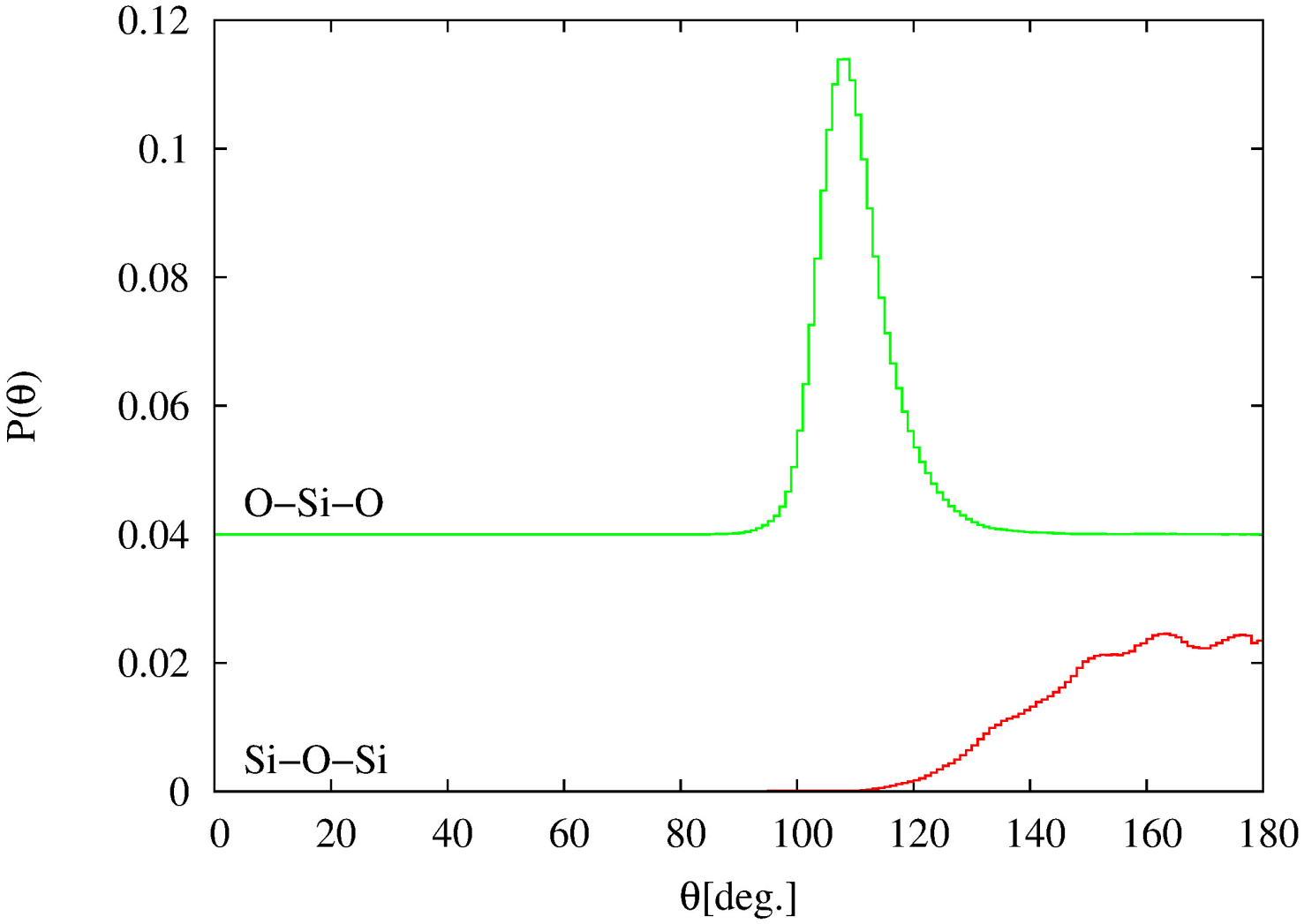


Coordination numbers:

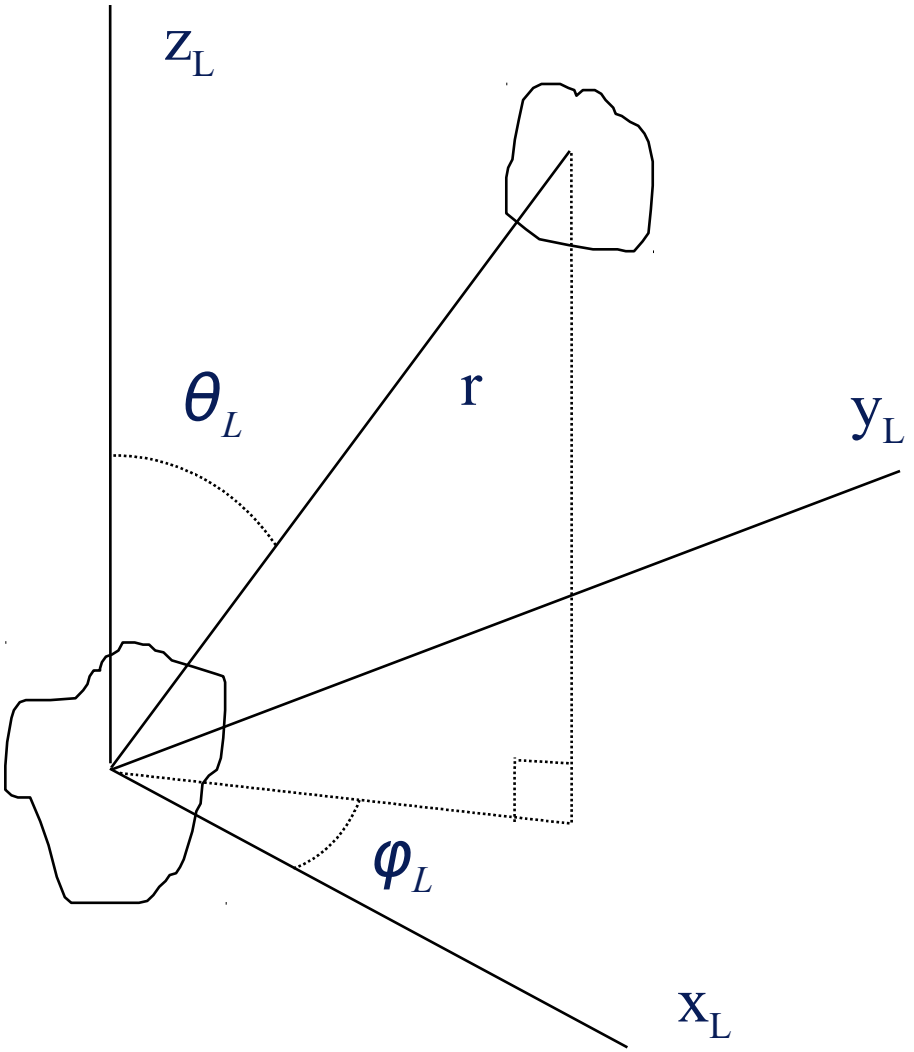


Triangle or “bond angle” distributions, a-SiO_2:

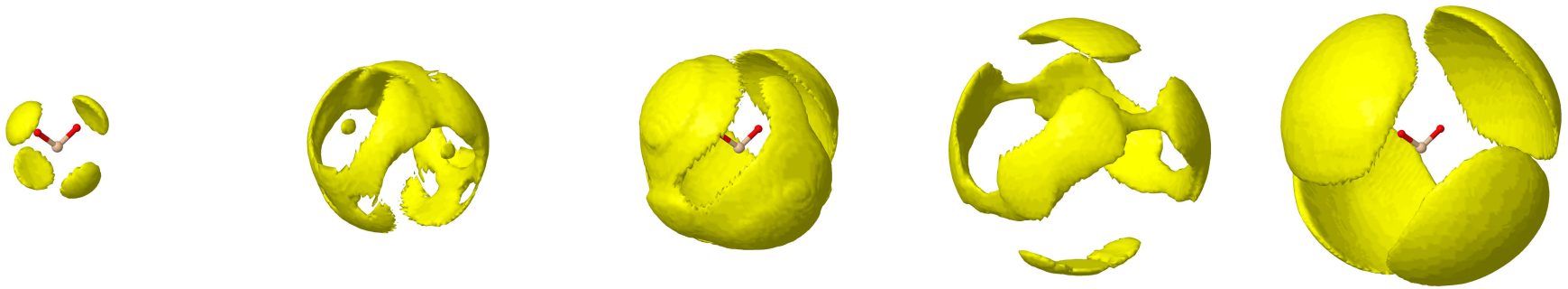




The spatial density function

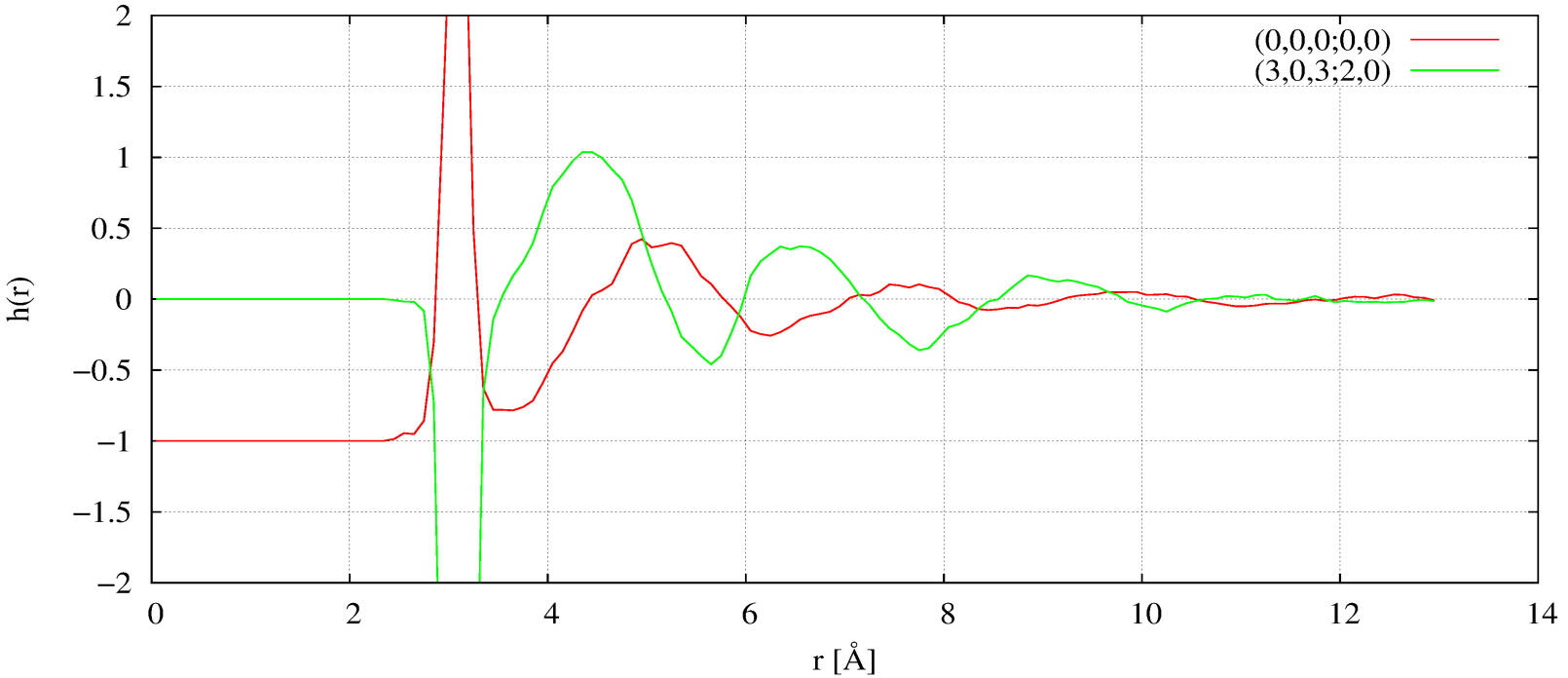


Spatial density function for amorphous SiO_2:



2.00 – 3.48 Å | 3.48 – 5.20 Å | 5.20 – 5.94 Å | 5.94 – 7.22 Å | 7.22 – 8.29 Å

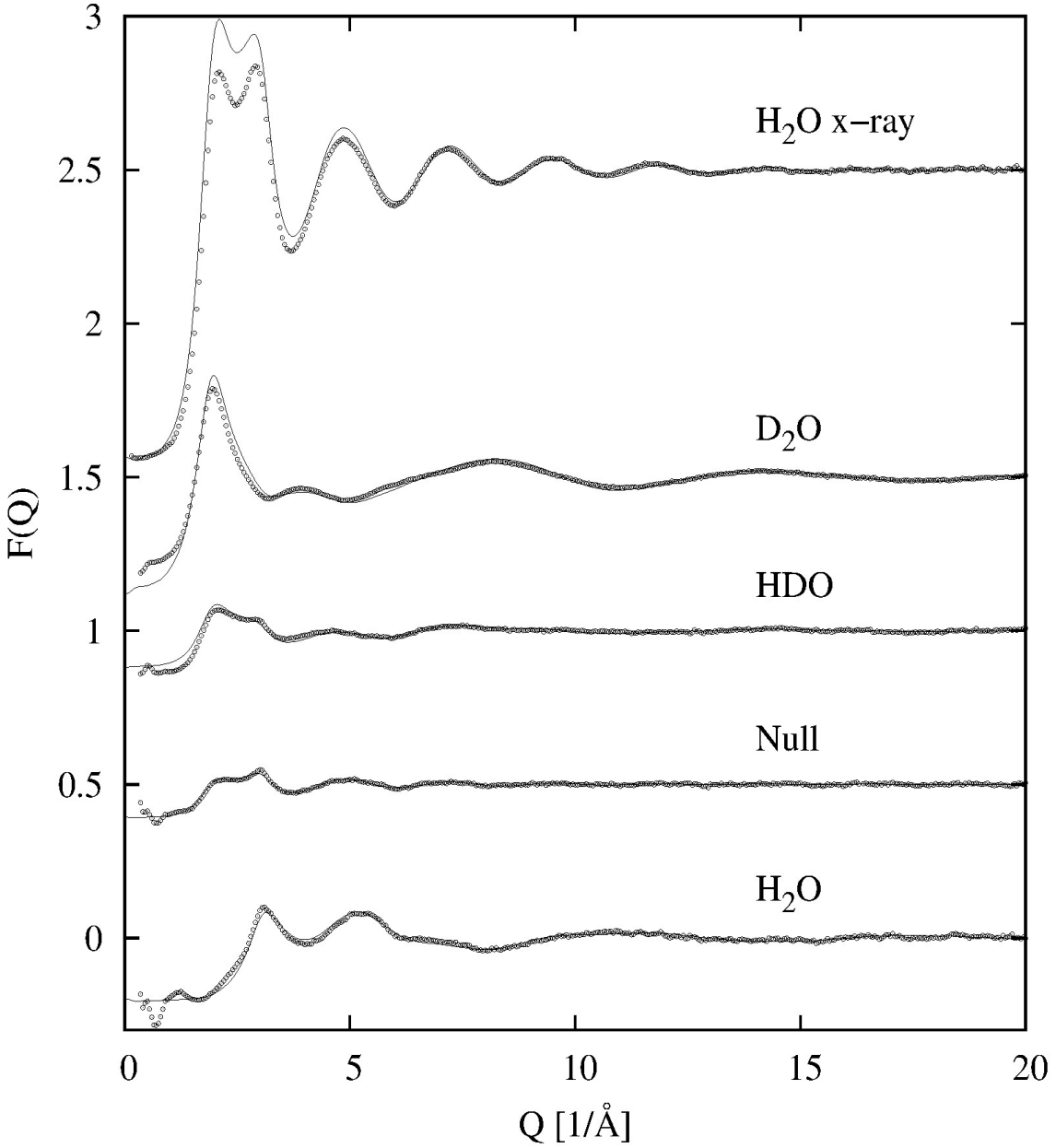
Spherical harmonic functions



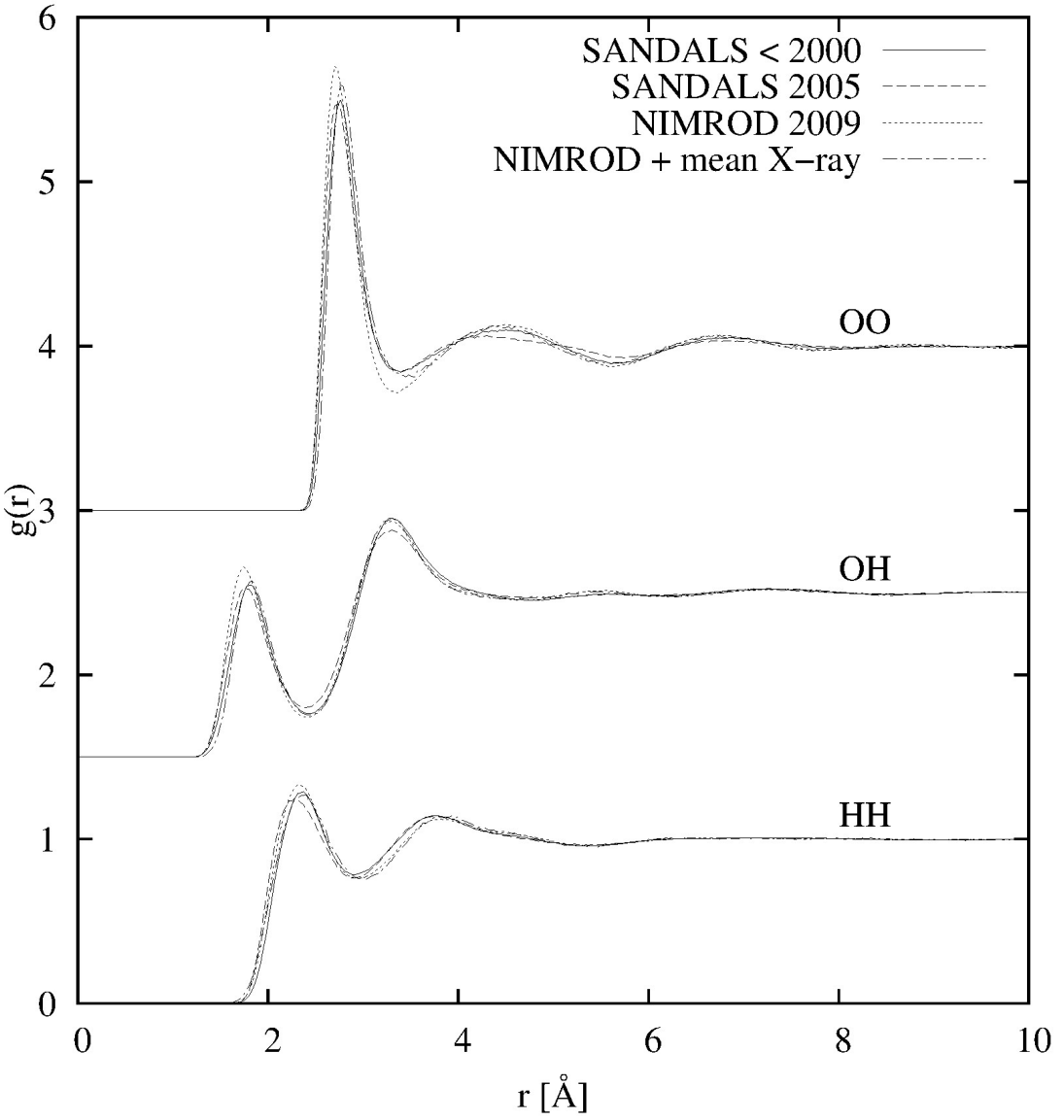
Structure refinement of liquid water

Water data

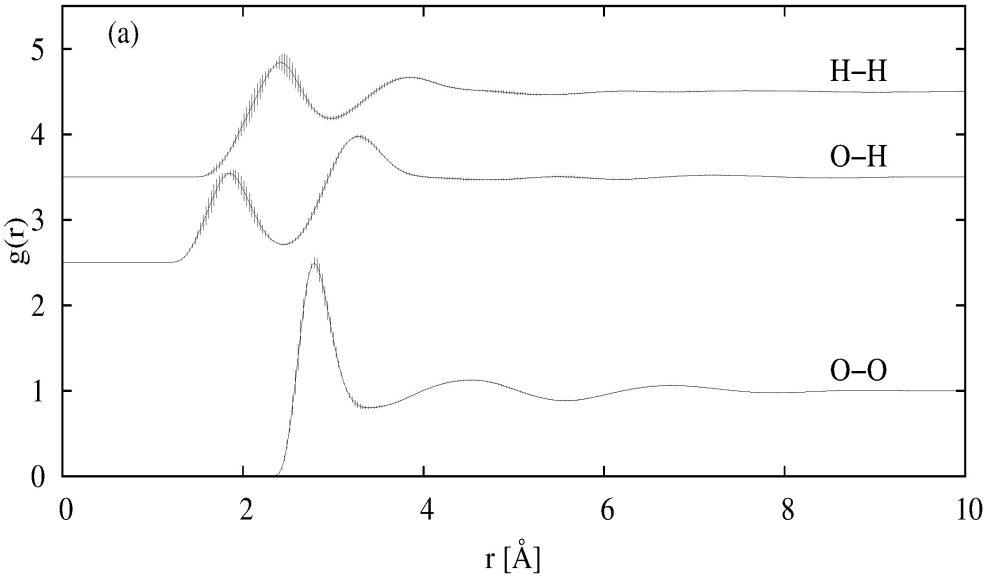
After structure refinement



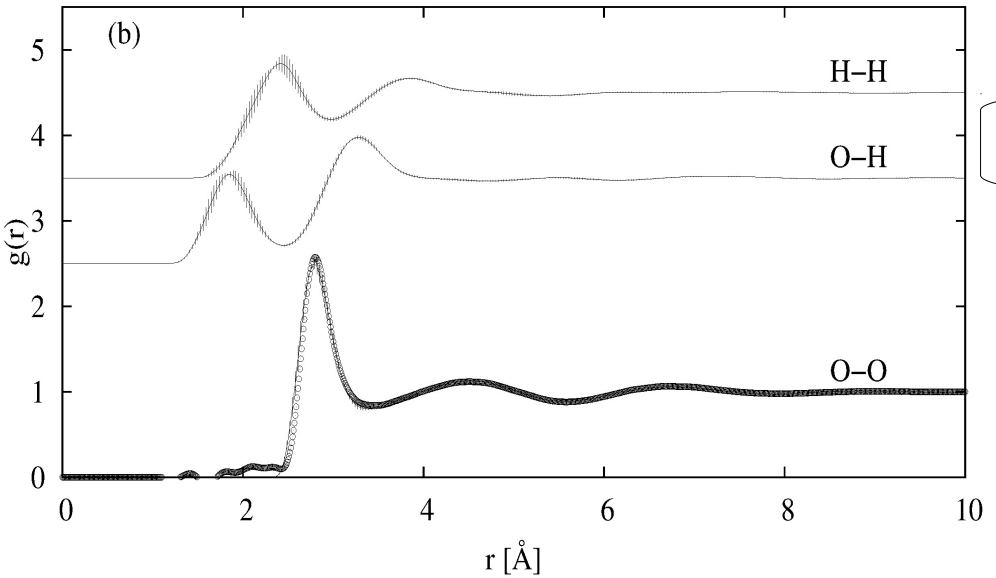
Water partial g(r)'s



The structure of bulk water: two recent papers

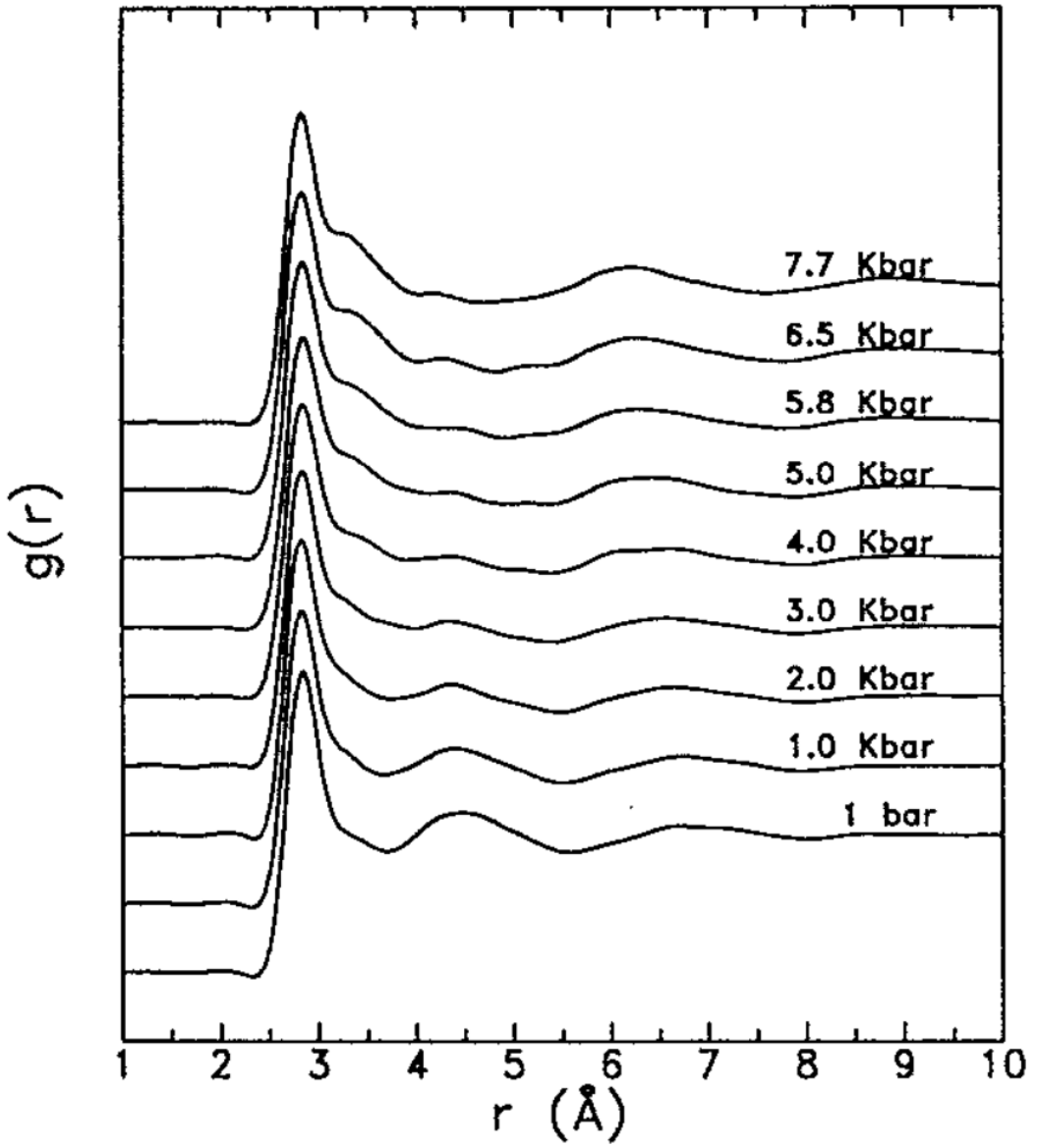


Soper 2013



Skinner *et al*. 2013

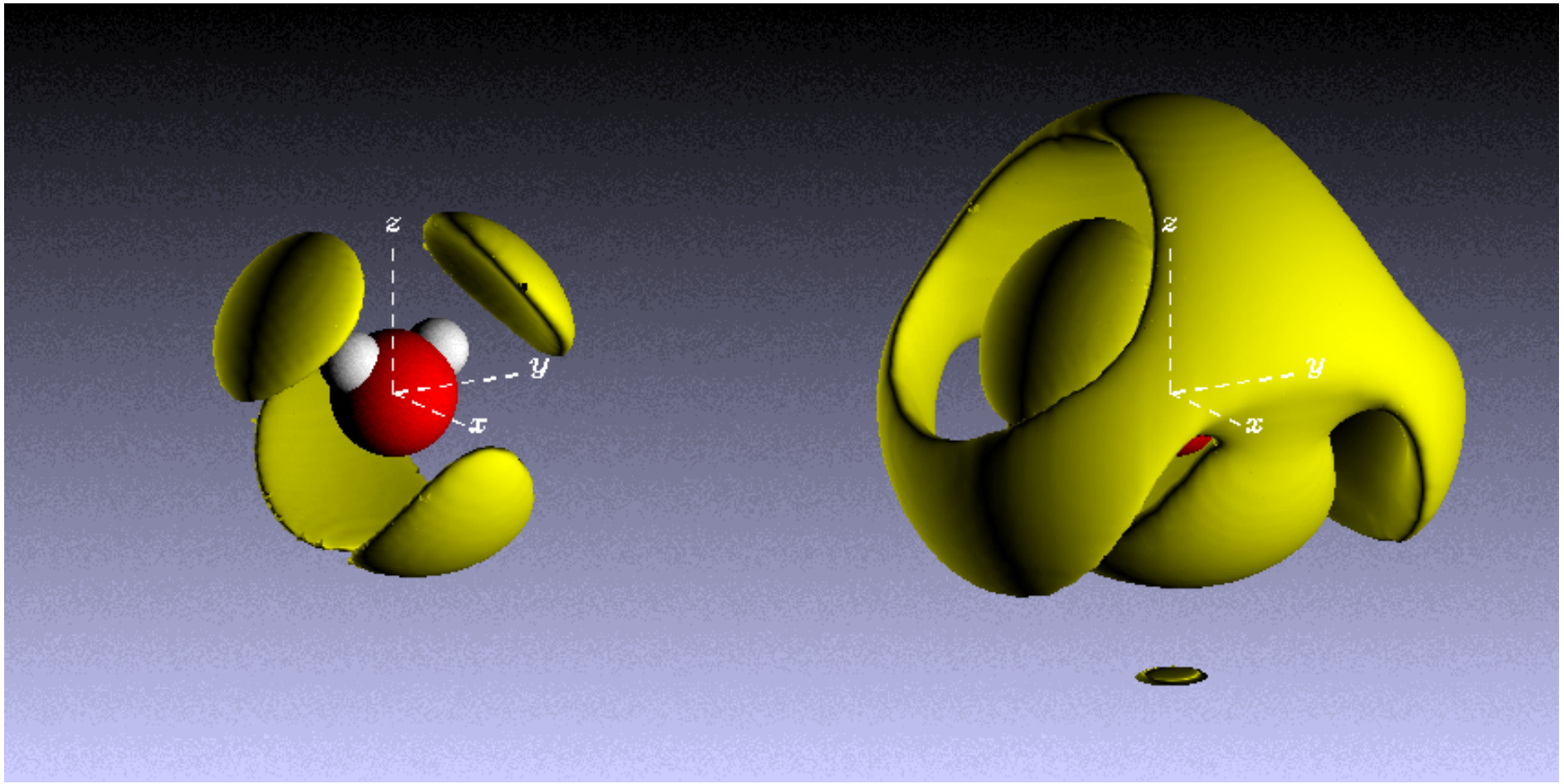
Water structure: effect of pressure



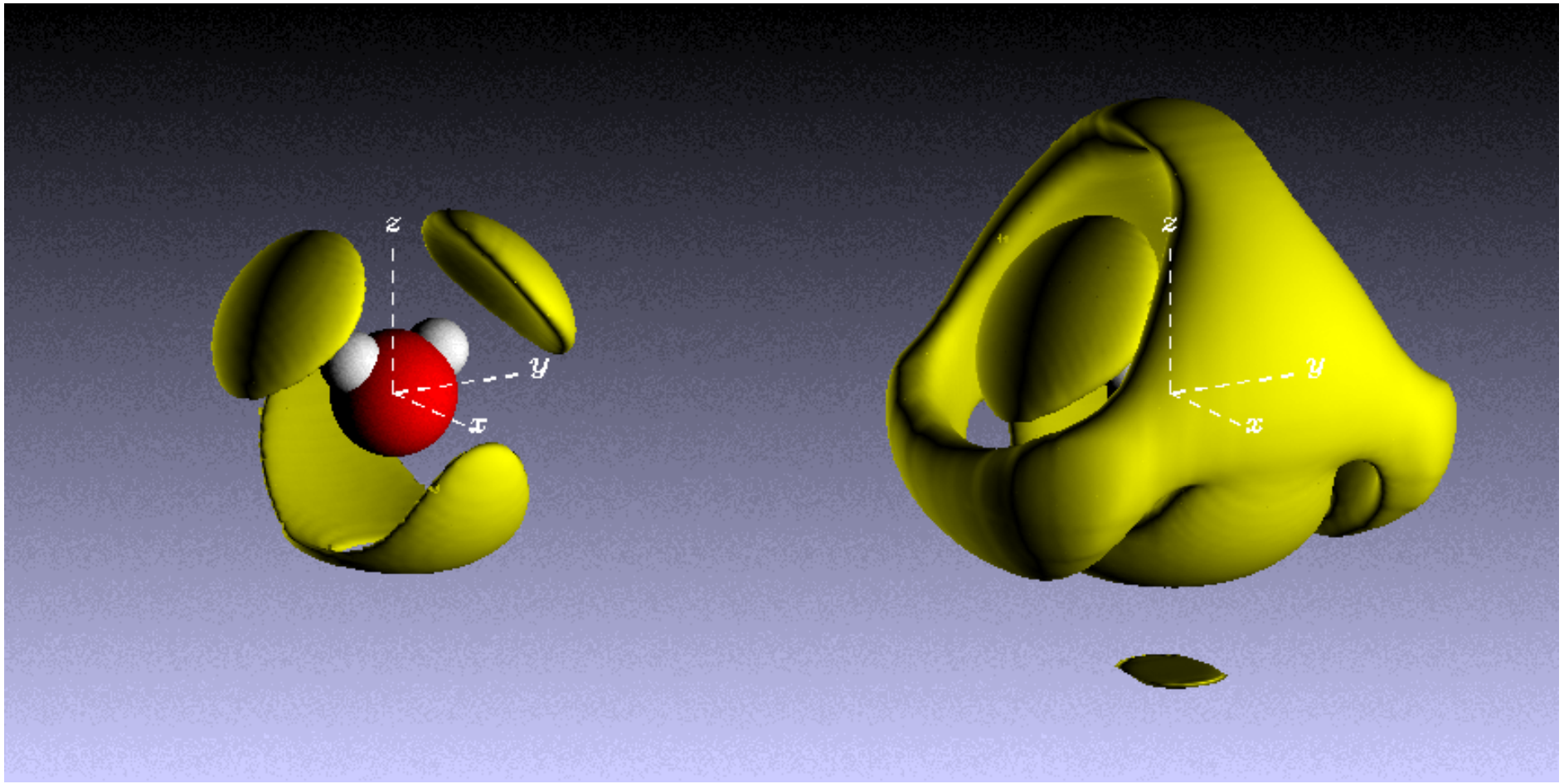
X-ray data

Okhulkov et al., 1994

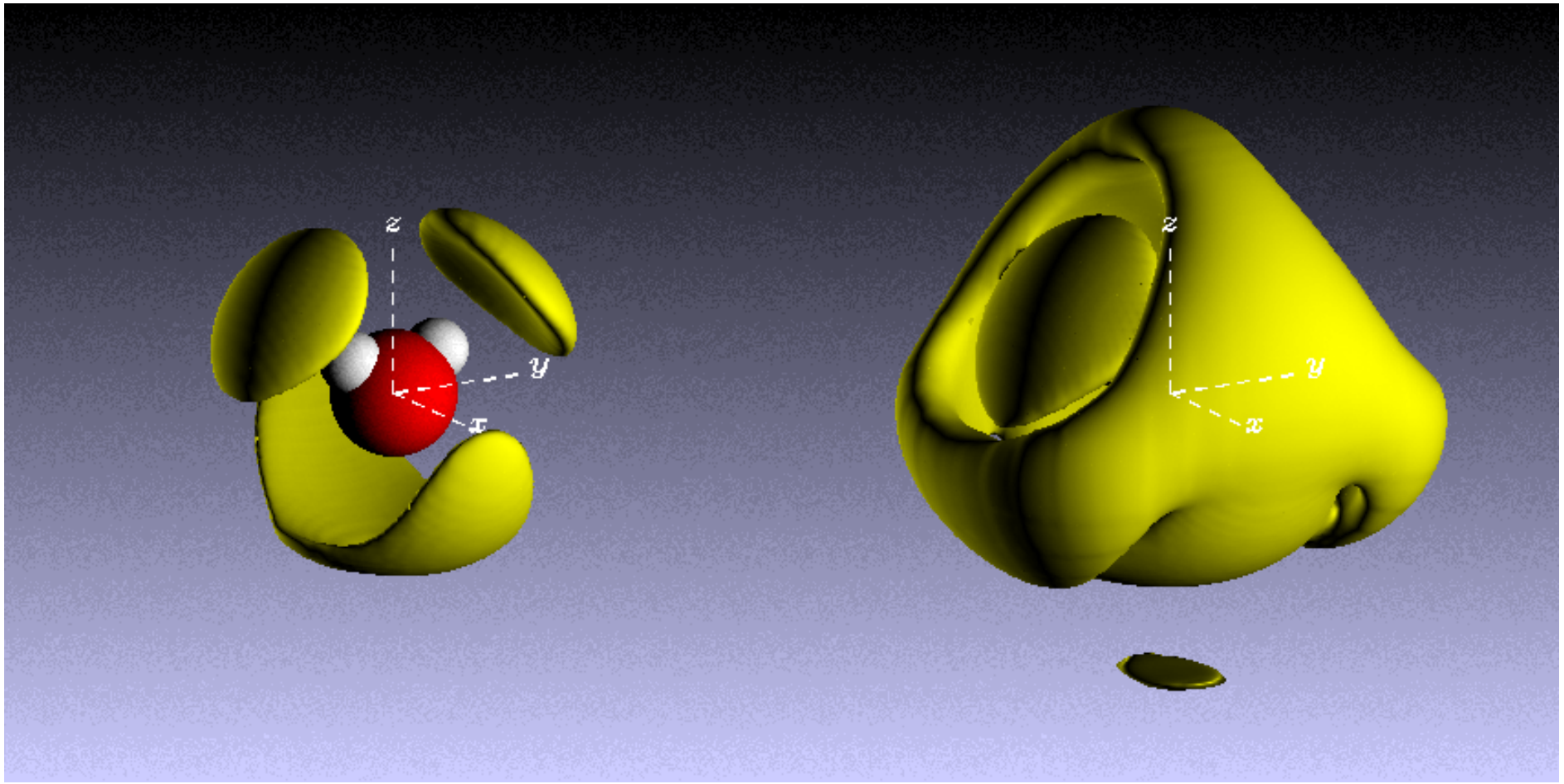
Water at 268K, 0.26kbar



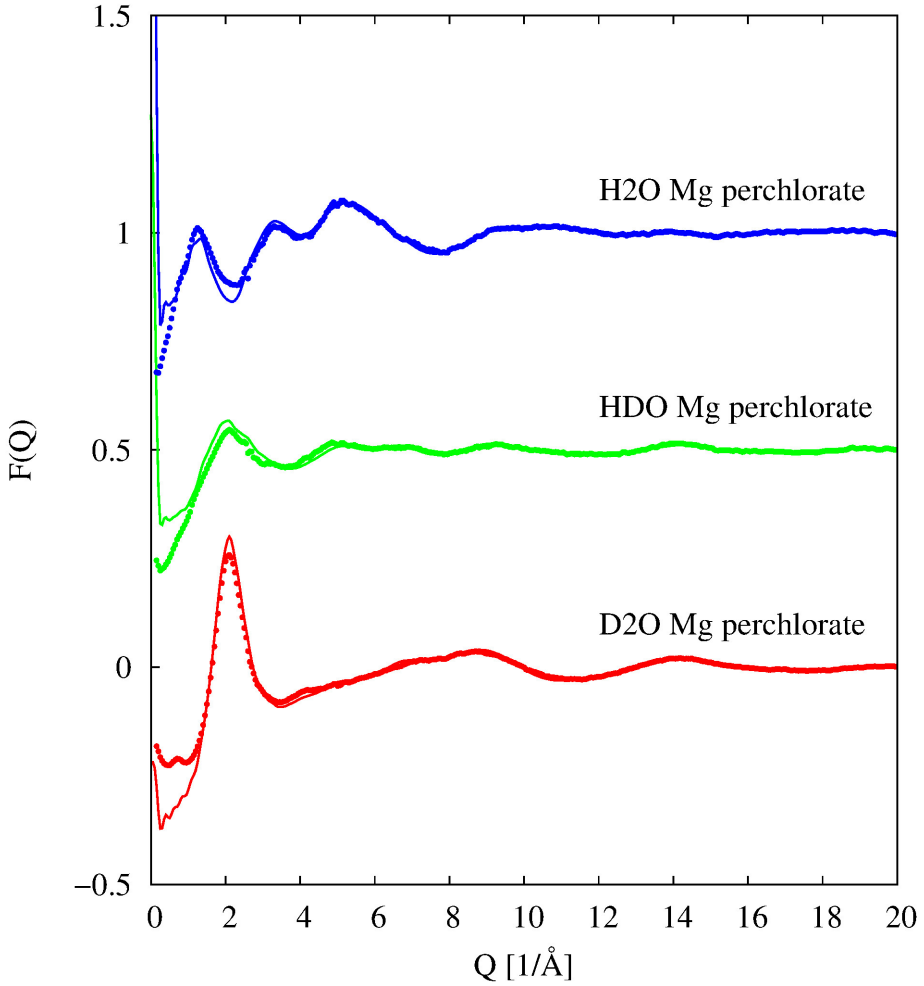
Water at 268K, 2.09kbar

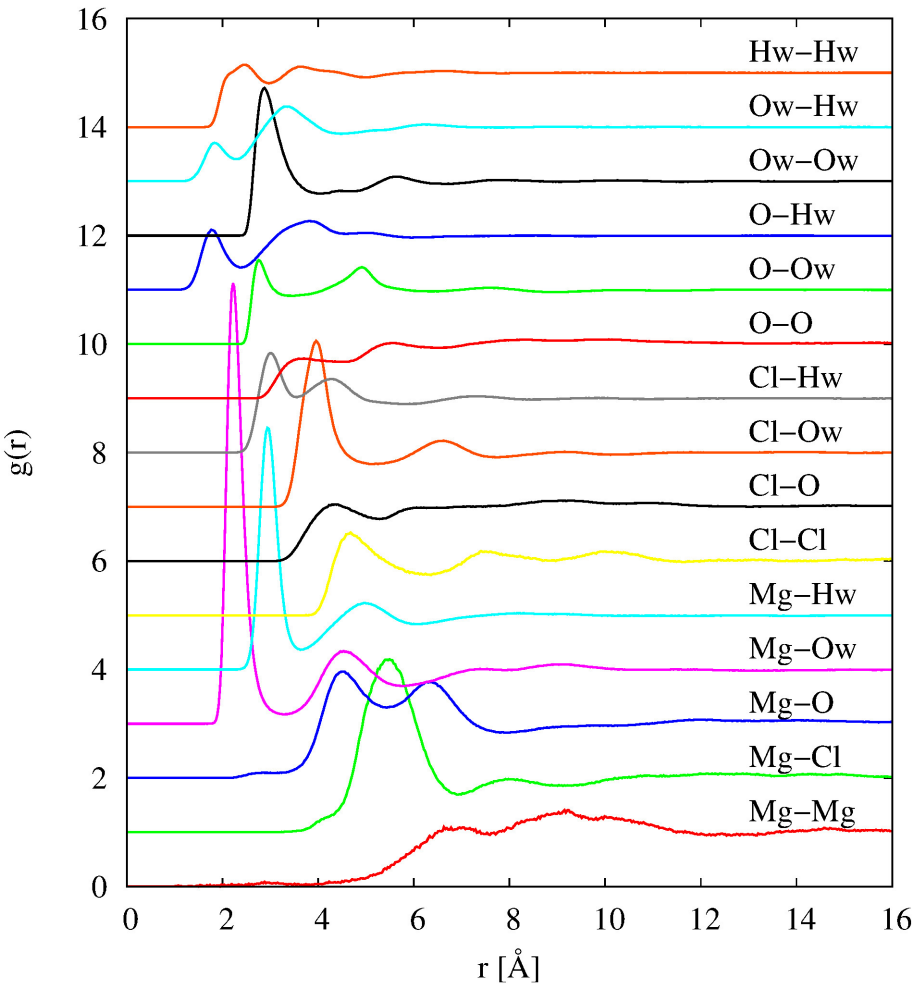


Water at 268K, 4.00kbar



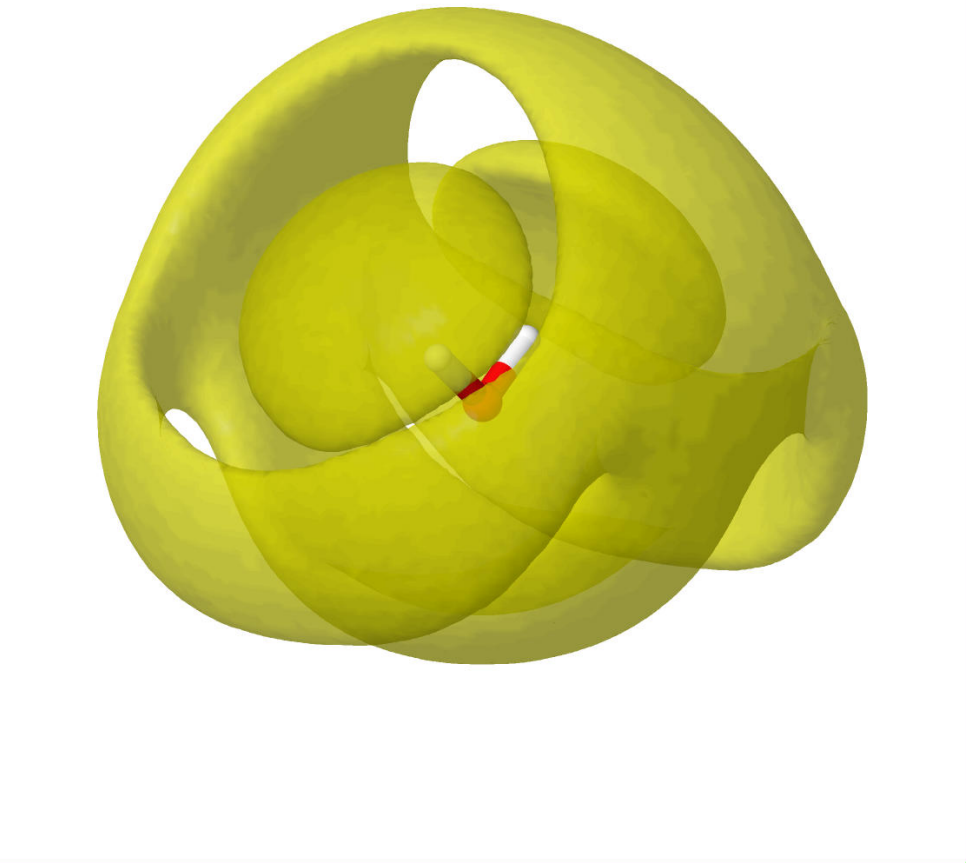
Pressure effect is ubiquitous in aqueous systems





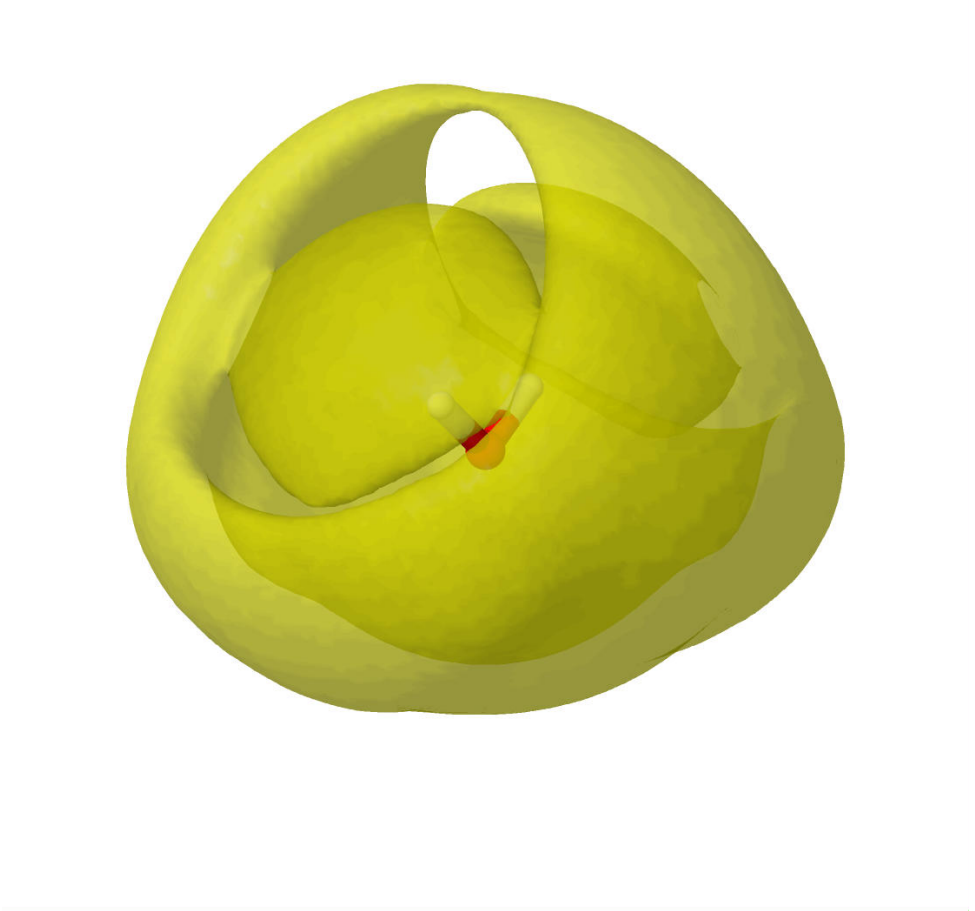
Water spatial density function

Pure water
0.3 kbar



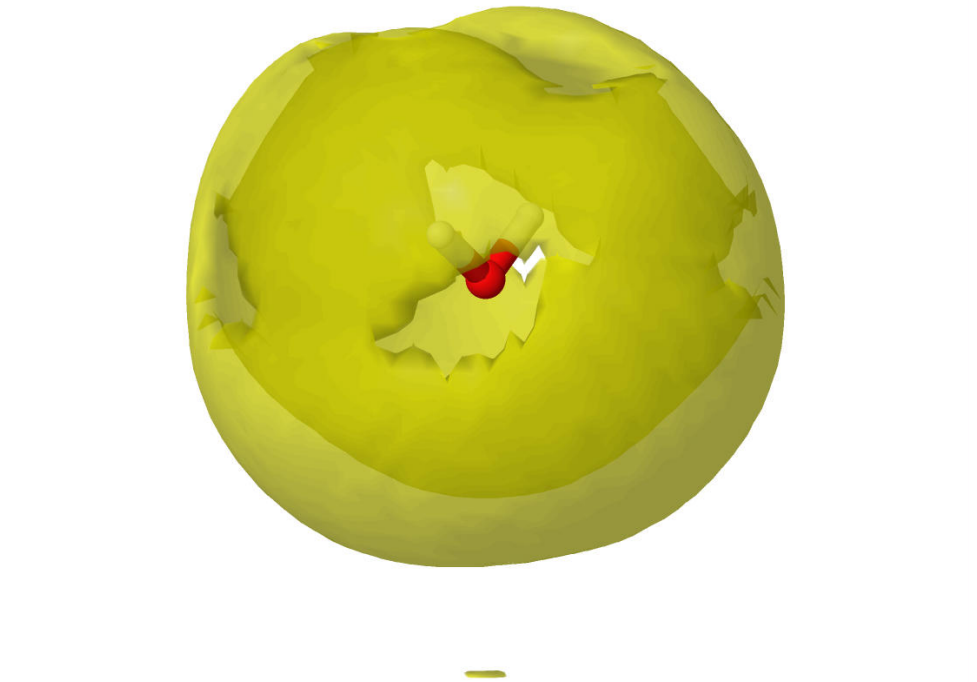
Water spatial density function

Pure water
4.0 kbar



Water spatial density function

Mg perchlorate
0.0 kbar



And so on … !