Disordered Materials:

Lecture II

Finding and refining a structural model

Alan Soper

Disordered Materials Group

ISIS

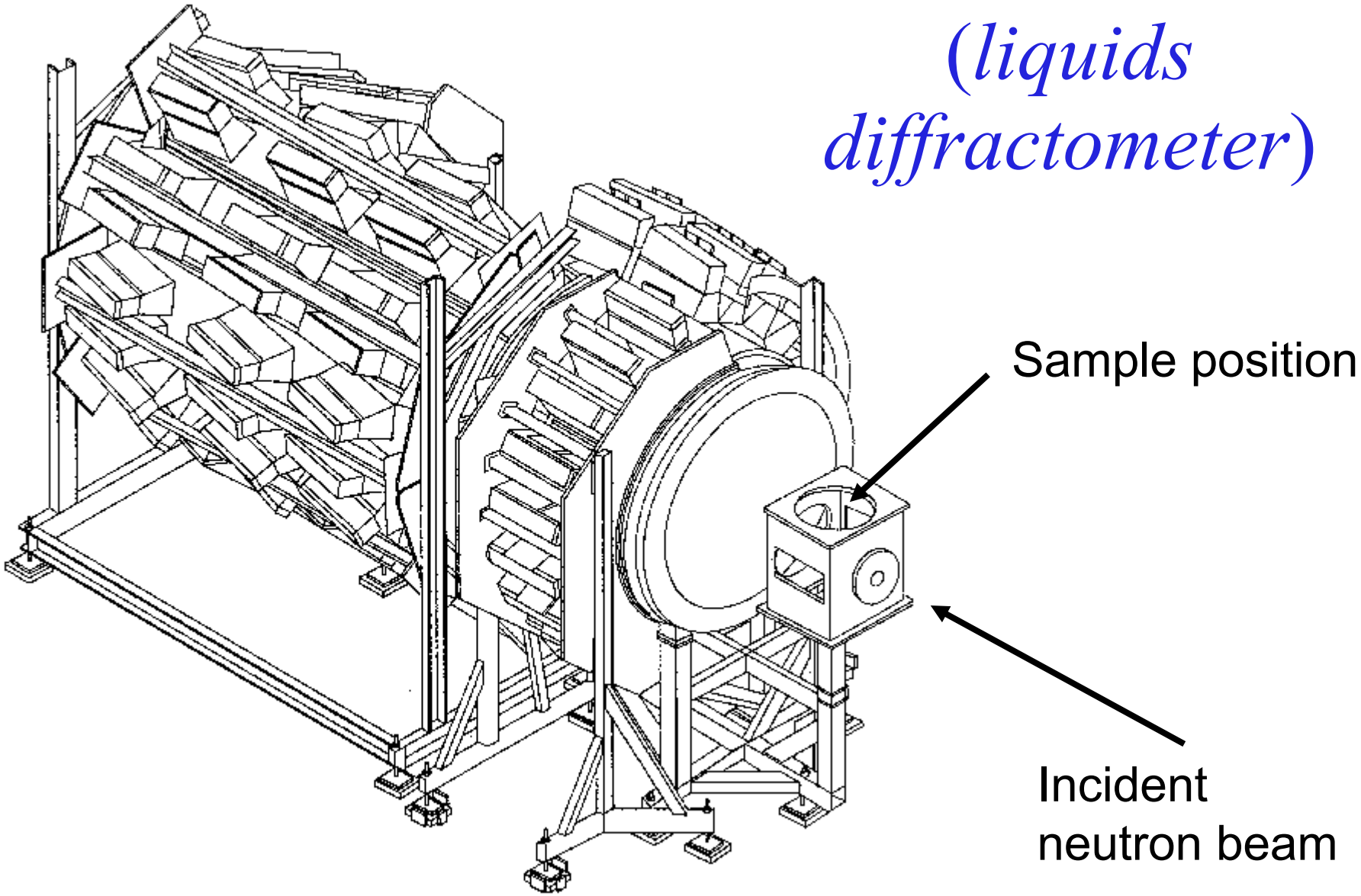
Summary of Lecture I

- Discussion of disorder in our world.
- Concept of correlation in disordered systems.
- Use of radial distribution function to characterise the correlations in a disordered system.
- Use of diffraction to count atoms as a function of distance.
- How to characterise structure in molecular systems:
  - –

Summary of lecture II

- Extracting the structure factor from the diffraction experiment.
- Computer simulation as a tool to model disordered materials
- Molecular systems:
  - SDF, bond angle distributions, OPCF
- Use of computer simulation to go from measurements (*D(Q), g(r)*) to SDF, bond angle distribution, OPCF, etc.
- Some case studies: molten alumina, water, amorphous phosphorus, silica, silicon...

ISIS SANDALS (liquids diffractometer)



The liquid structure factor:

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

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

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

Atomic fraction of component "α"

The atom scattering factor or "form factor"

A much more tricky question: how do we interpret the data?

- For many years the next step was to simply invert our scattering equation:

$$d(r) = \frac{1}{2\pi^2 \rho} \int_0^\infty Q^2 D(Q) \frac{\sin Qr}{Qr} dQ$$

$$= \sum_{\alpha, \beta \geq \alpha} \left(2 - \delta_{\alpha\beta}\right) c_\alpha c_\beta b_\alpha b_\beta \left(g_{\alpha\beta}(r) - 1\right)$$

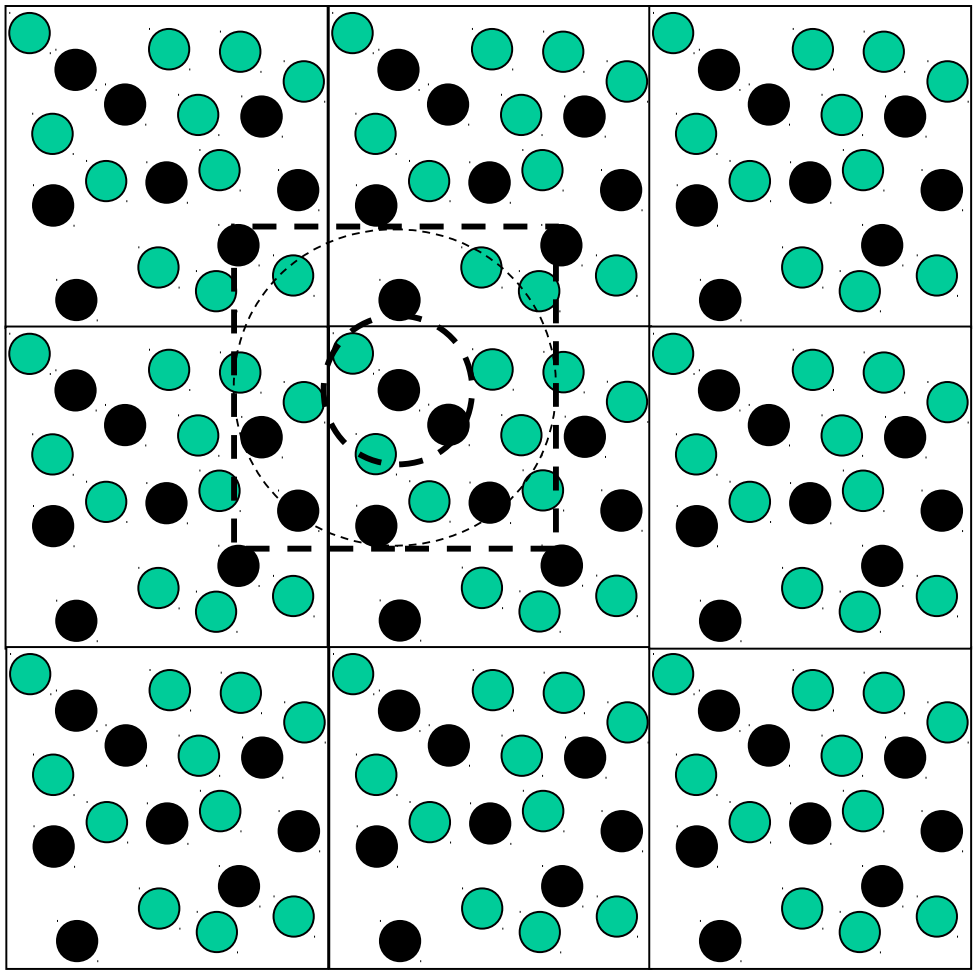
This leads to many problems

- Truncation errors.
- Systematic errors.
- Finite measuring statistics.
- Some site-site terms are more strongly weighted than others.
- These all make interpretation of the data unreliable.
- Radial distribution functions (*g(r)*) do not yield the Orientational Pair Correlation Function (OPCF).

Introduce: computer simulation

- Requires an atom-atom potential energy function.
- Place computer atoms in a (parallelpiped) box at same density as experiment.
- Apply periodic boundary conditions
  - the box repeats itself indefinitely throughout space.
- Apply minimum image convention.

Minimum image convention



Count atoms out to *D/2*

Monte Carlo computer simulation

1. Using the specifed atom-atom potential function, calculate energy of atomic ensemble.
2. Displace one atom or molecule by a random amount in the interval $\pm\delta$.
3. Calculate change in energy of ensemble, ΔU.
4. Always accept move if $\Delta U < 0$
5. If $\Delta U > 0$, accept move with probability $\exp[-\Delta U/kT]$.
6. Go back to 2 and repeat sequence.

But there is a problem:

We don’t know the potential energy function!

Introduce Reverse Monte Carlo, RMC

1. Build a box of atoms as before. Calculate $\chi^2=[D(Q)-F(Q)]^2/\sigma^2$
2. Displace one atom or molecule by a random amount in the interval $\pm\delta$.
3. Calculate change in χ^2 of ensemble, $\Delta\chi^2$.
4. Always accept move if $\Delta\ \chi^2 < 0$
5. If $\Delta\ \chi^2 > 0$, accept move with probability $\exp[-\Delta\ \chi^2]$.
6. Go back to 2 and repeat sequence.

This approach has problems, particularly with molecules.

- Molecules are usually introduced via unphysical coordination constraints.
- Especially with molecules the ensemble of atoms can get “stuck” i.e. it does not sample phase space correctly.
- Various reasons why this can occur.

Introduce Empirical Potential Structure Refinement, EPSR

- 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).
- Use the diffraction data to perturb this reference potential, so that the simulated structure factor looks like the measured data.

Introducing the data

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

- M measured datasets, N partial structure factors: (Usually $M < N$)
- Assign a "feedback" factor f for the data:

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

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

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

- Form inversion of $w'_{ij},\ 1\leq i\leq M+N,\ 1\leq j\leq N$

Refining the potential: M datasets, N partial structure factors

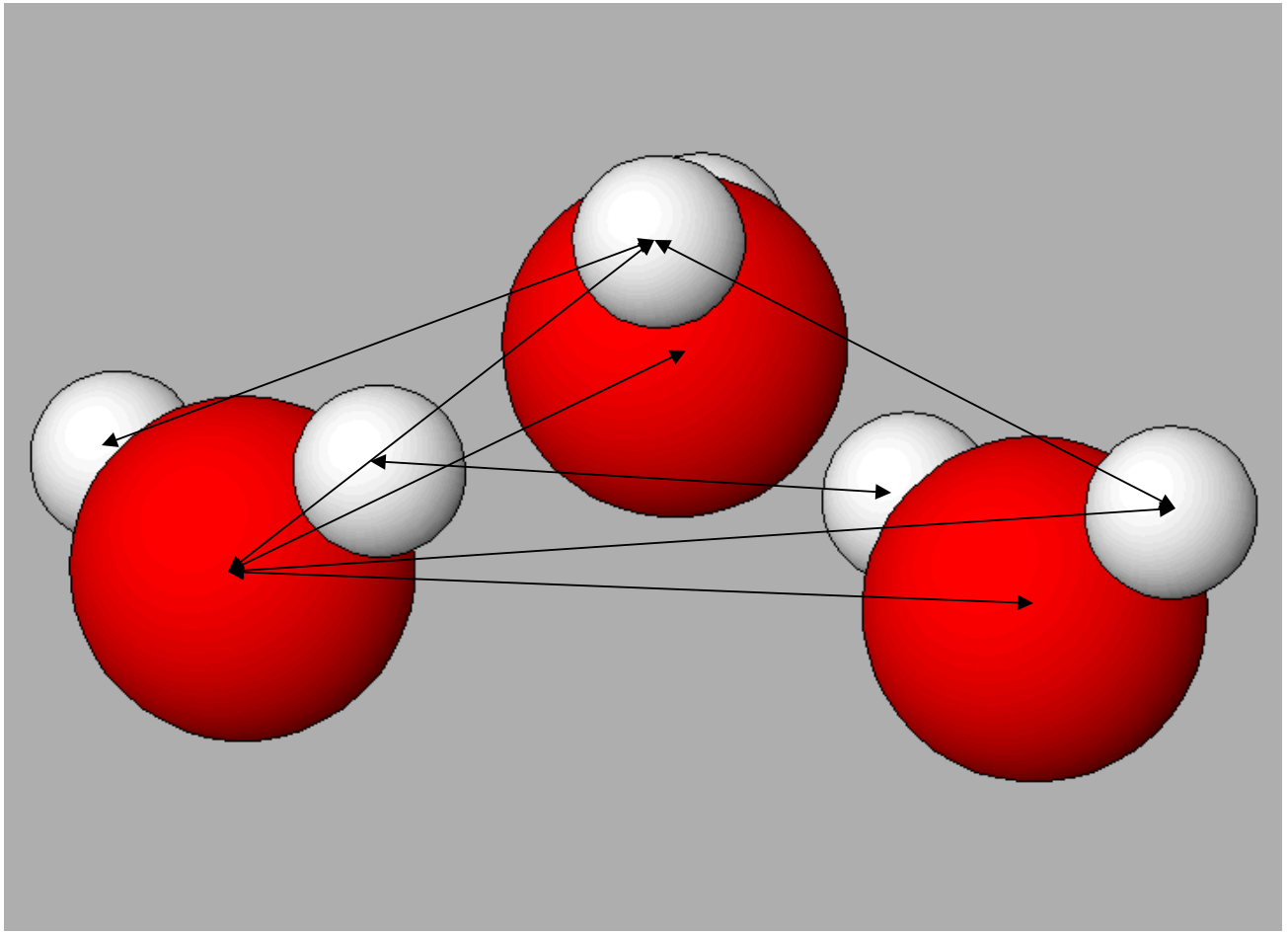
$$F_{i(=1,M+N)}(Q) = \begin{bmatrix} & & & & & & & & & \\ fw_{11} & fw_{12} & \cdots & & & & & \cdots & fw_{1N} \\ fw_{21} & fw_{22} & \cdots & & & & & \cdots & fw_{2N} \\ \cdots & \cdots & & & & & & & \cdots \\ \cdots & \cdots & & & & & & & \cdots \\ fw_{M1} & fw_{M2} & & & & & & & fw_{MN} \\ (1-f) & 0.0 & 0.0 & \cdots & & & & \cdots & 0.0 \\ 0.0 & (1-f) & 0.0 & \cdots & & & & \cdots & \cdots \\ 0.0 & 0.0 & (1-f) & \cdots & & & & & \\ \cdots & \cdots & \cdots & \cdots & & & & & \\ & & & & \cdots & & & & \\ & & & & & \cdots & & & \\ & & & & & & \cdots & \cdots & \cdots & \cdots \\ \cdots & & & & & & \cdots & (1-f) & 0.0 & 0.0 \\ \cdots & \cdots & & & & & \cdots & 0.0 & (1-f) & 0.0 \\ 0.0 & \cdots & \cdots & & & & \cdots & 0.0 & 0.0 & (1-f) \end{bmatrix} \times \begin{bmatrix} S_1 \\ S_2 \\ \cdots \\ \\ \\ \\ \\ \\ \cdots \\ S_N \end{bmatrix}$$

Data

Simulation

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

What do we measure if there are molecules present?



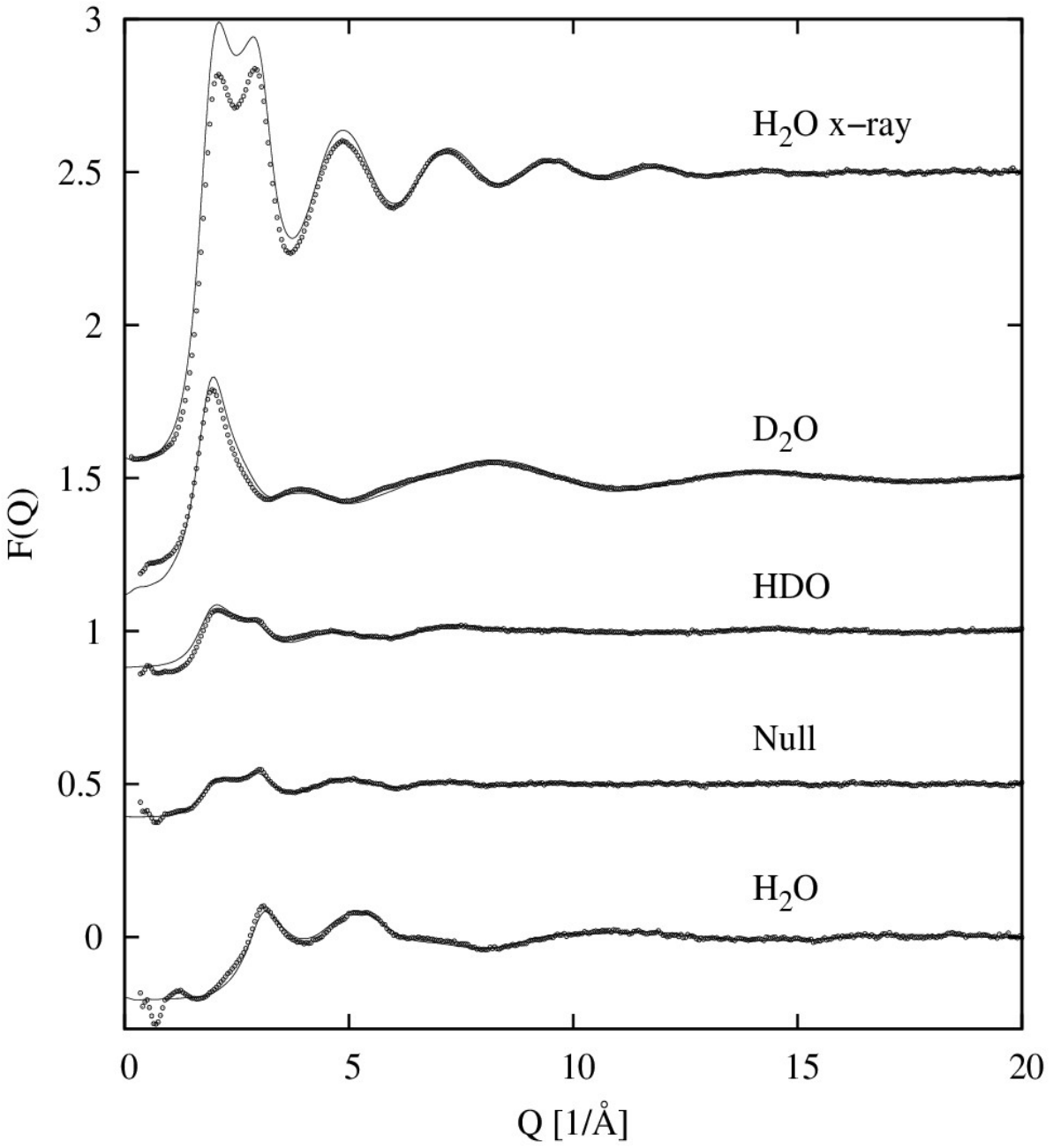
However, two issues need to be addressed:-

- *Issue 1: Often not possible to measure all partial structure factors.*
- *Issue 2: Even if we could, what do they mean?*

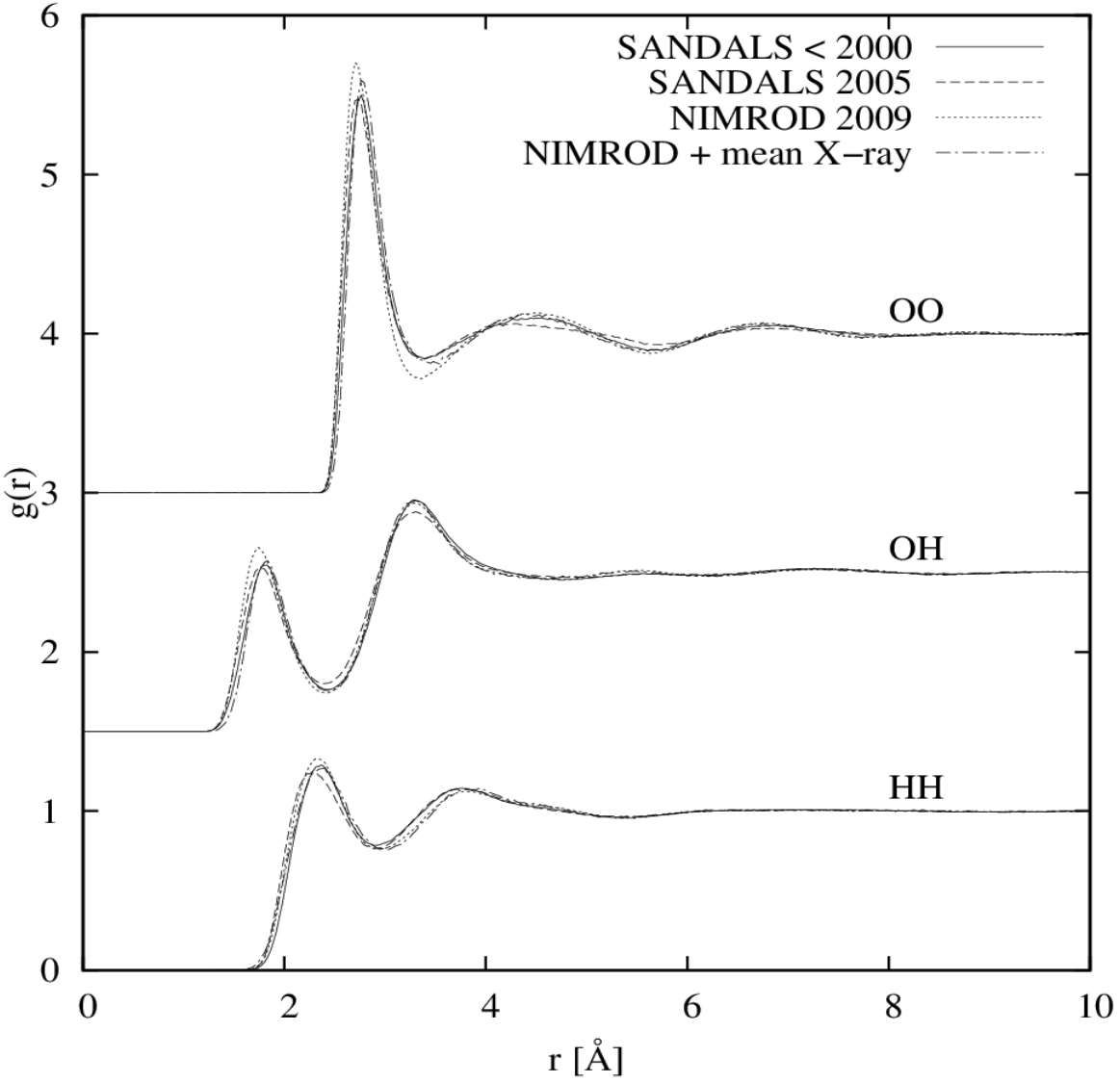
Structure refinement of liquid water

Water data

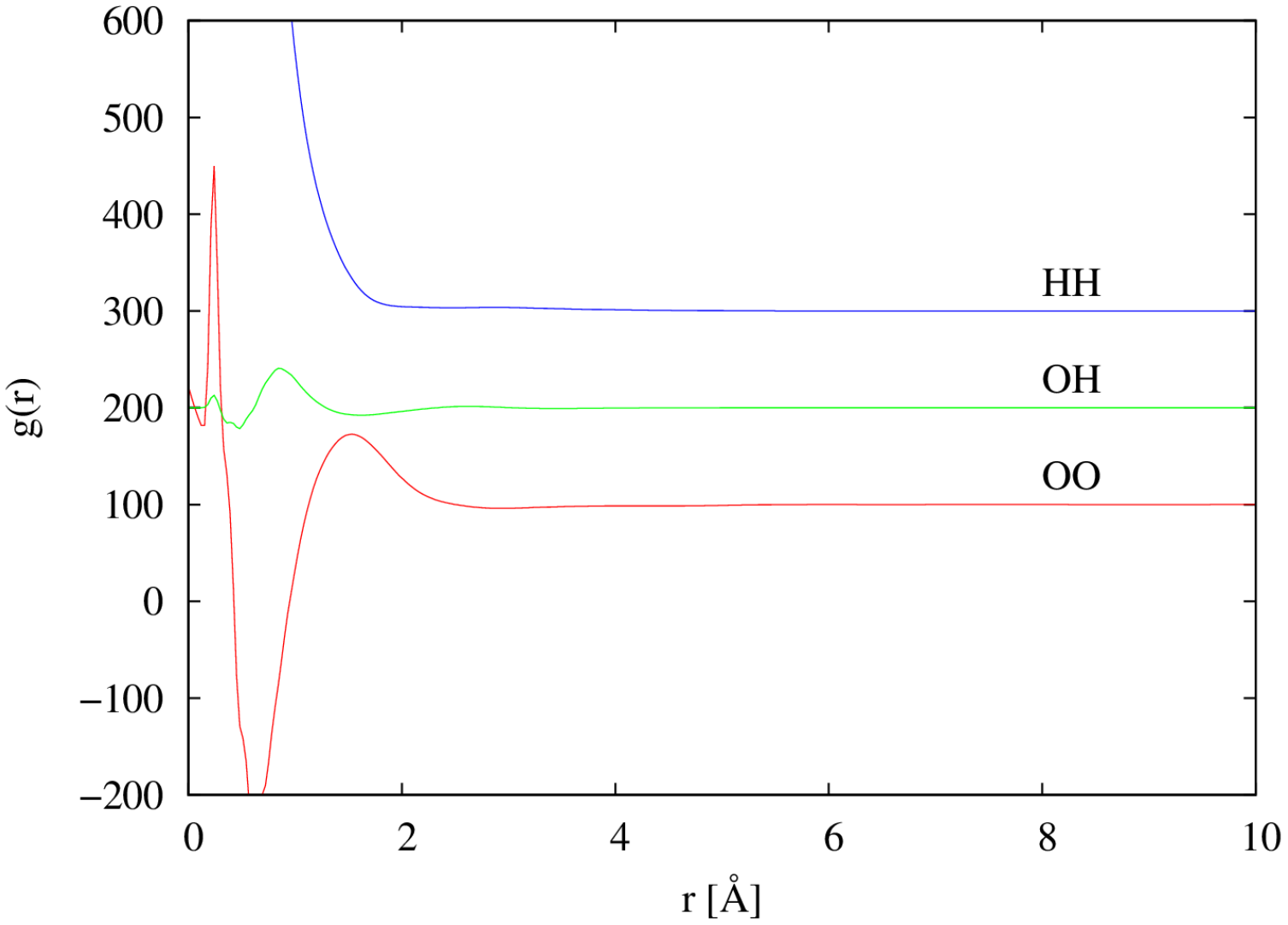
After structure refinement



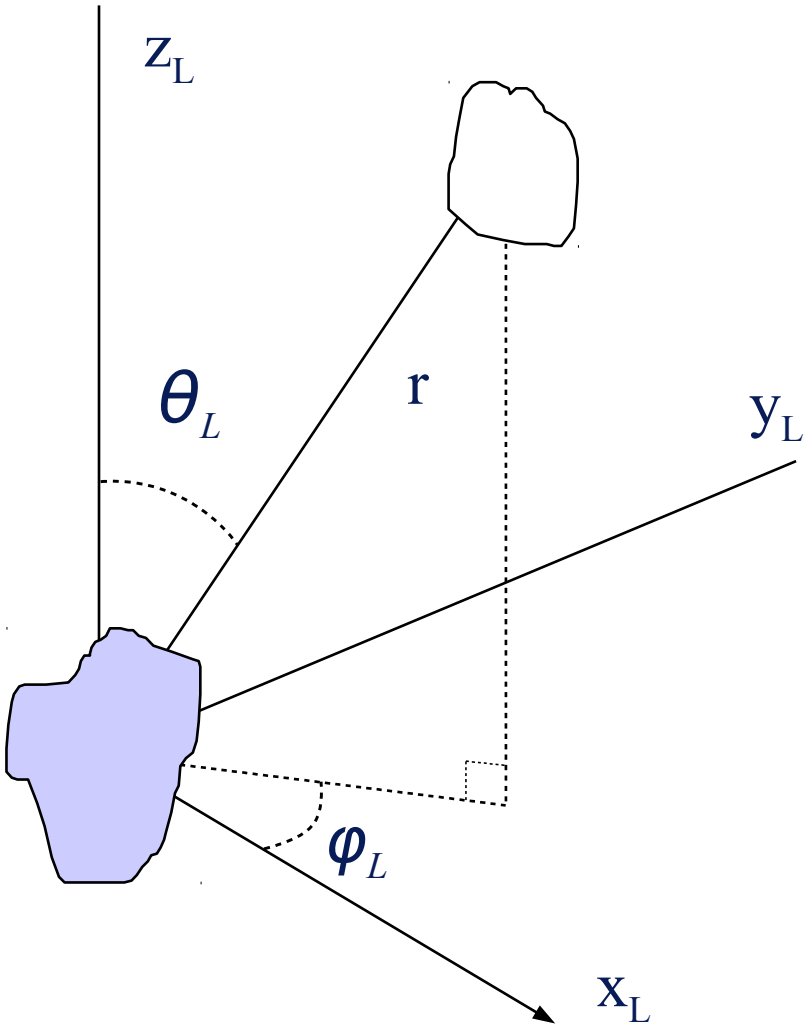
Water partial g(r)'s



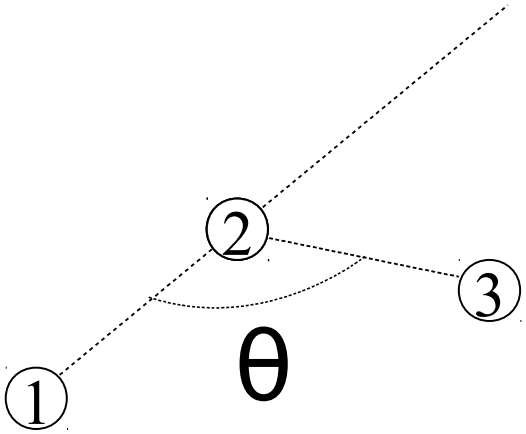
Water empirical potentials



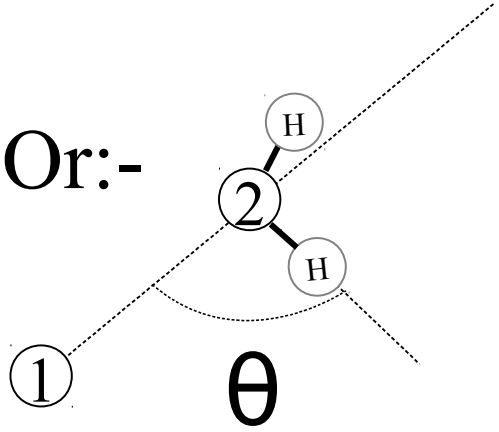
Beyond g(r): the spatial density function



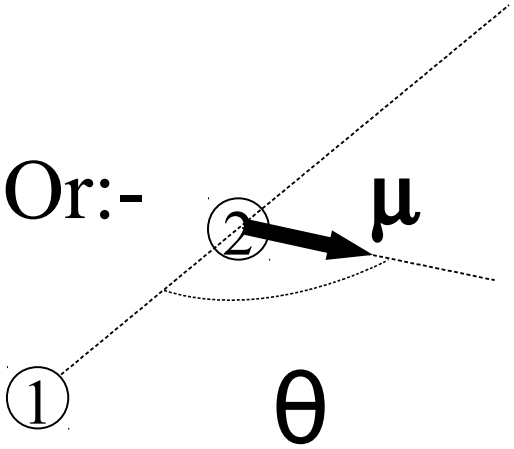
Bond angle distributions



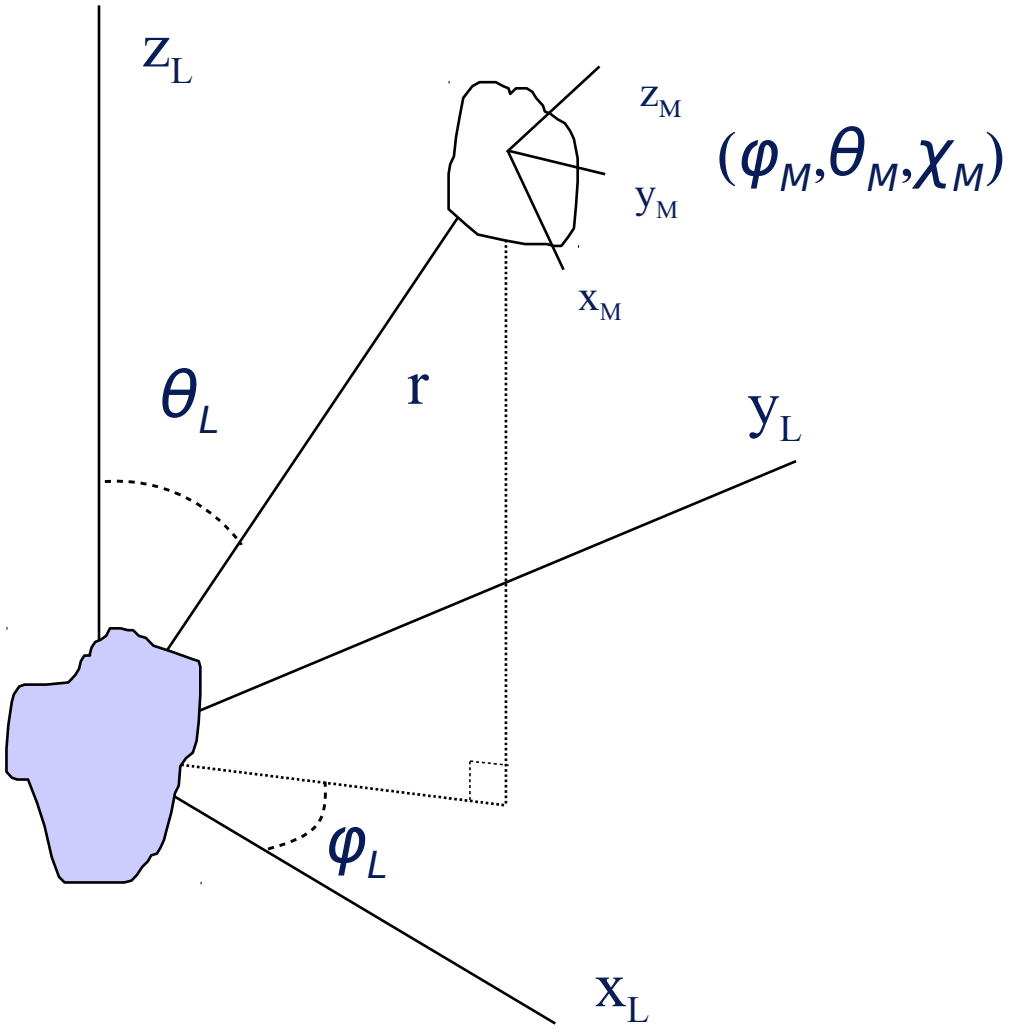
Or:-



Or:-

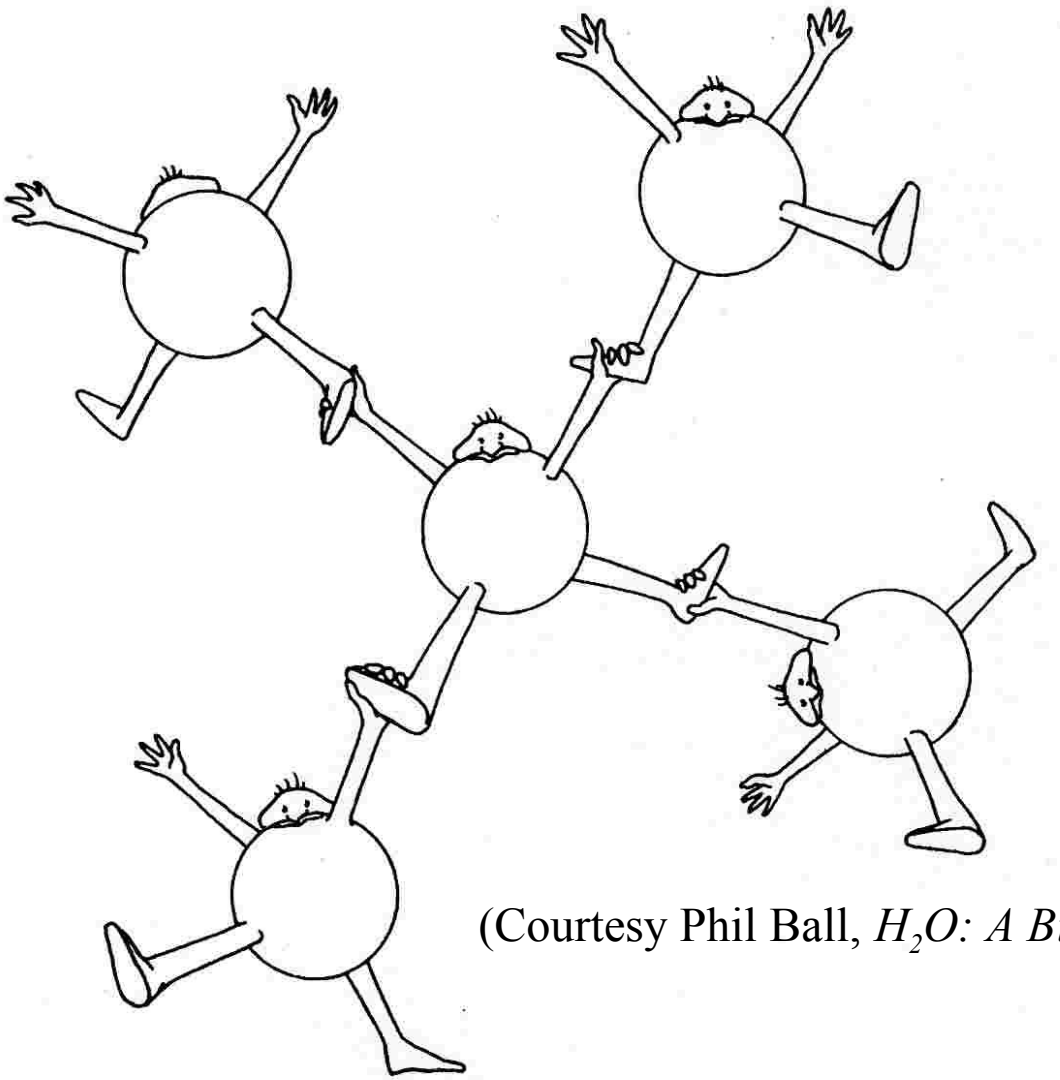


A step further: the orientational pair correlation function



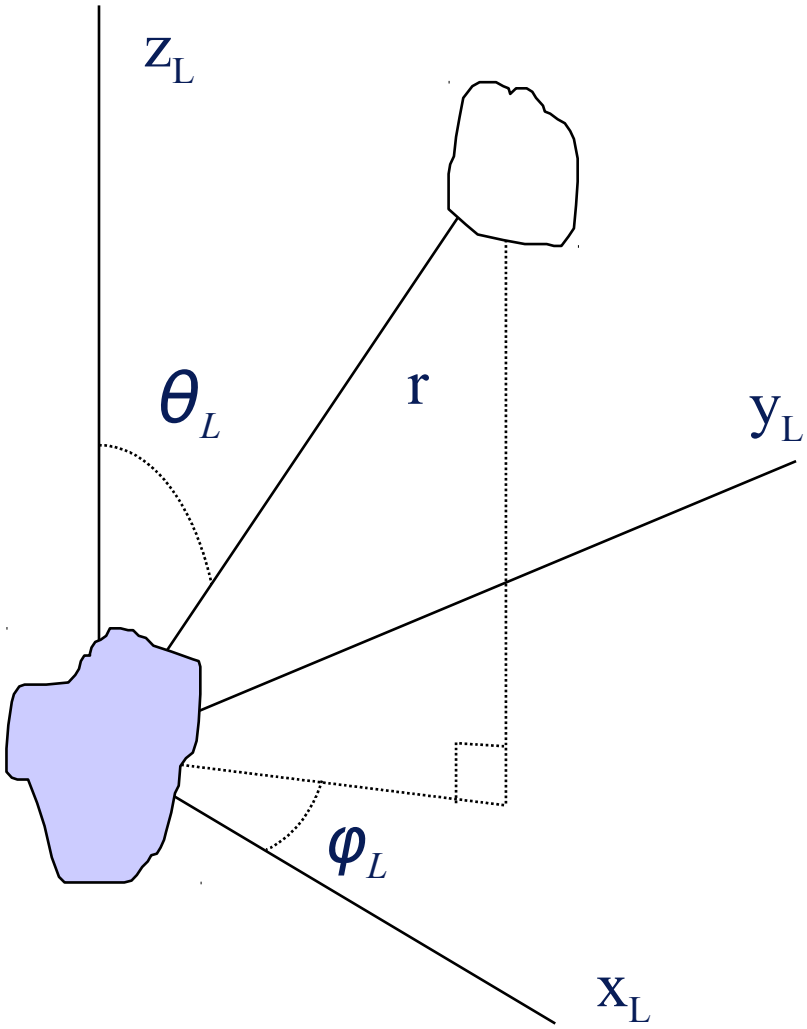
The spatial density function of water...

Water structure



(Courtesy Phil Ball, *H_2O: A Biography of Water*)

Beyond g(r): the spatial density function

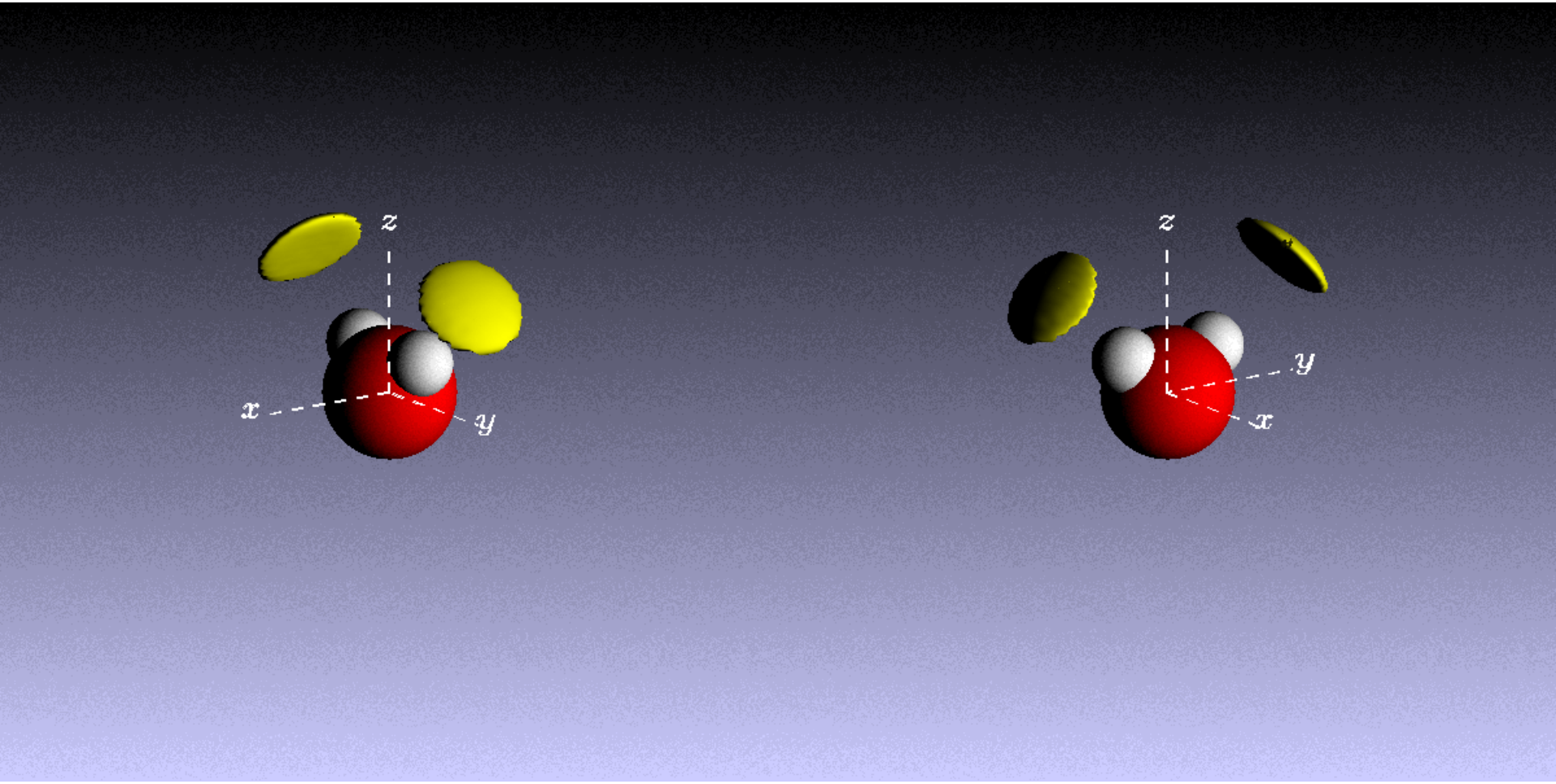


Choose distance range (0-5.7Å)

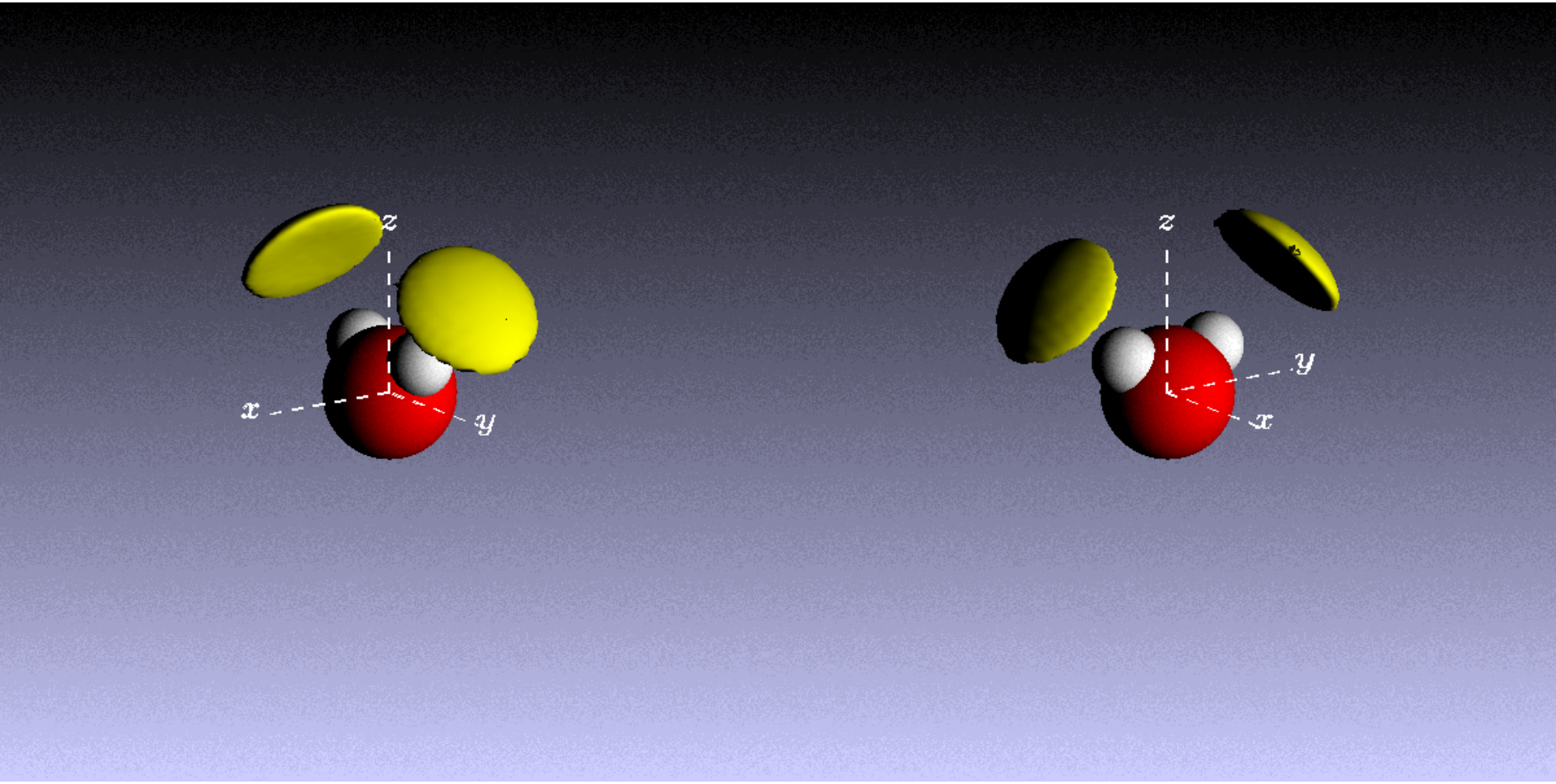
and a contour level

(% of all molecules in distance range)

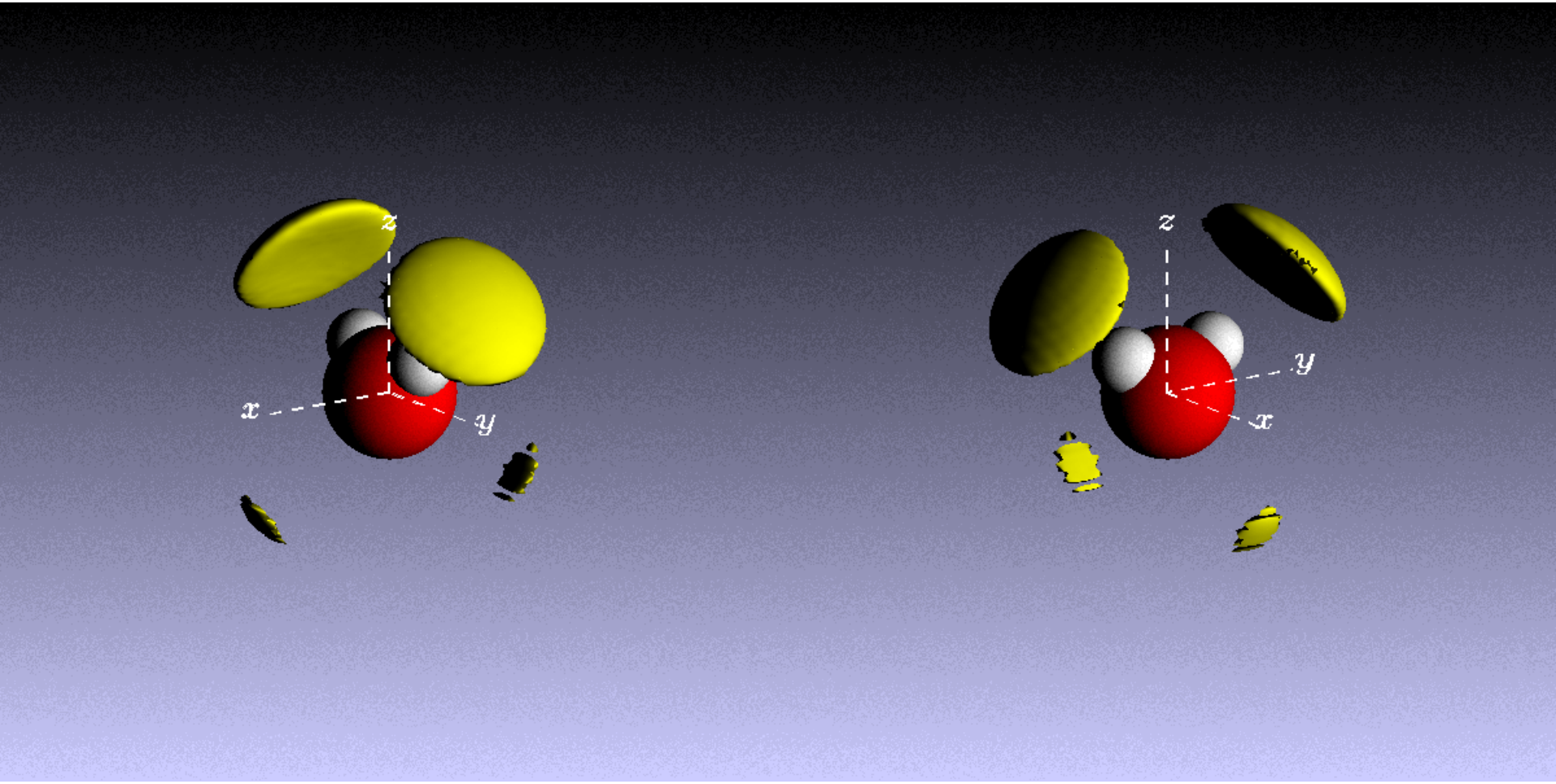
1%



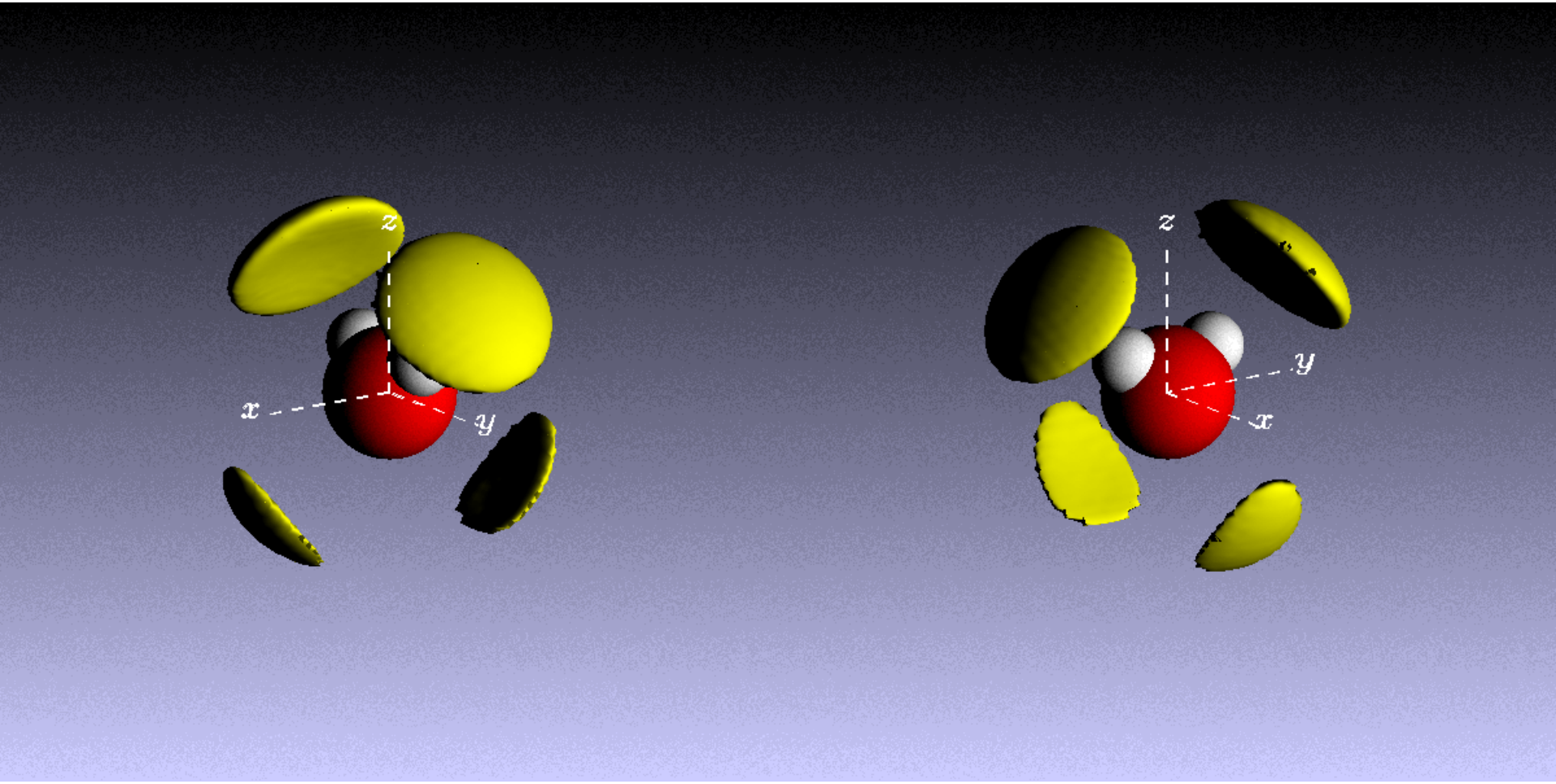
2%



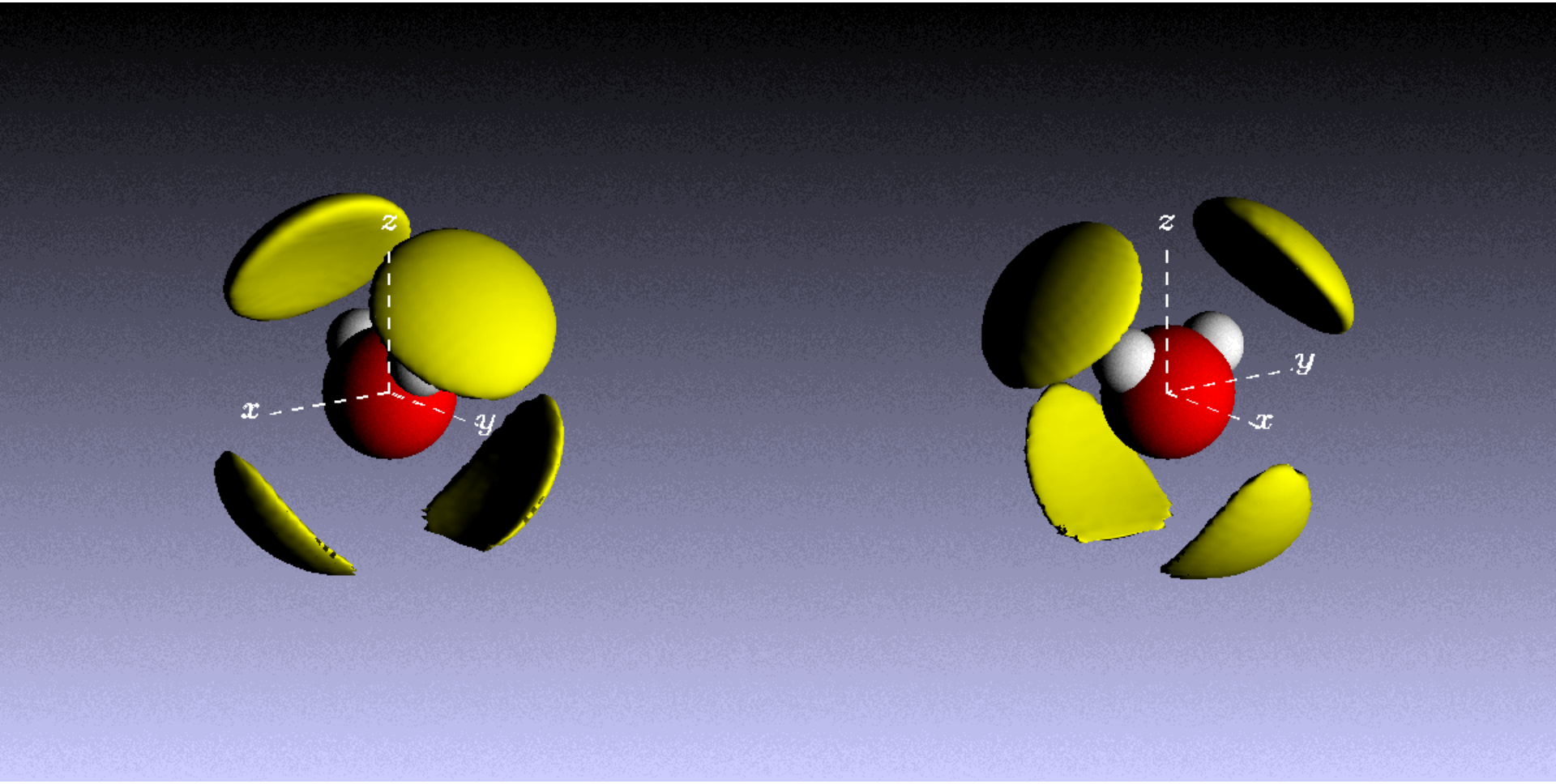
3%



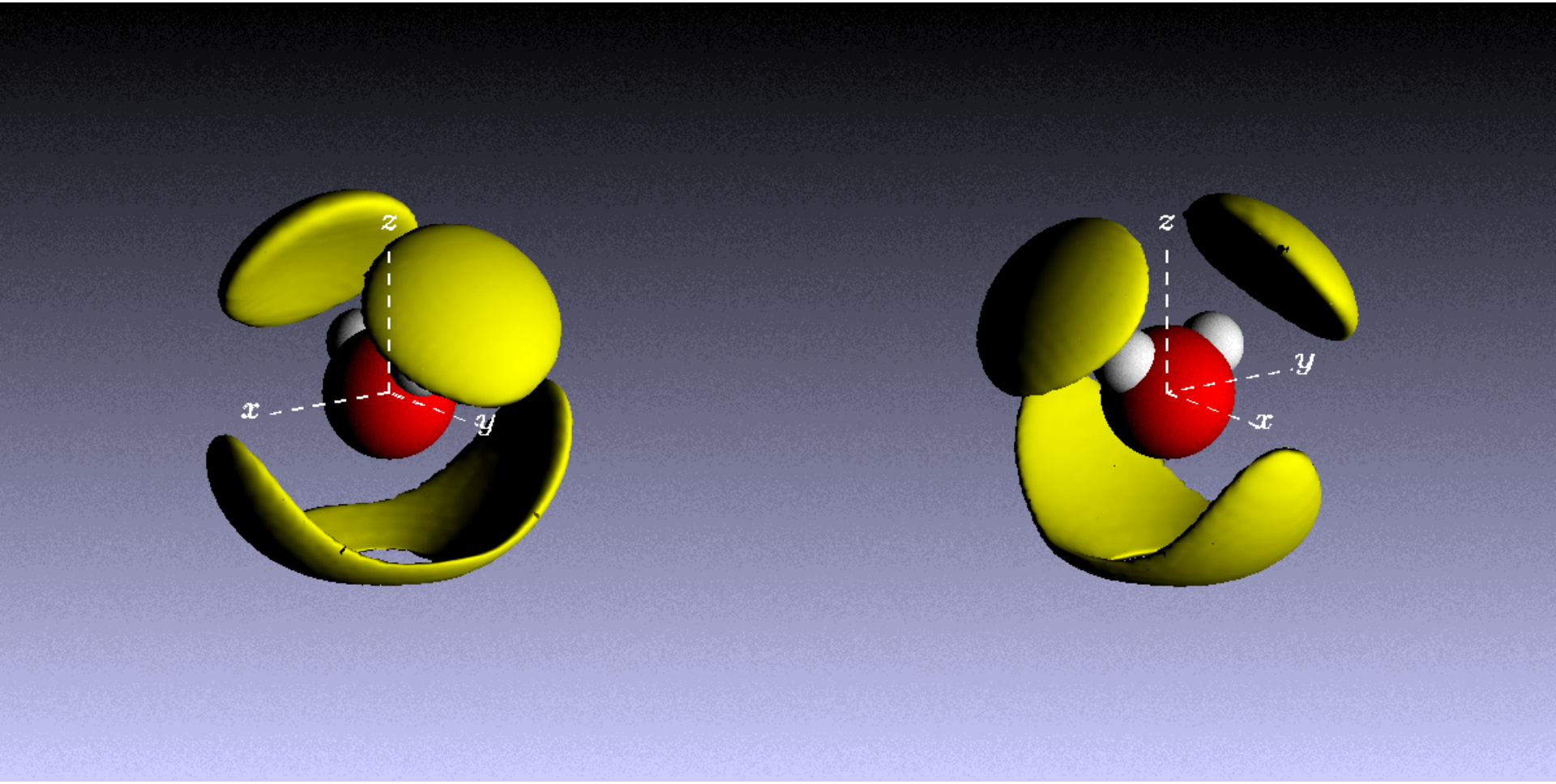
4%



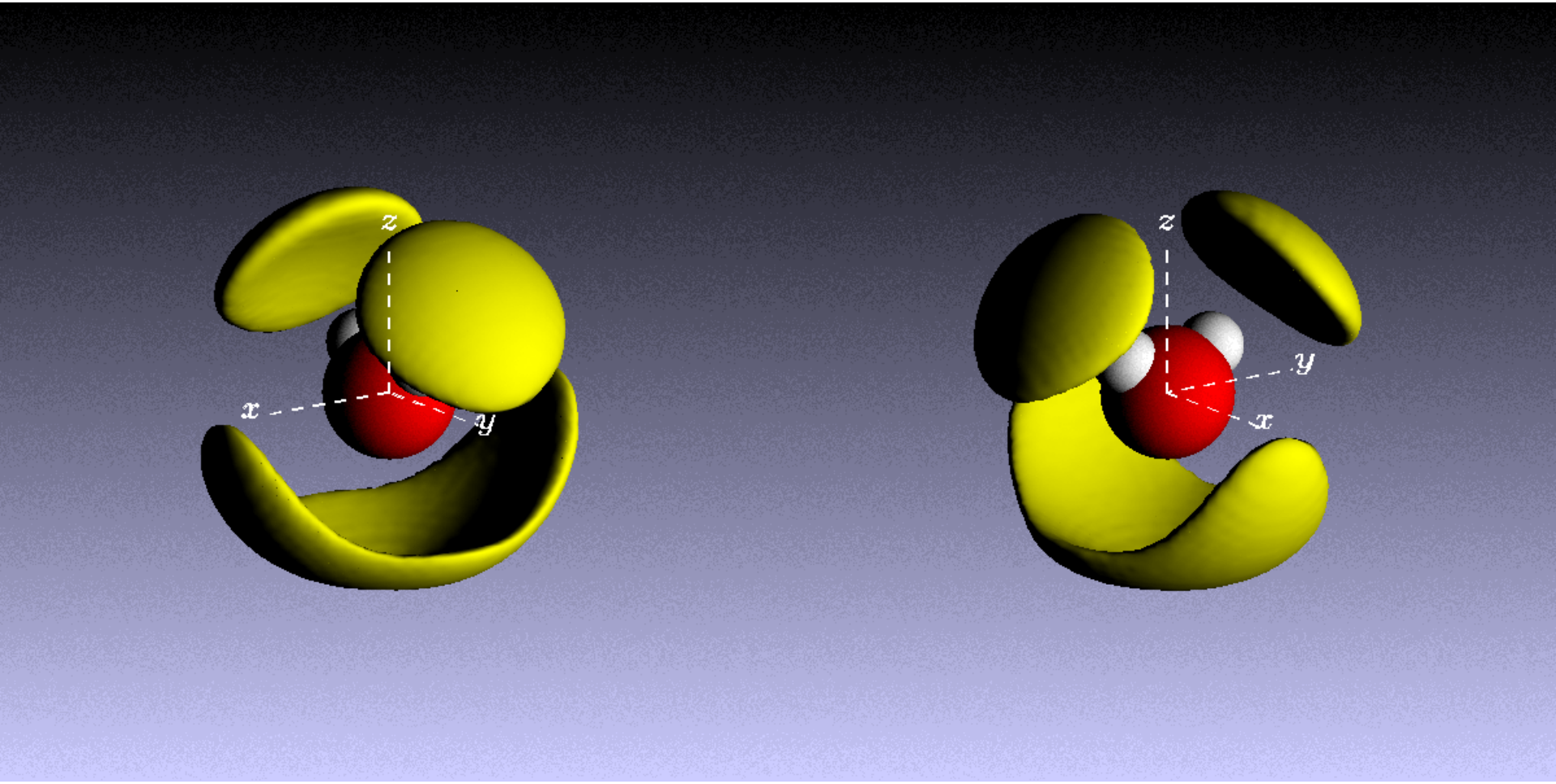
5%



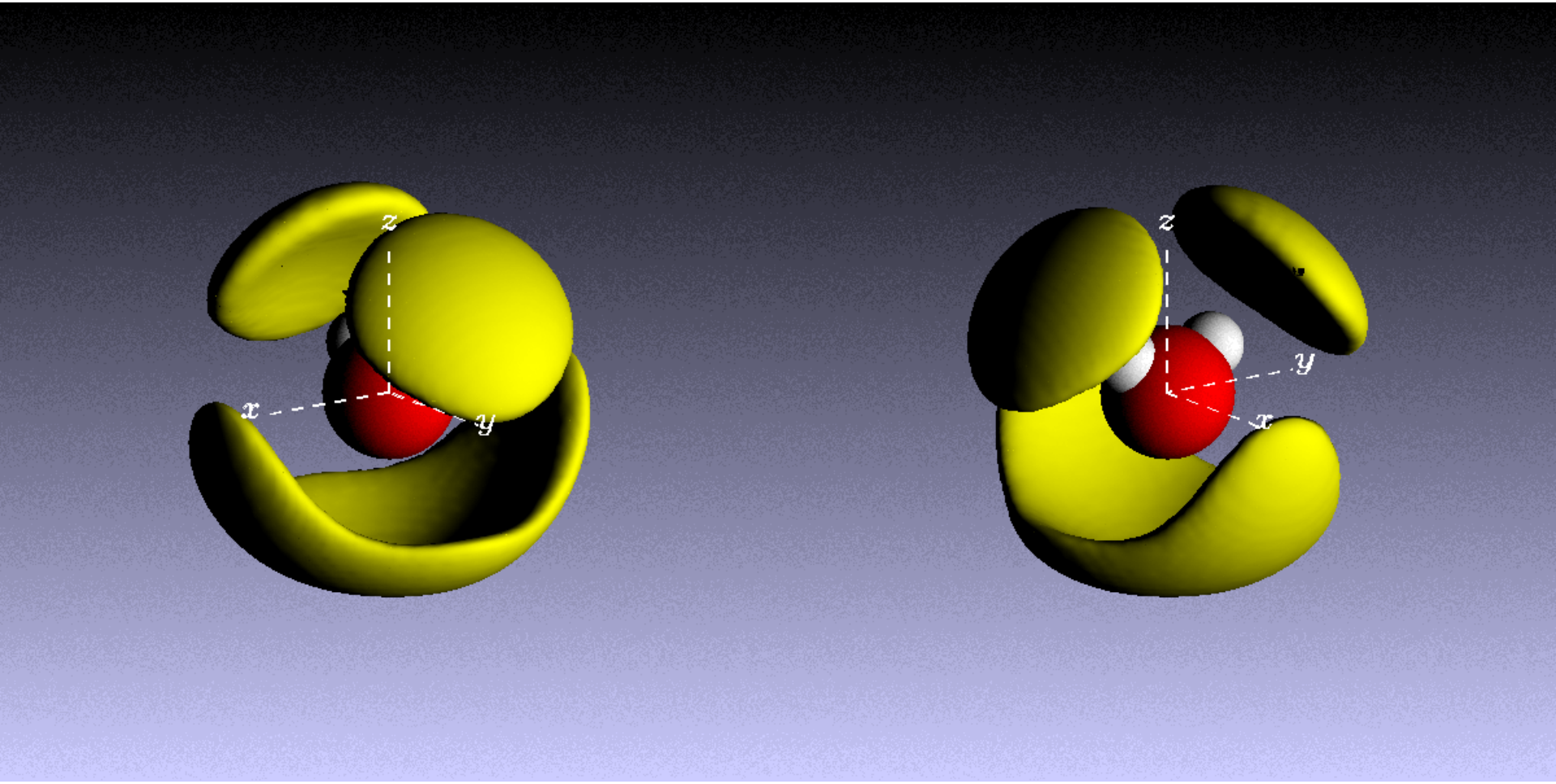
7%



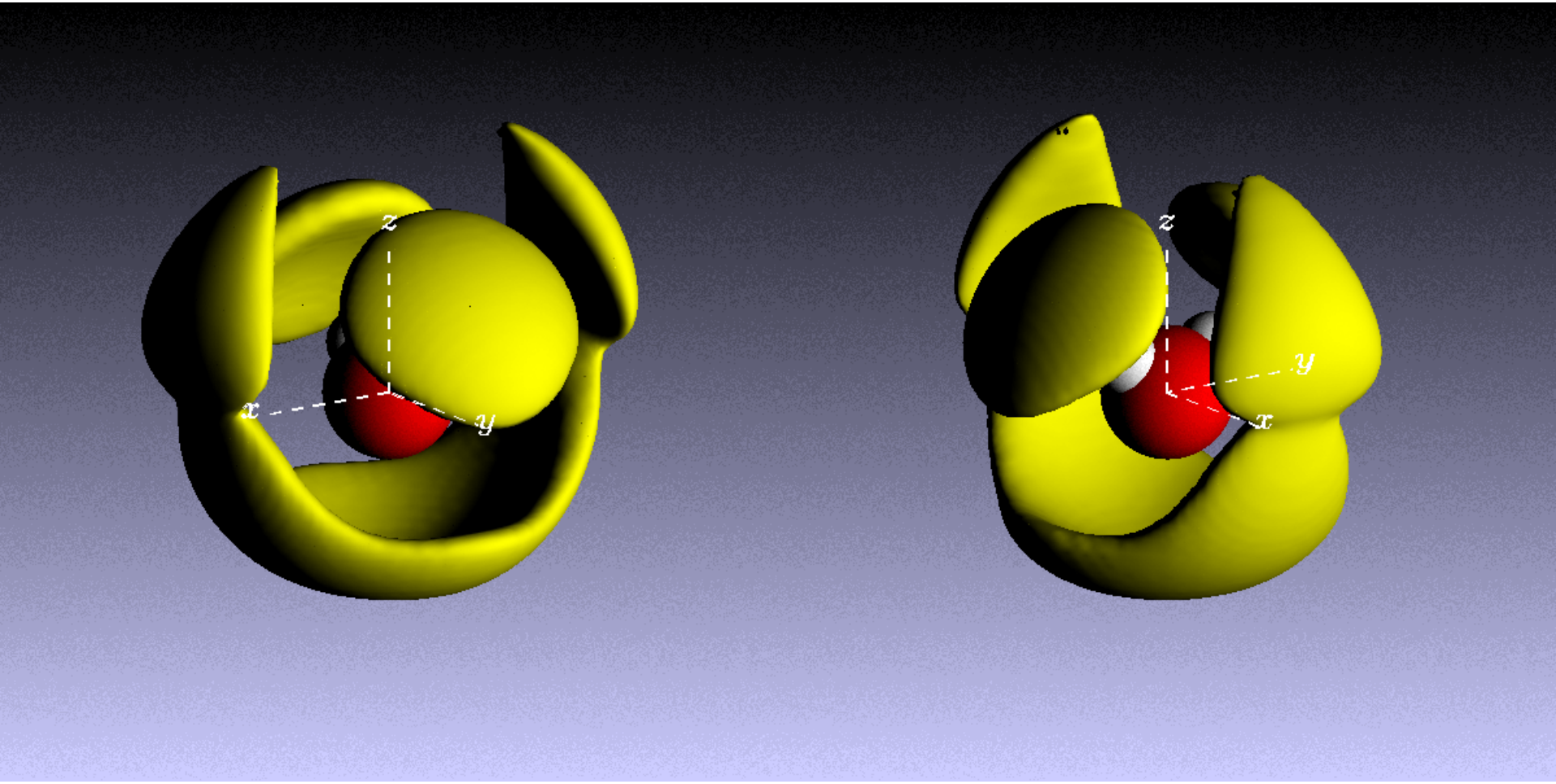
9%



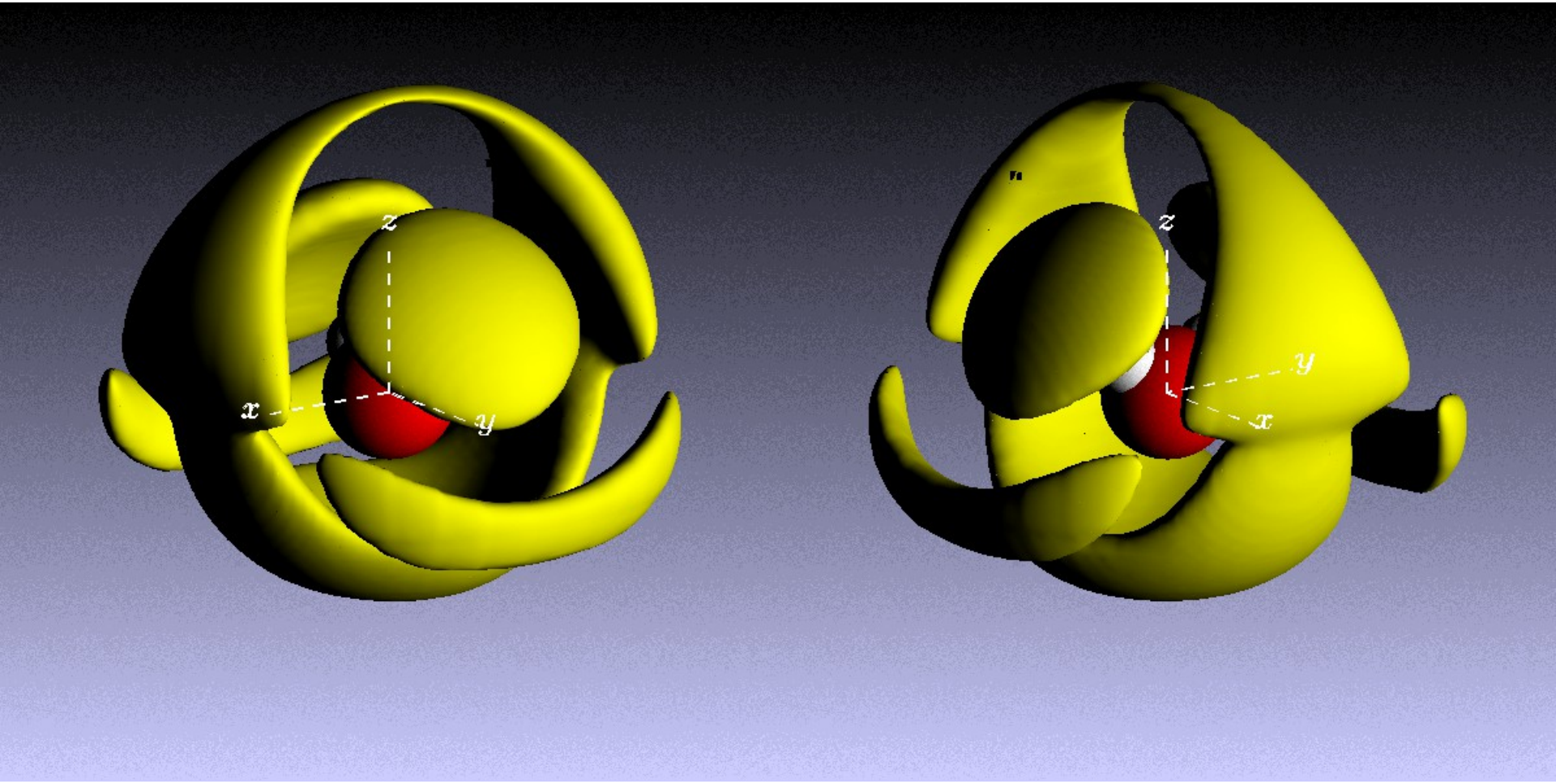
12%



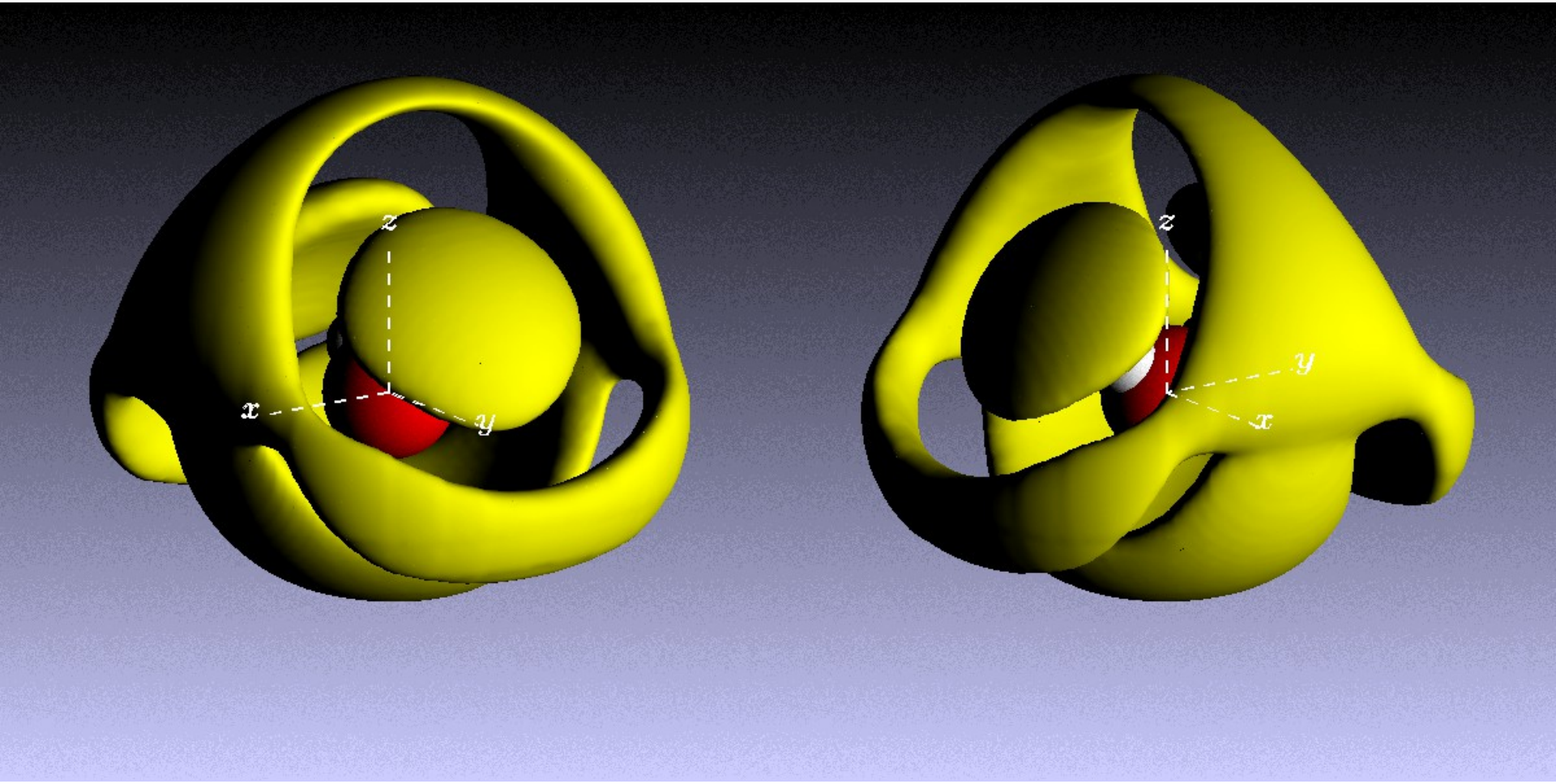
15%



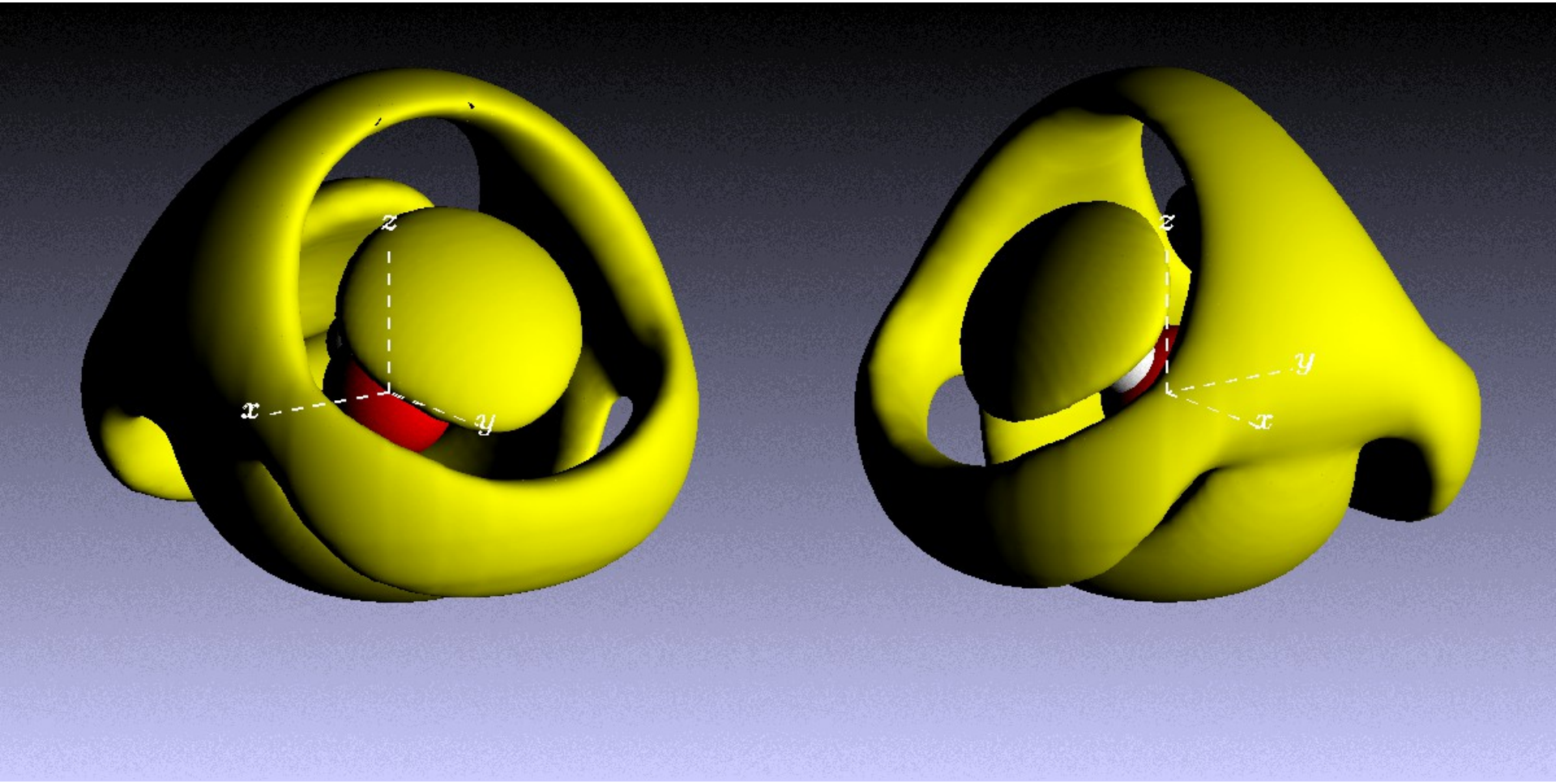
18%



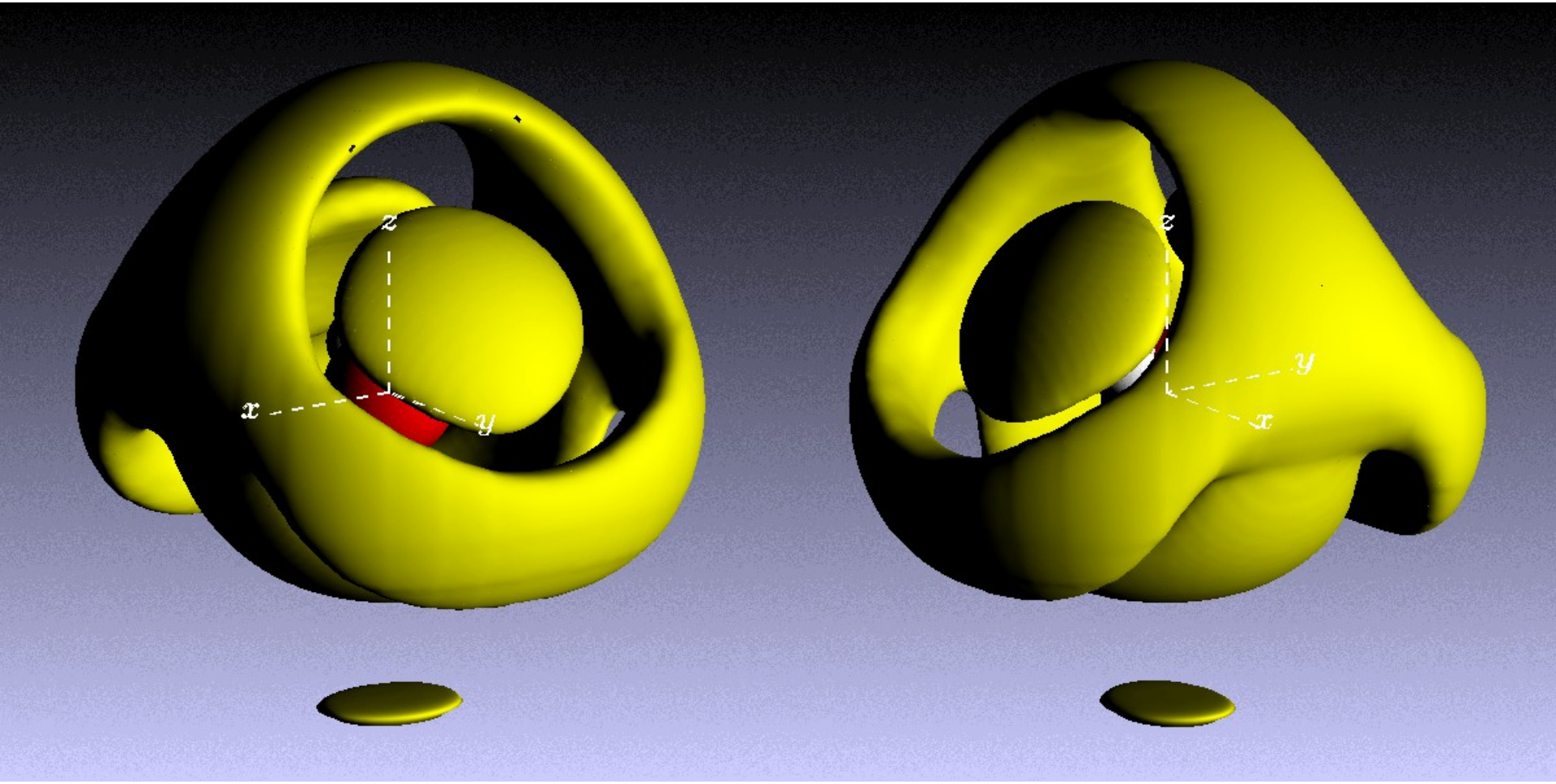
21%



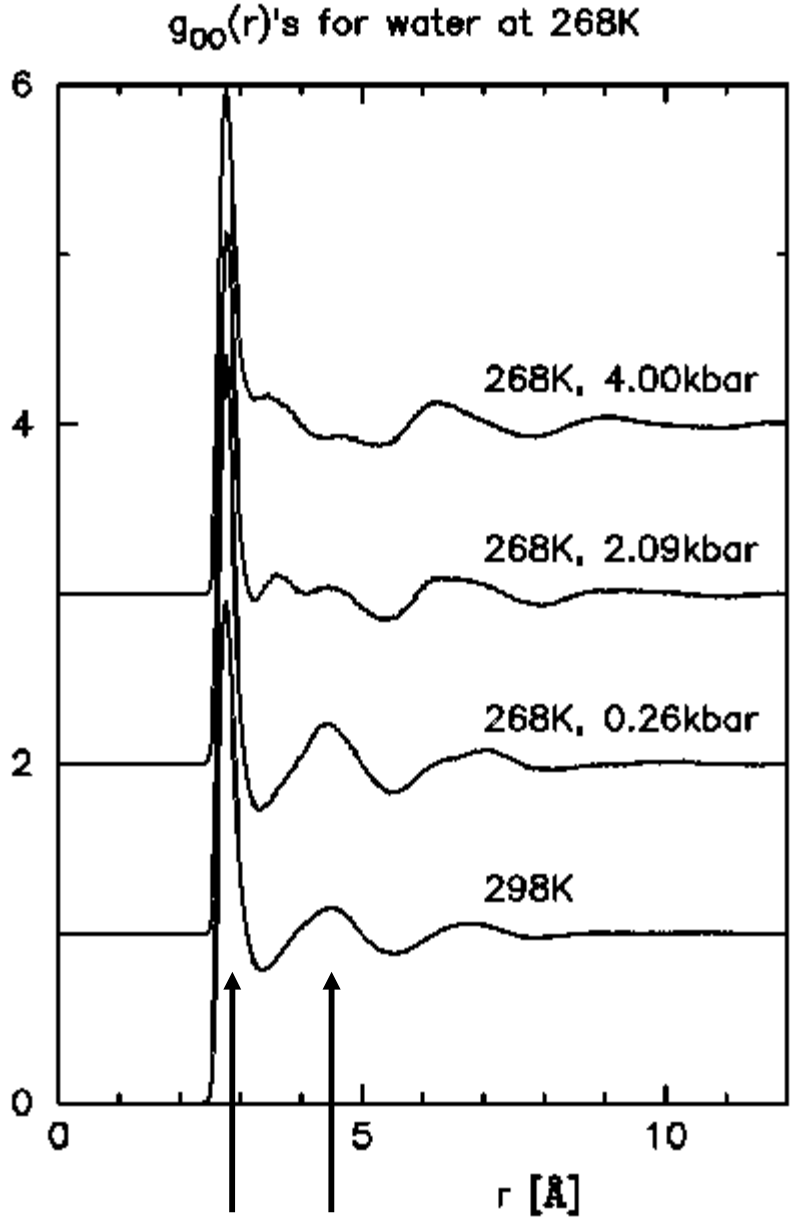
25%



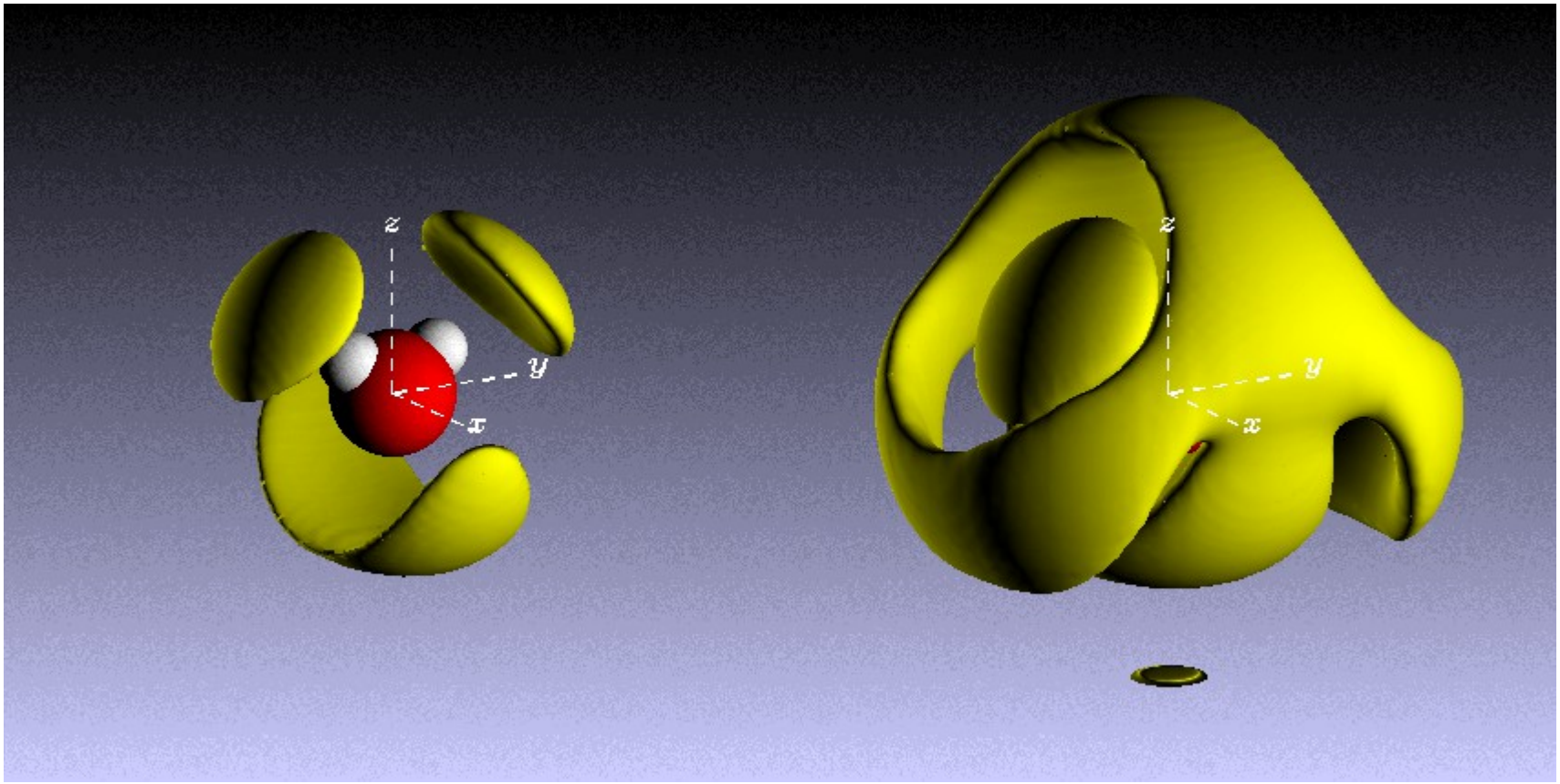
30%



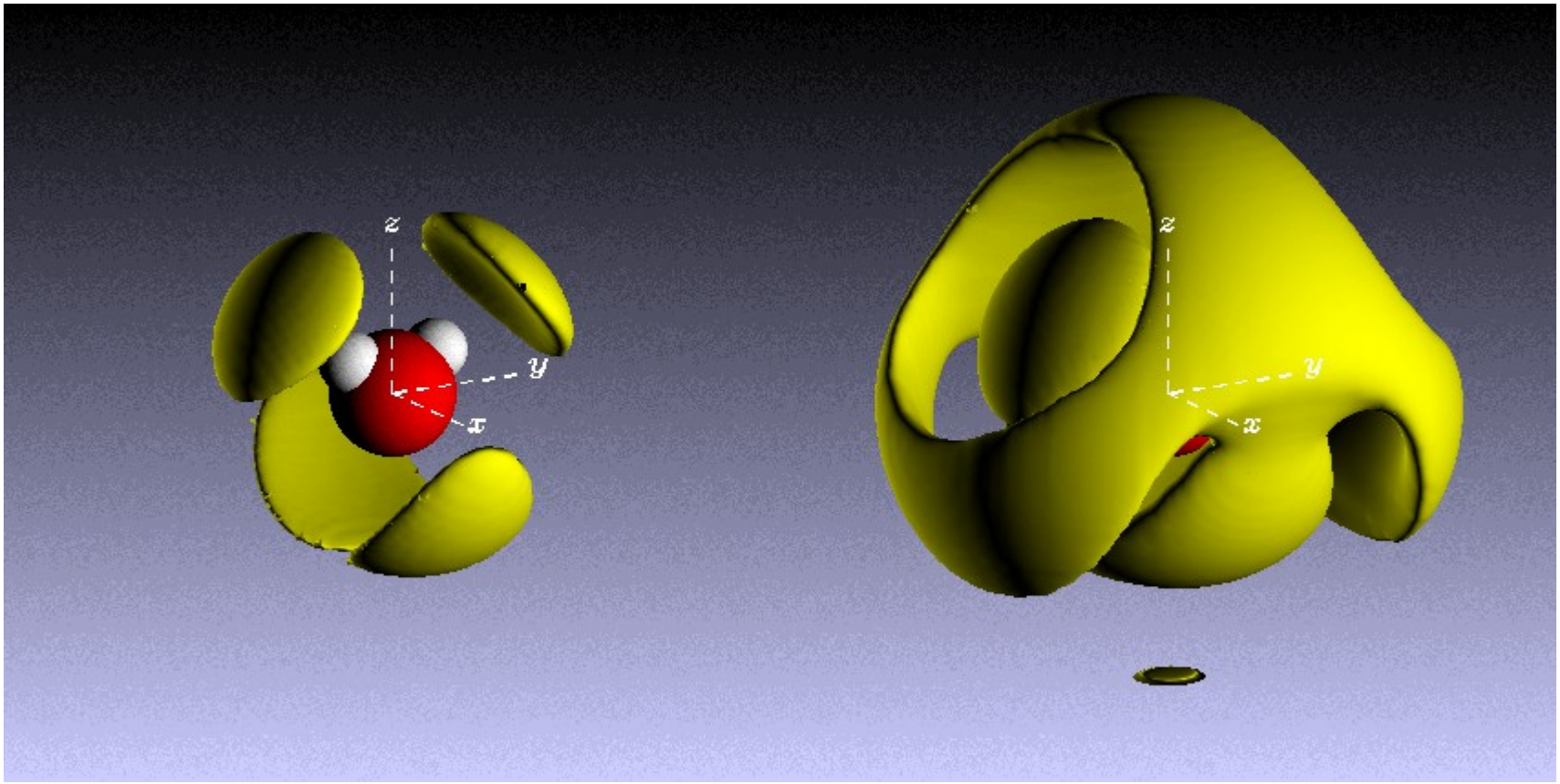
Water under pressure


$g_{OO}(r)$'s for water at 268K
6
4
2
0
268K, 4.00kbar
268K, 2.09kbar
268K, 0.26kbar
298K
0
5
10
r [Å]

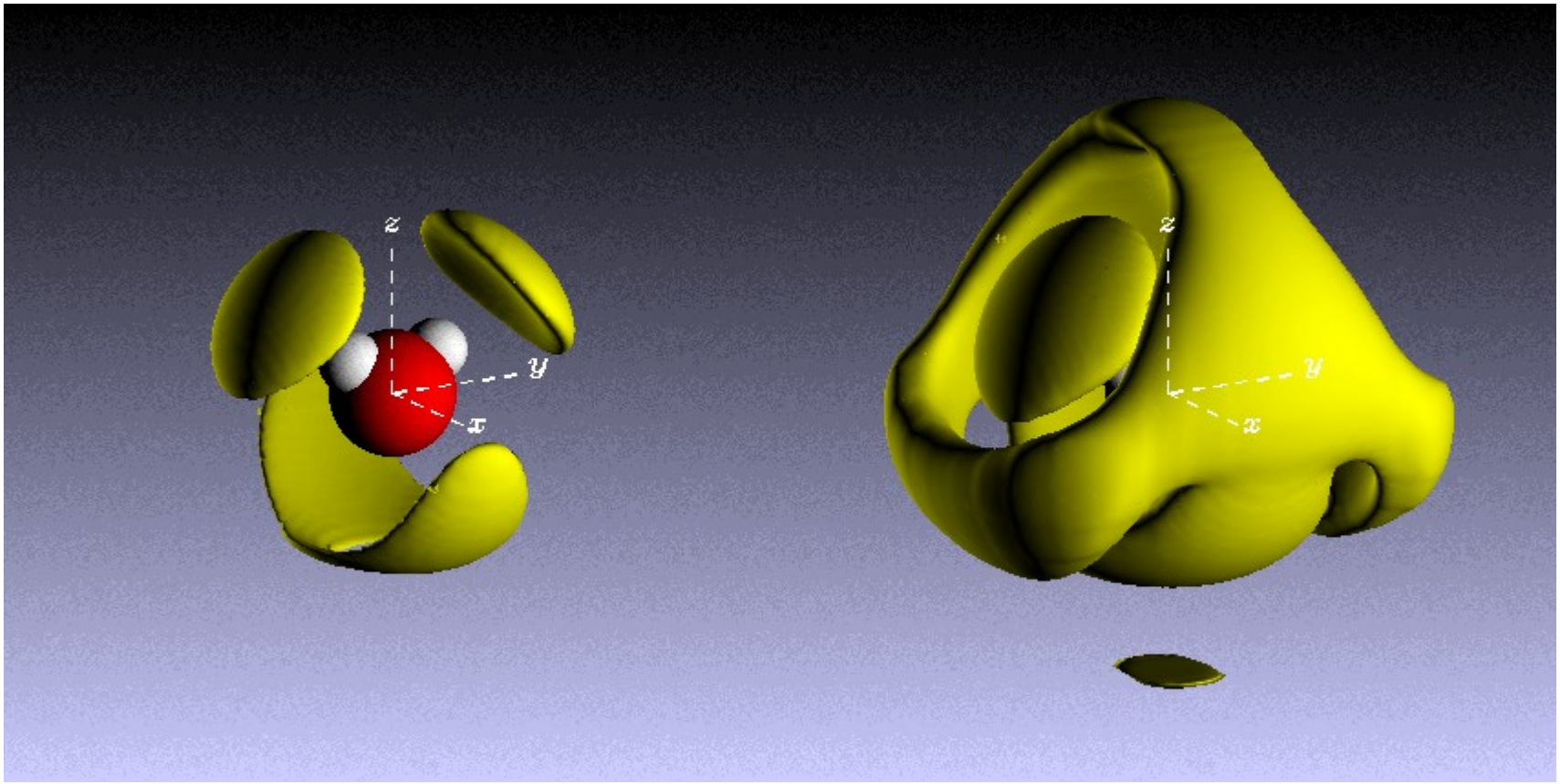
Water at 298K, 0kbar



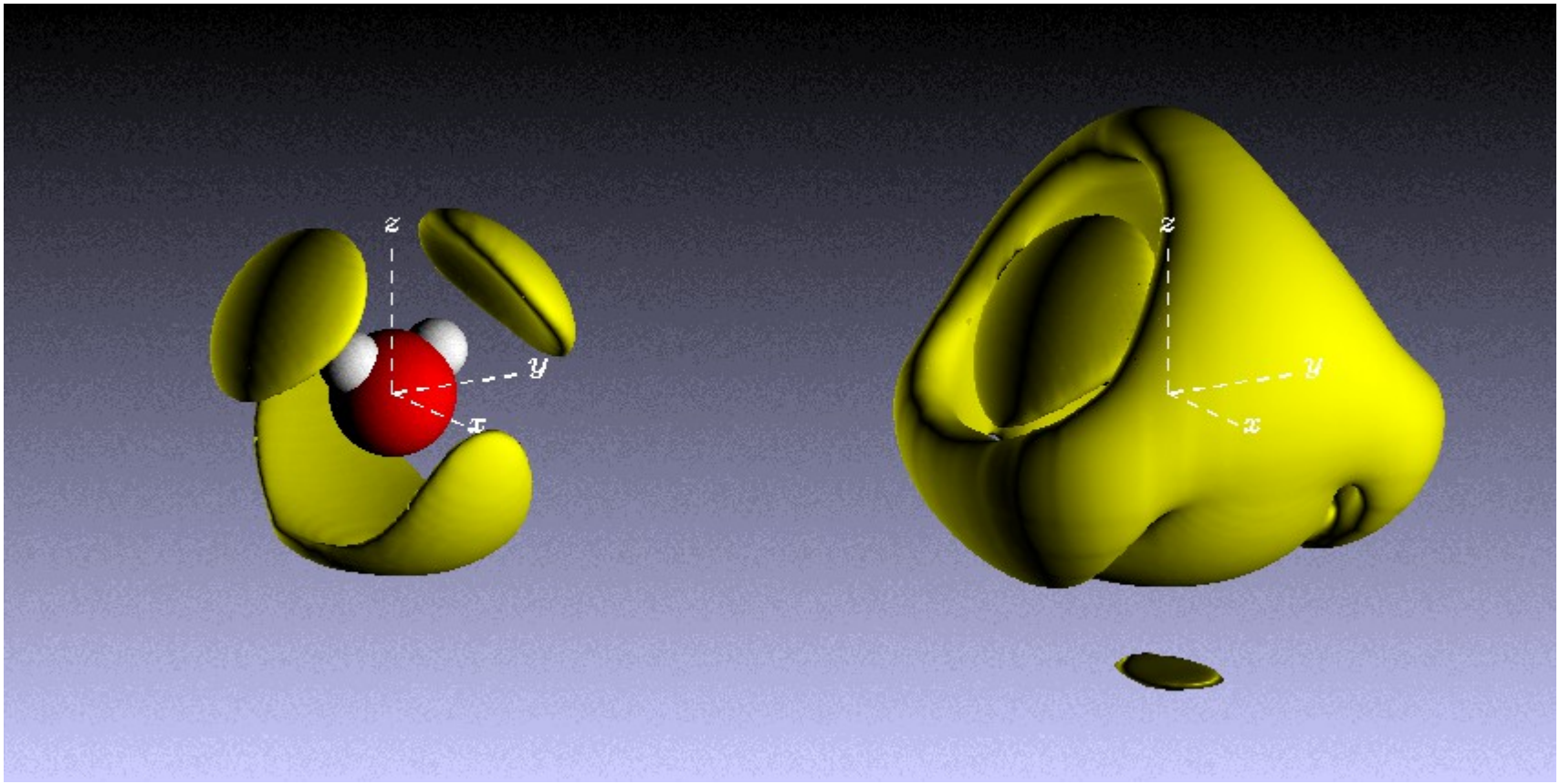
Water at 268K, 0.26kbar



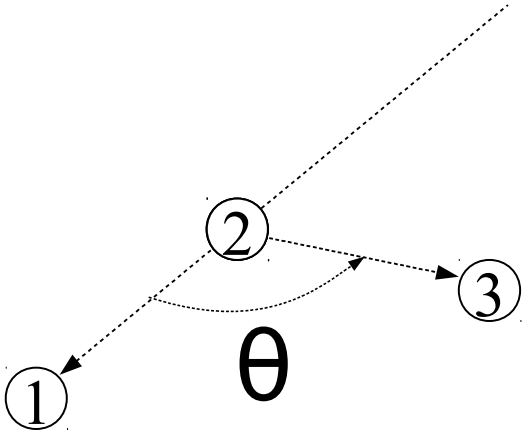
Water at 268K, 2.09kbar

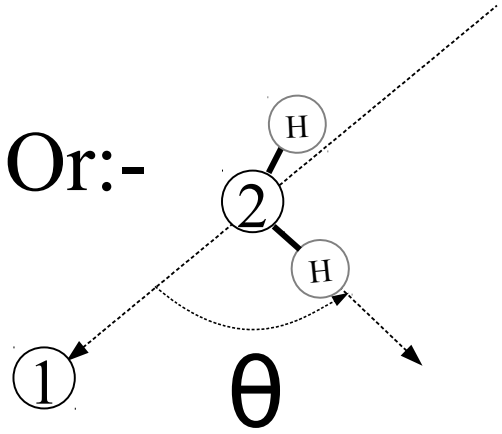


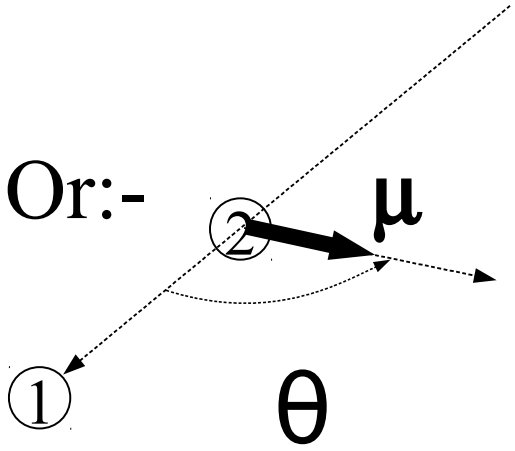
Water at 268K, 4.00kbar



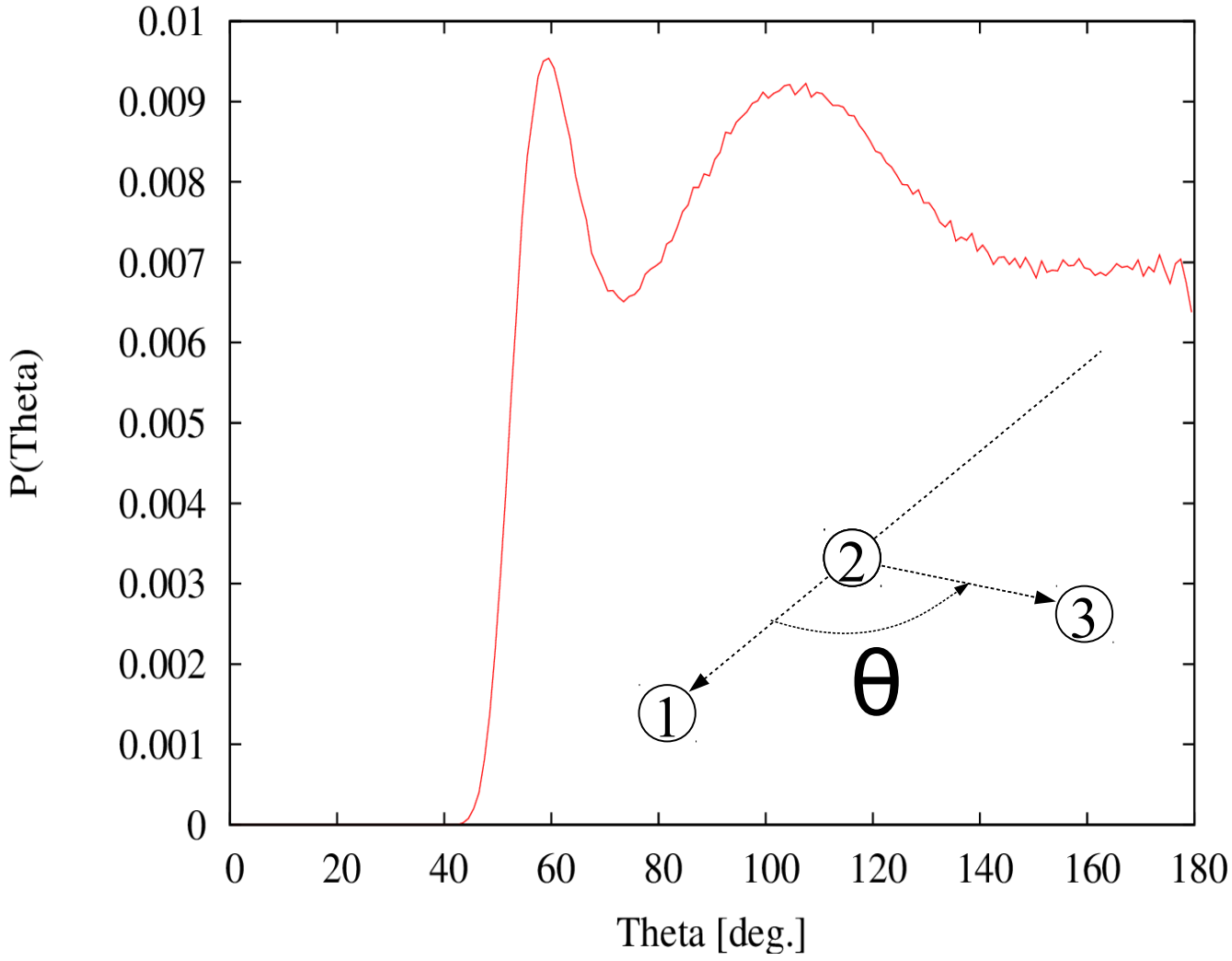
Bond angle distributions



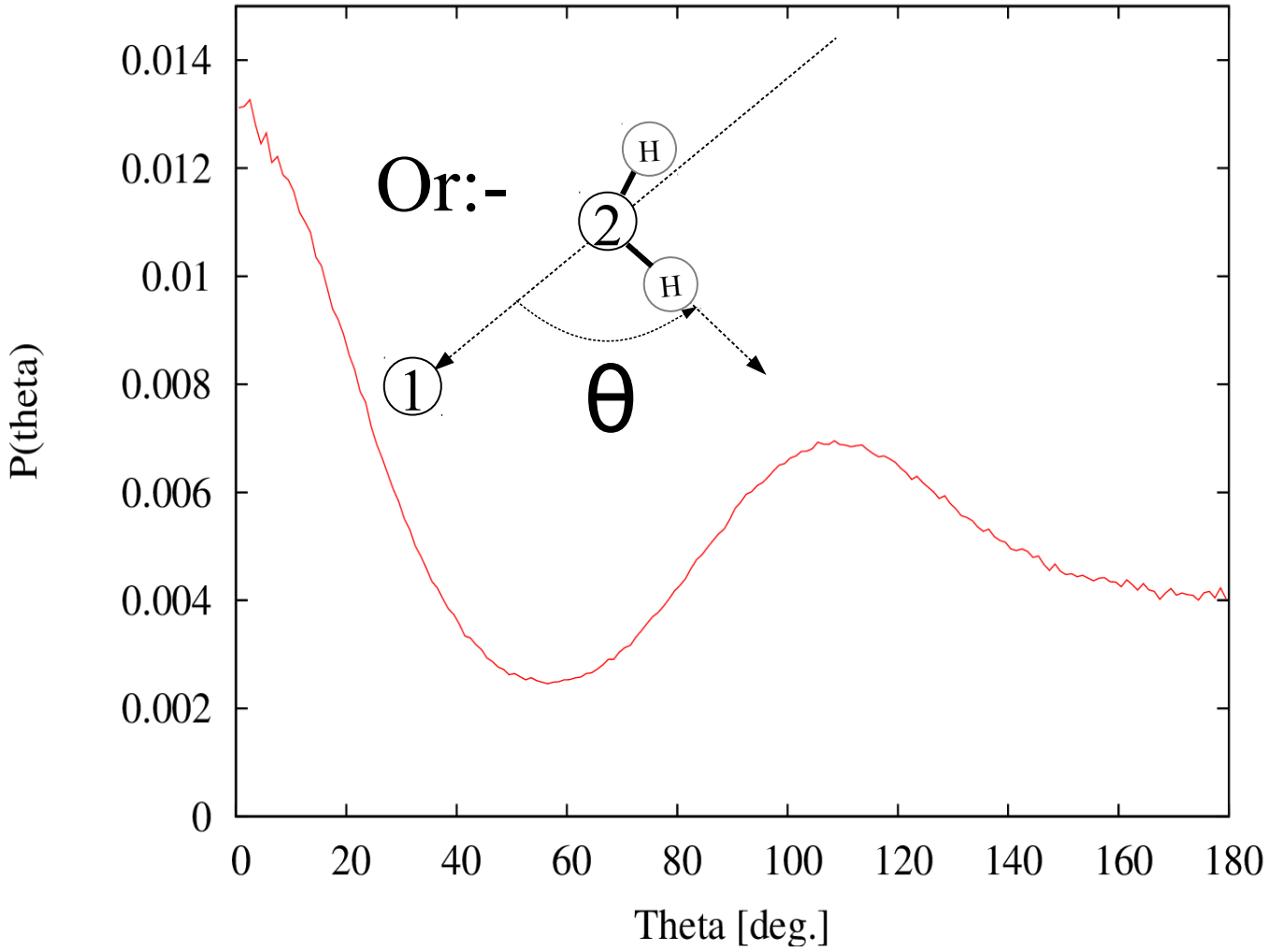




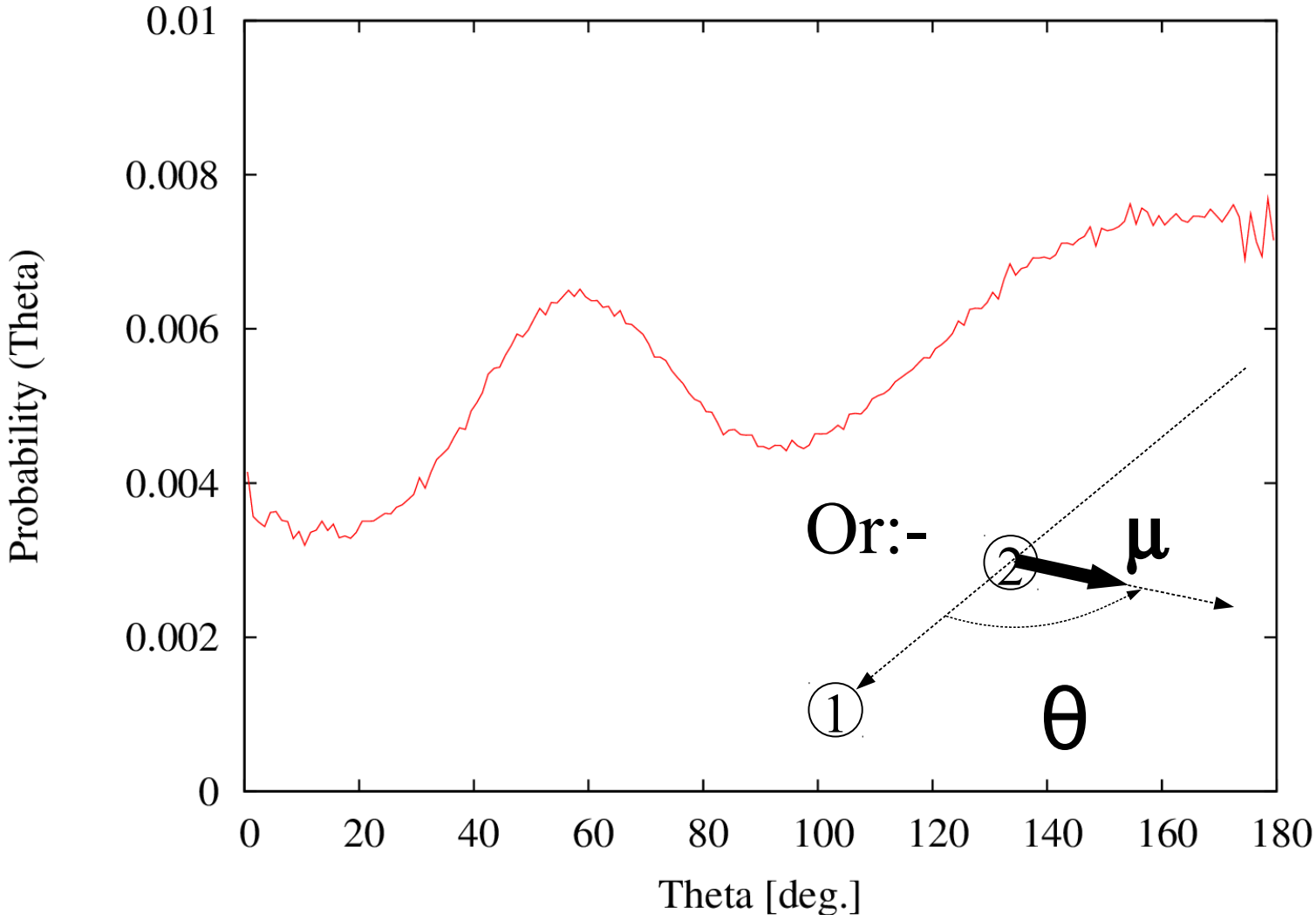
O-O-O angle distribution



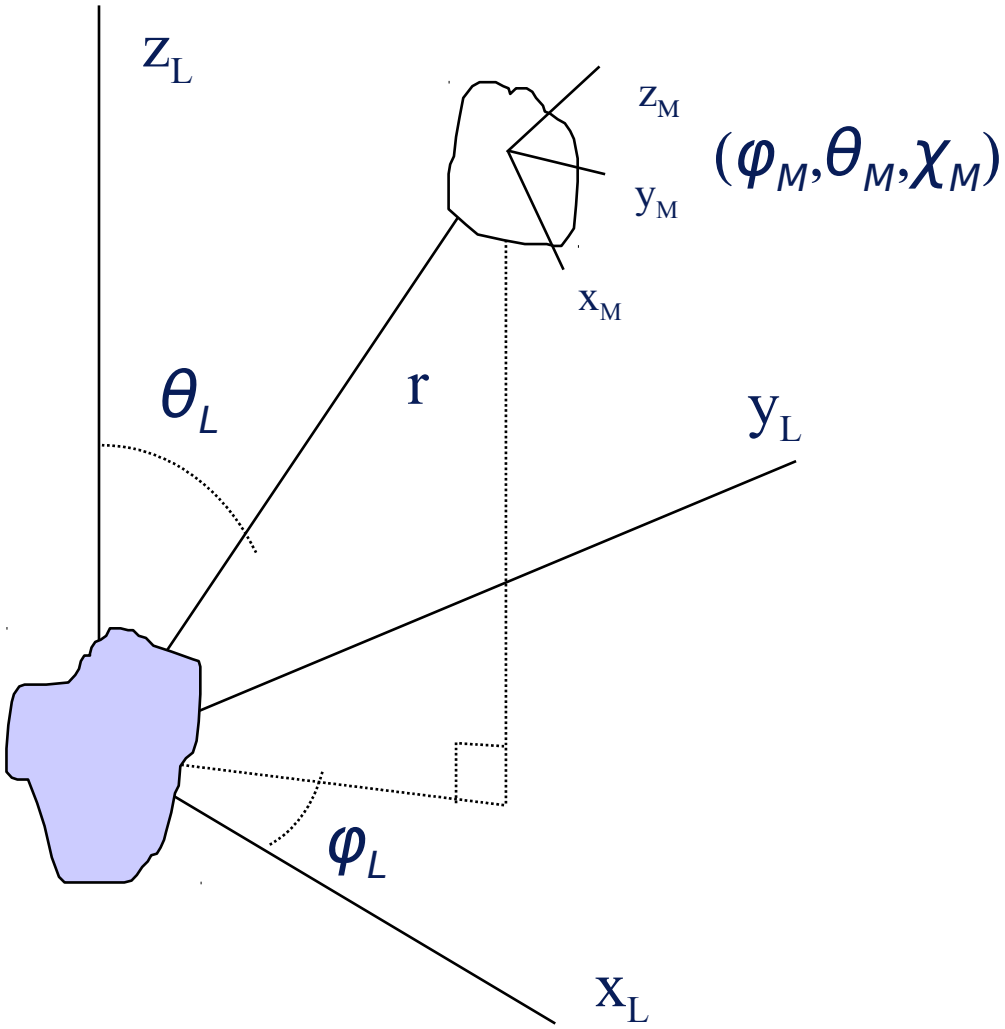
O-O-H angle distribution



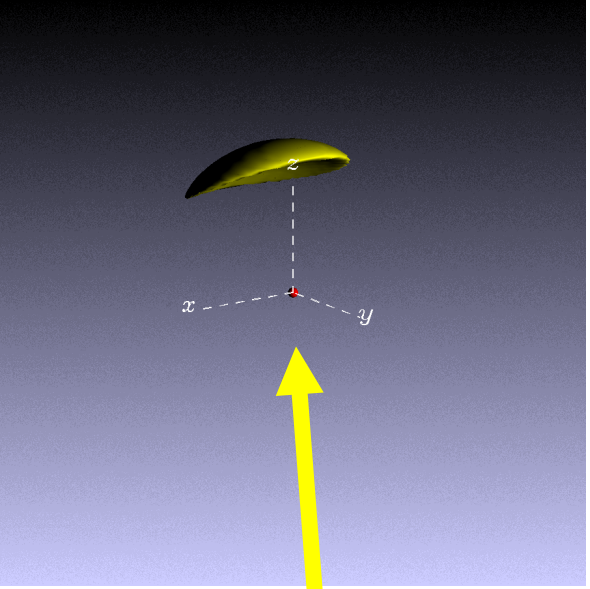
O-μ angle distribution

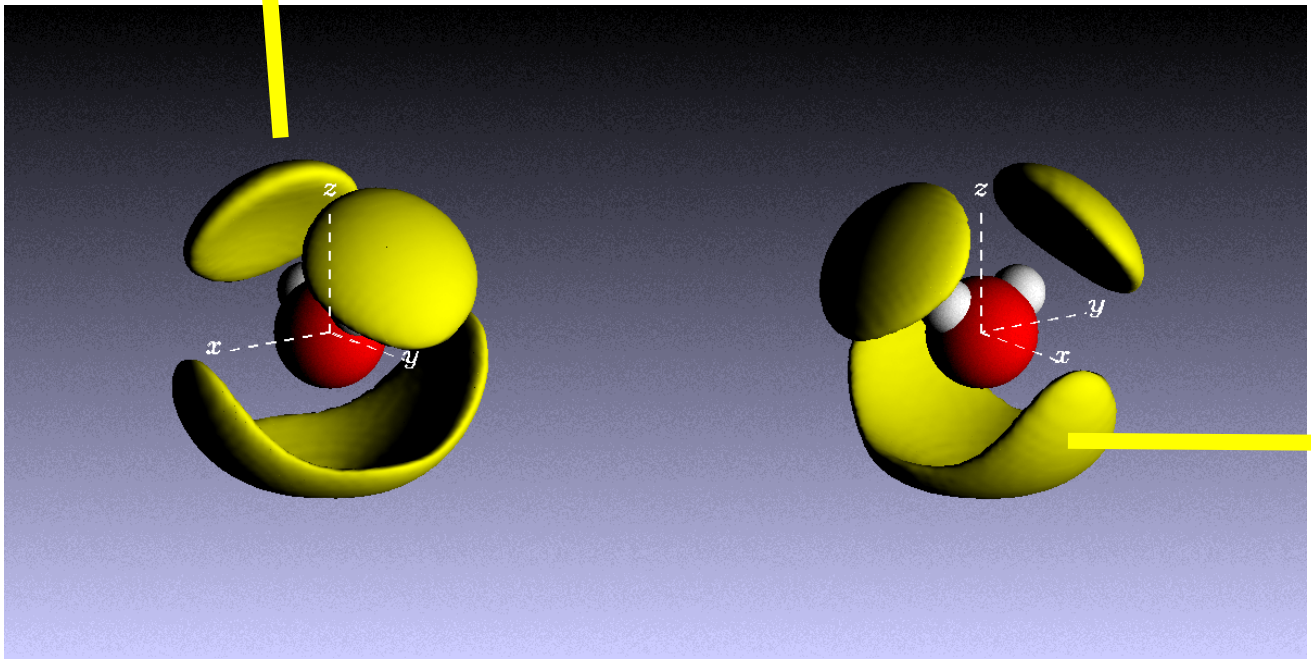


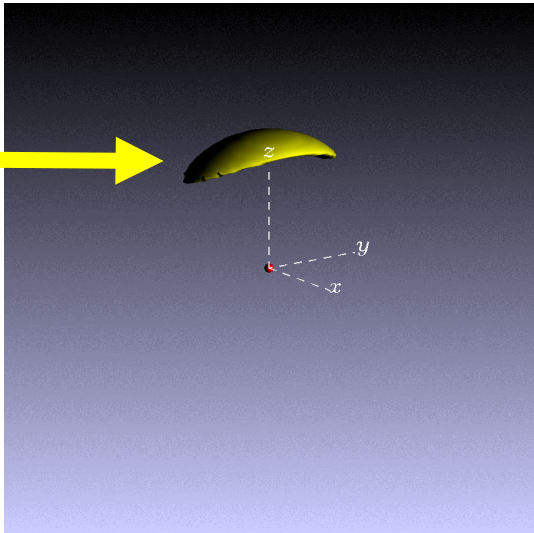
A step further: the orientational pair correlation function



Dipole orientations in water

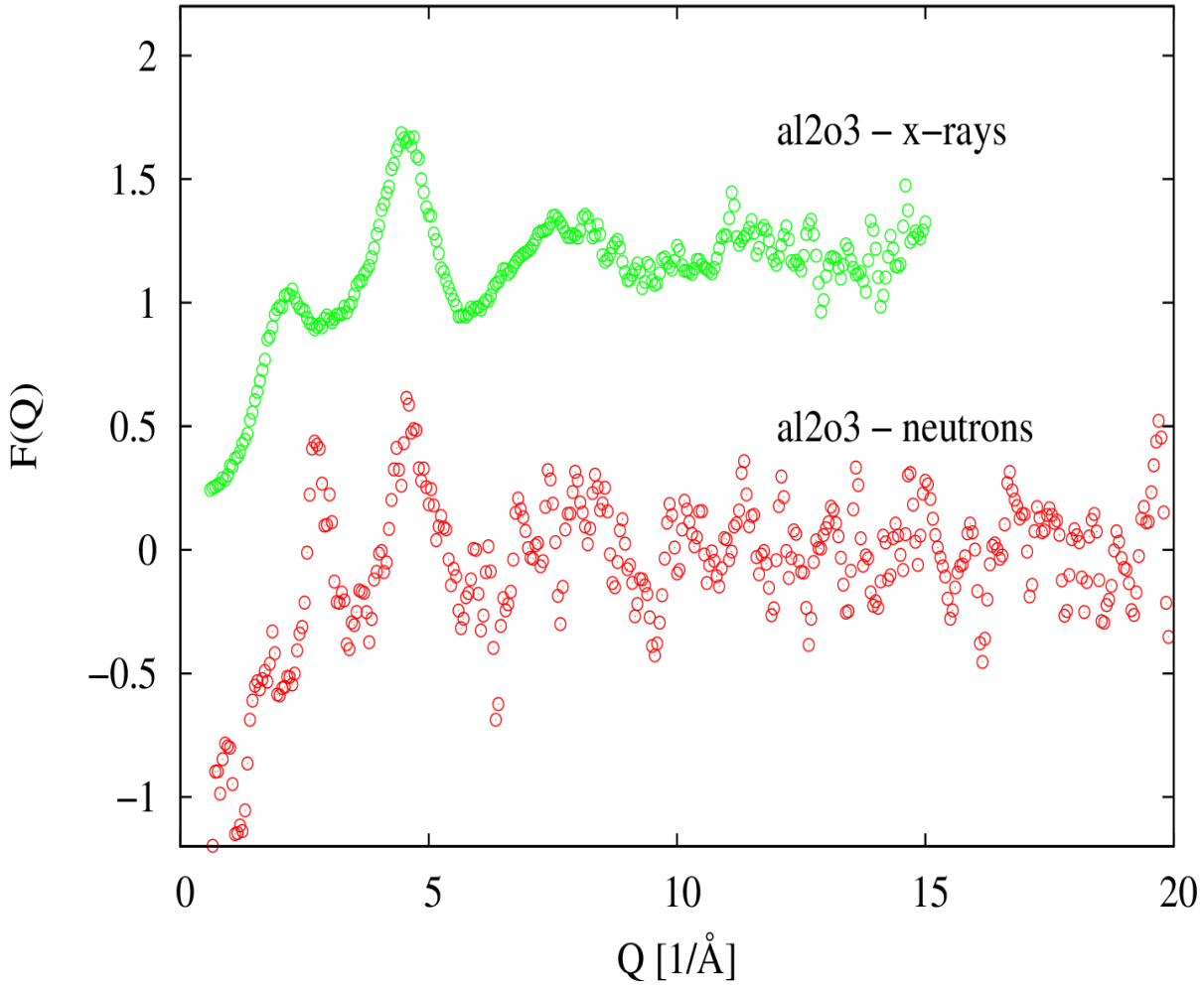






Another example:

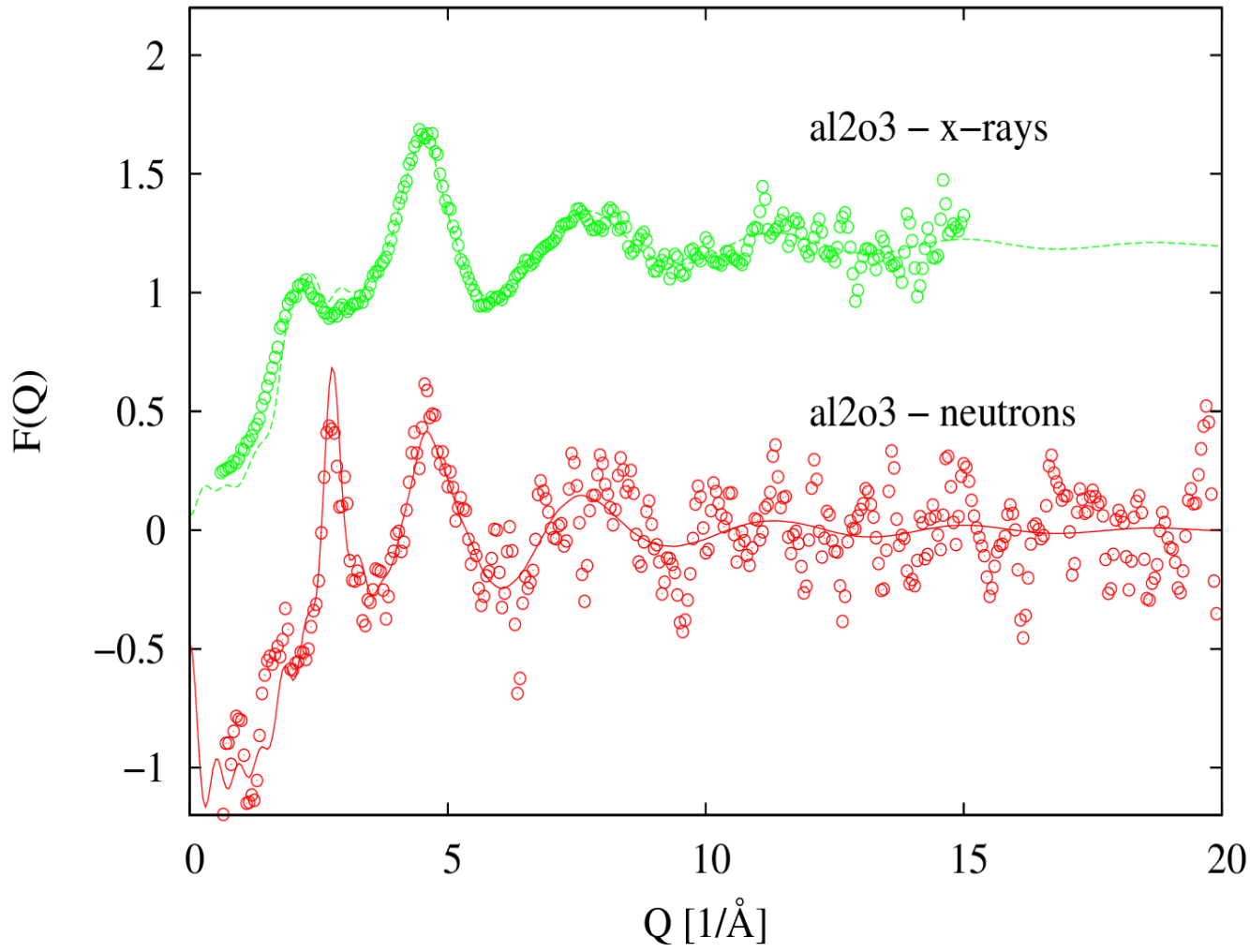
Molten Al_2O_3



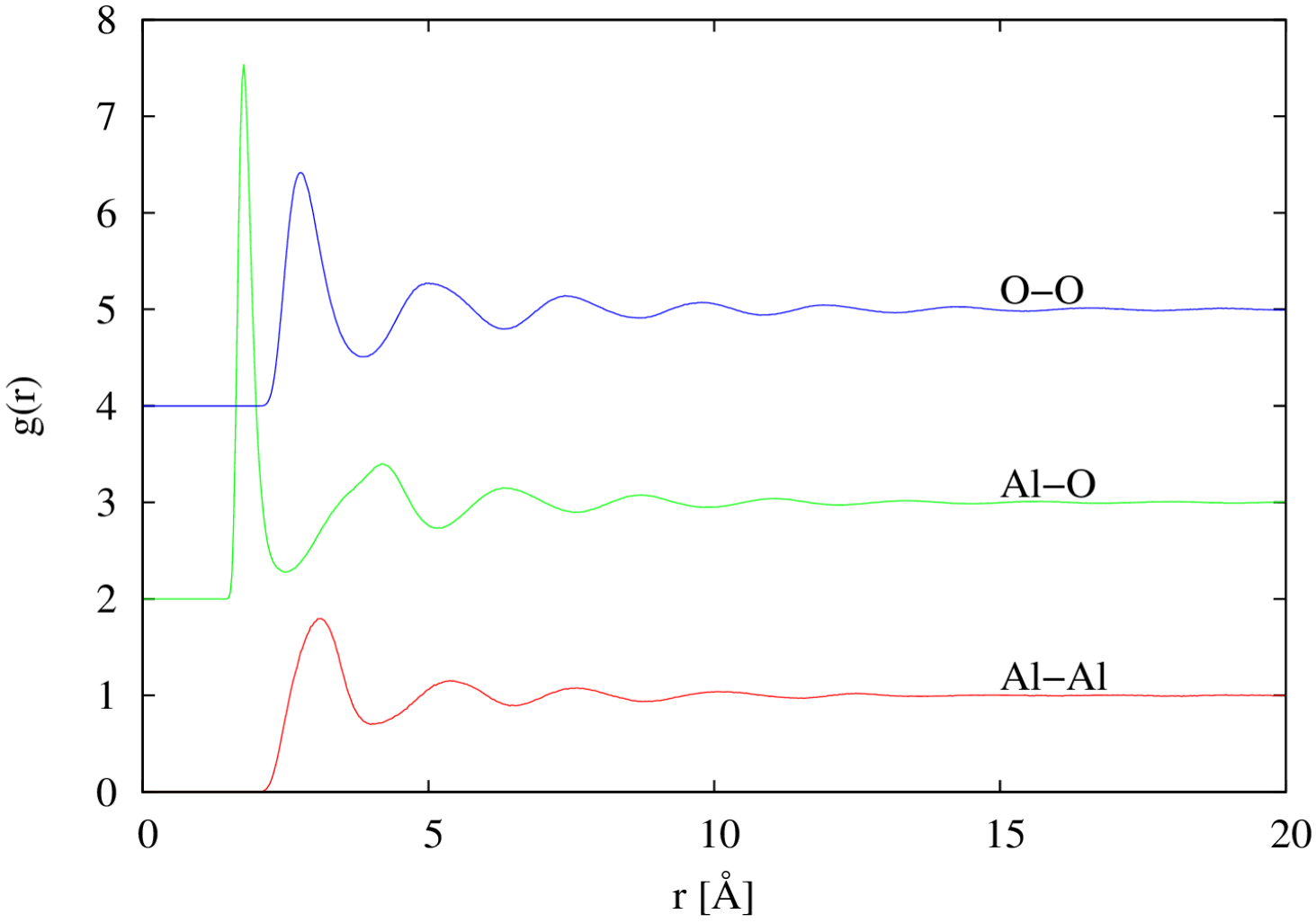
[*Courtesy of Neville Greaves (Aberystwth) and Claude Landron (Orleans)*]

Molten Al_2O_3

Final fit after Empirical Potential Structure Refinemen



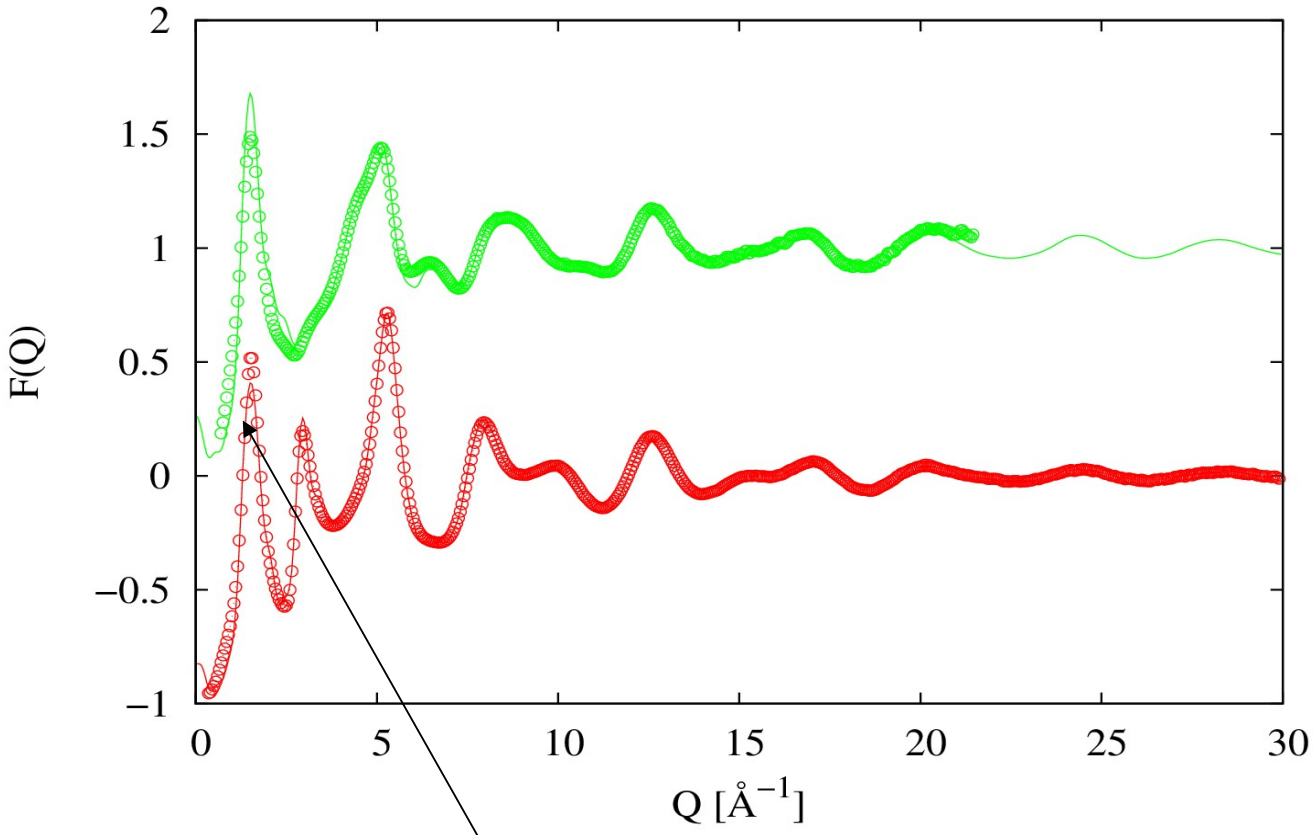
Partial g(r)'s for Al_2O_3



The problem of tetrahedrally coordinated glasses and liquids

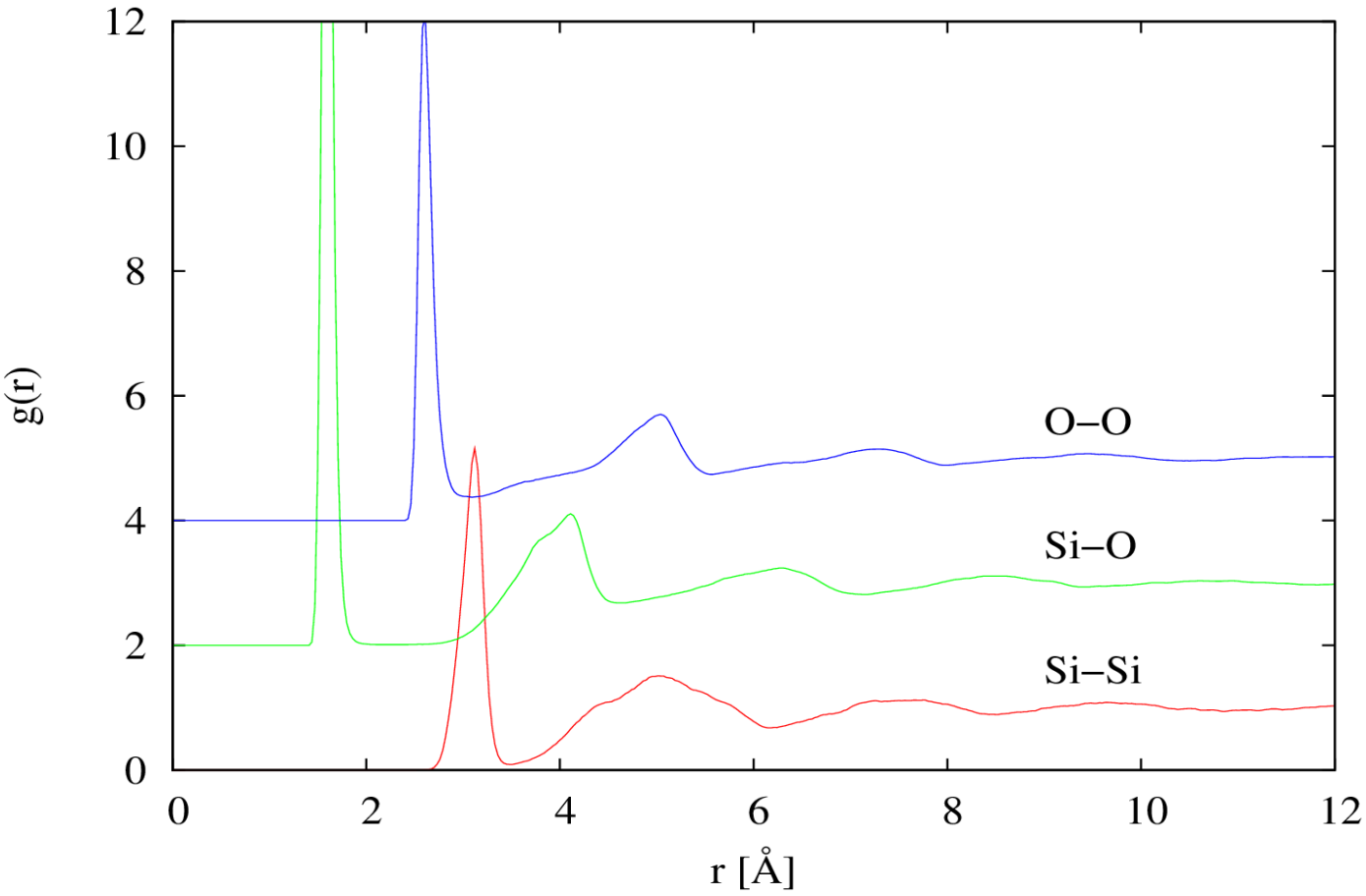
(water, a-MX_2, a-Si, a-Ge)

Amorphous SiO_2

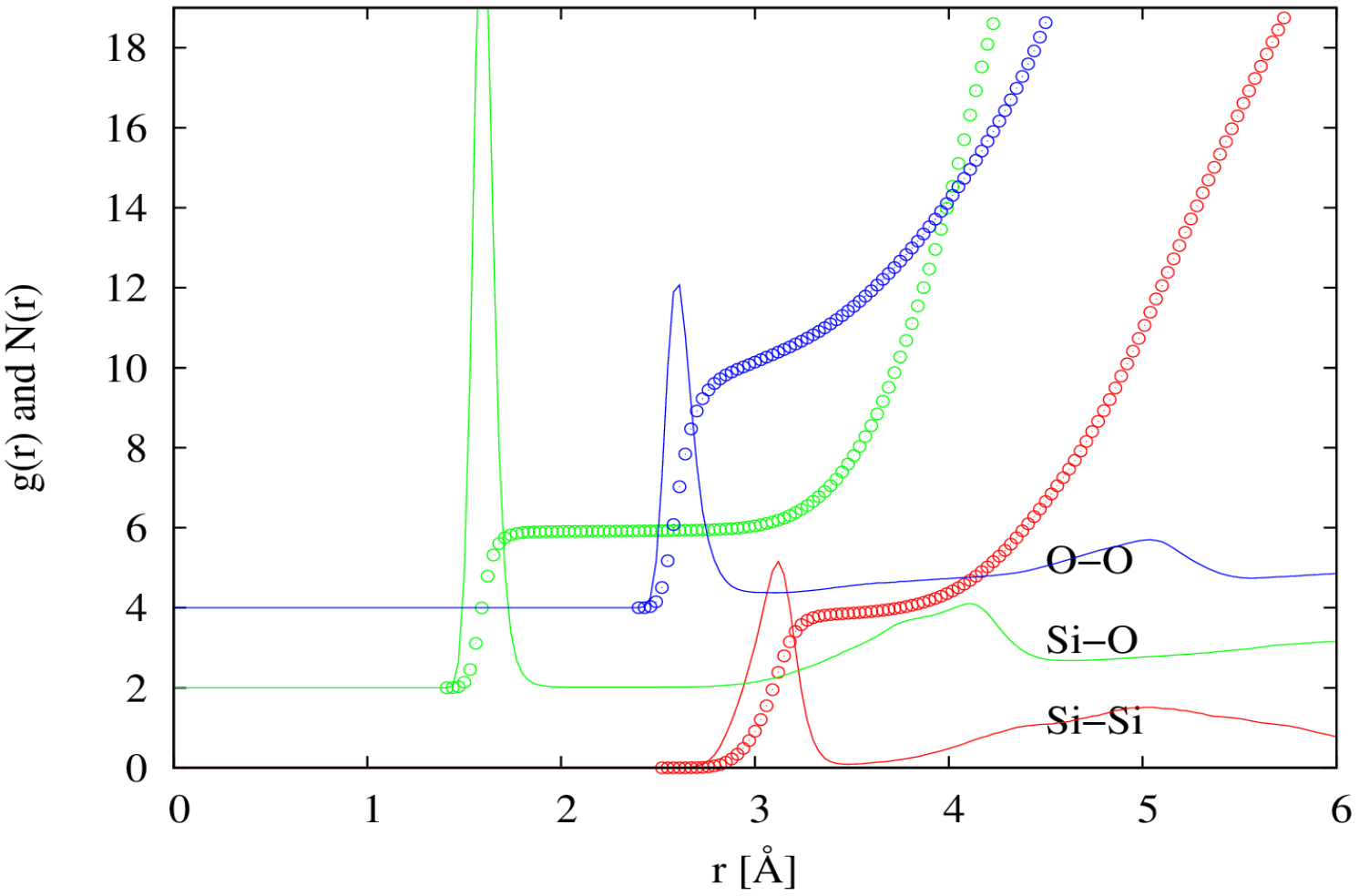


"First sharp diffraction peak" - FSDP

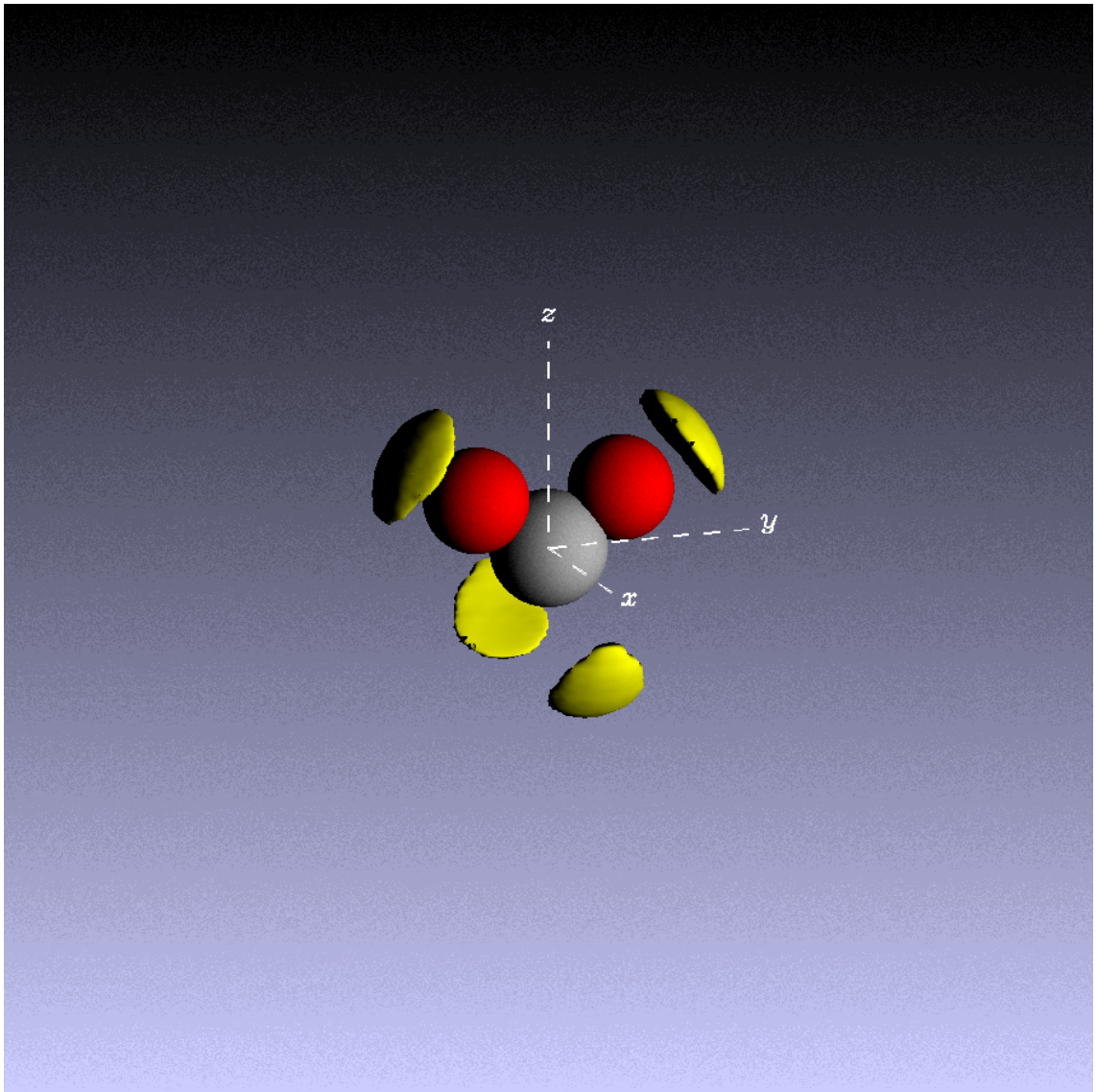
Radial distribution functions:



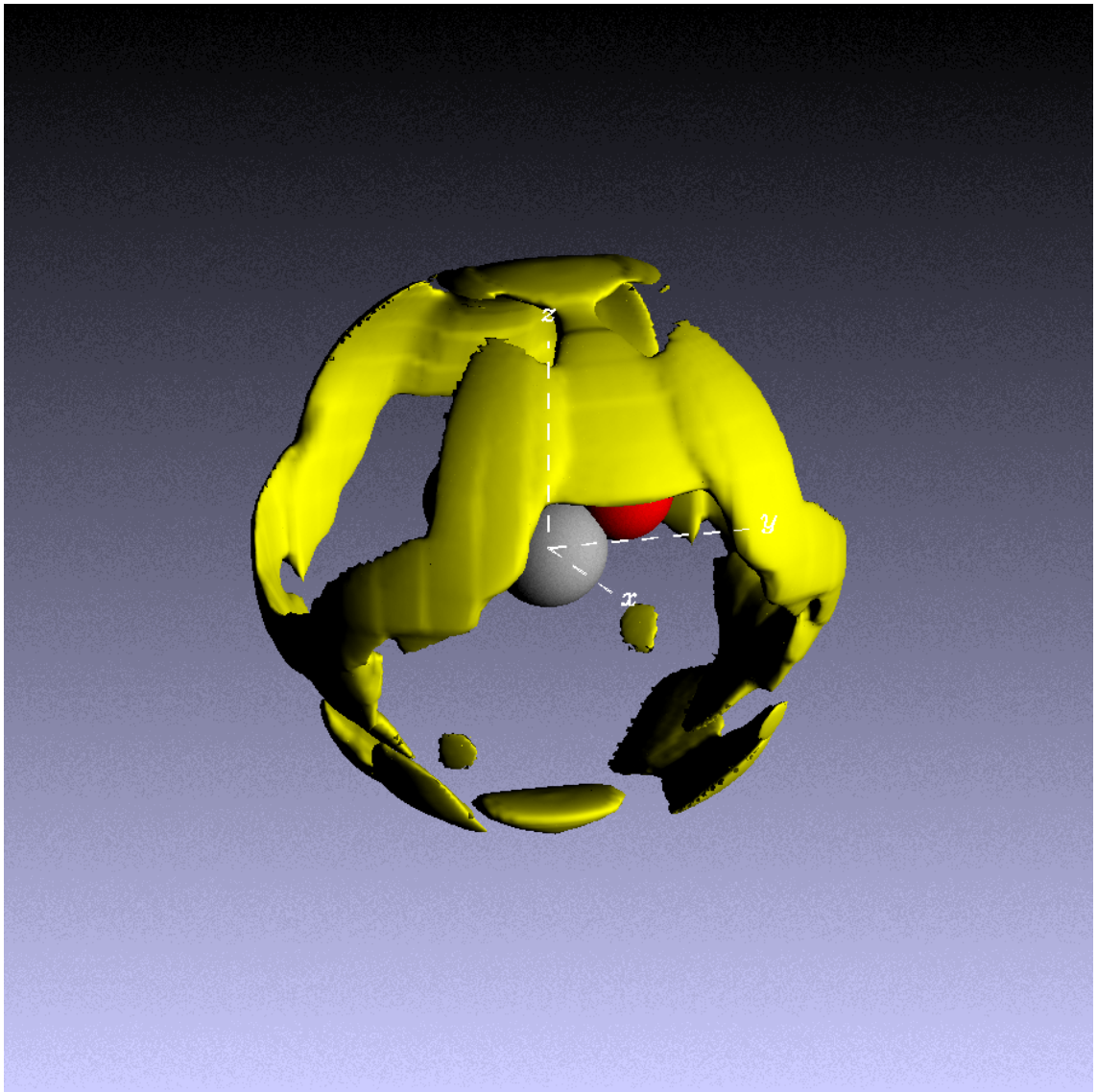
Coordination numbers:



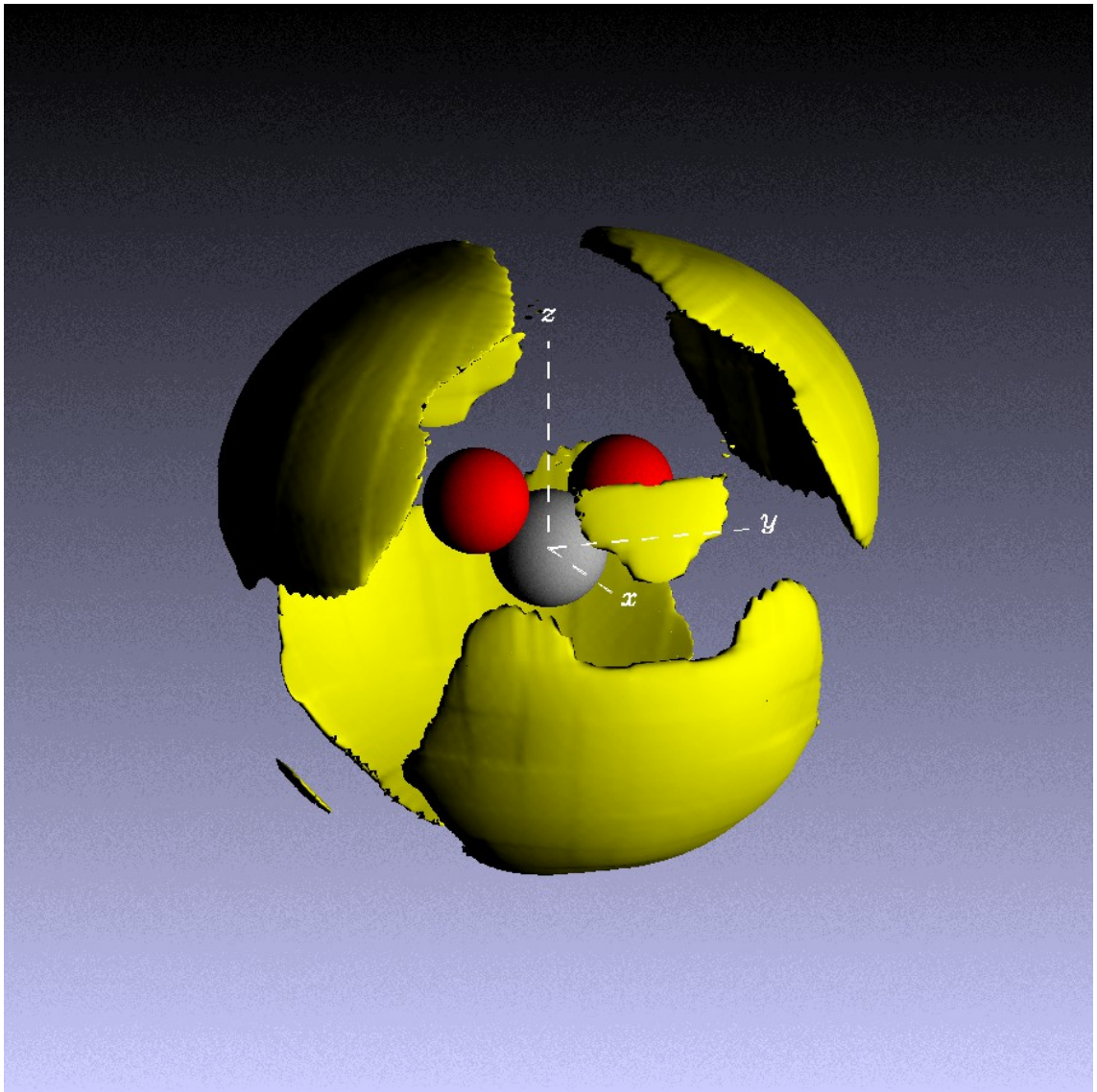
Spatial density function for a-SiO_2:



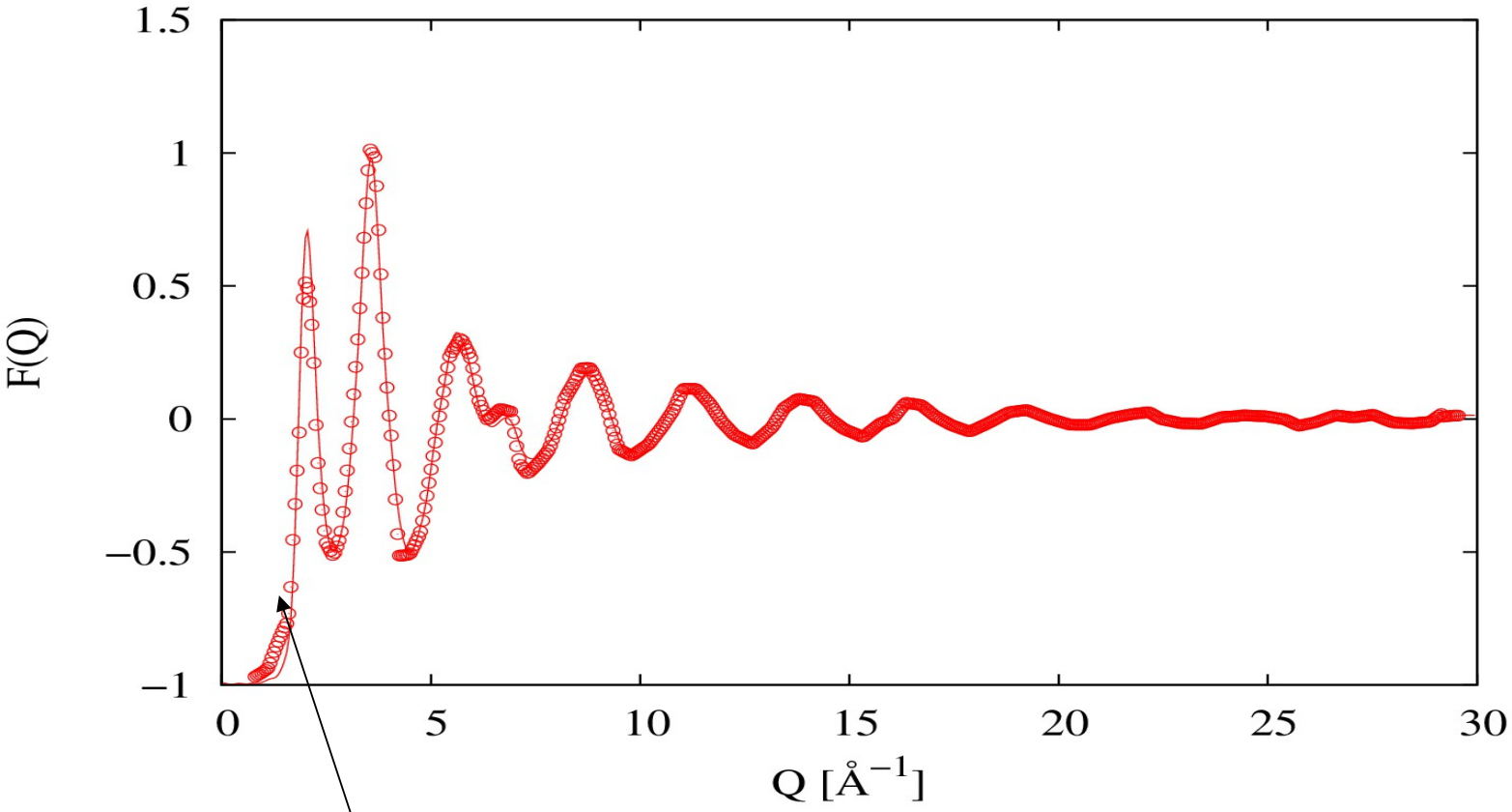
Spatial density function for a-SiO_2:



Spatial density function for a-SiO_2:

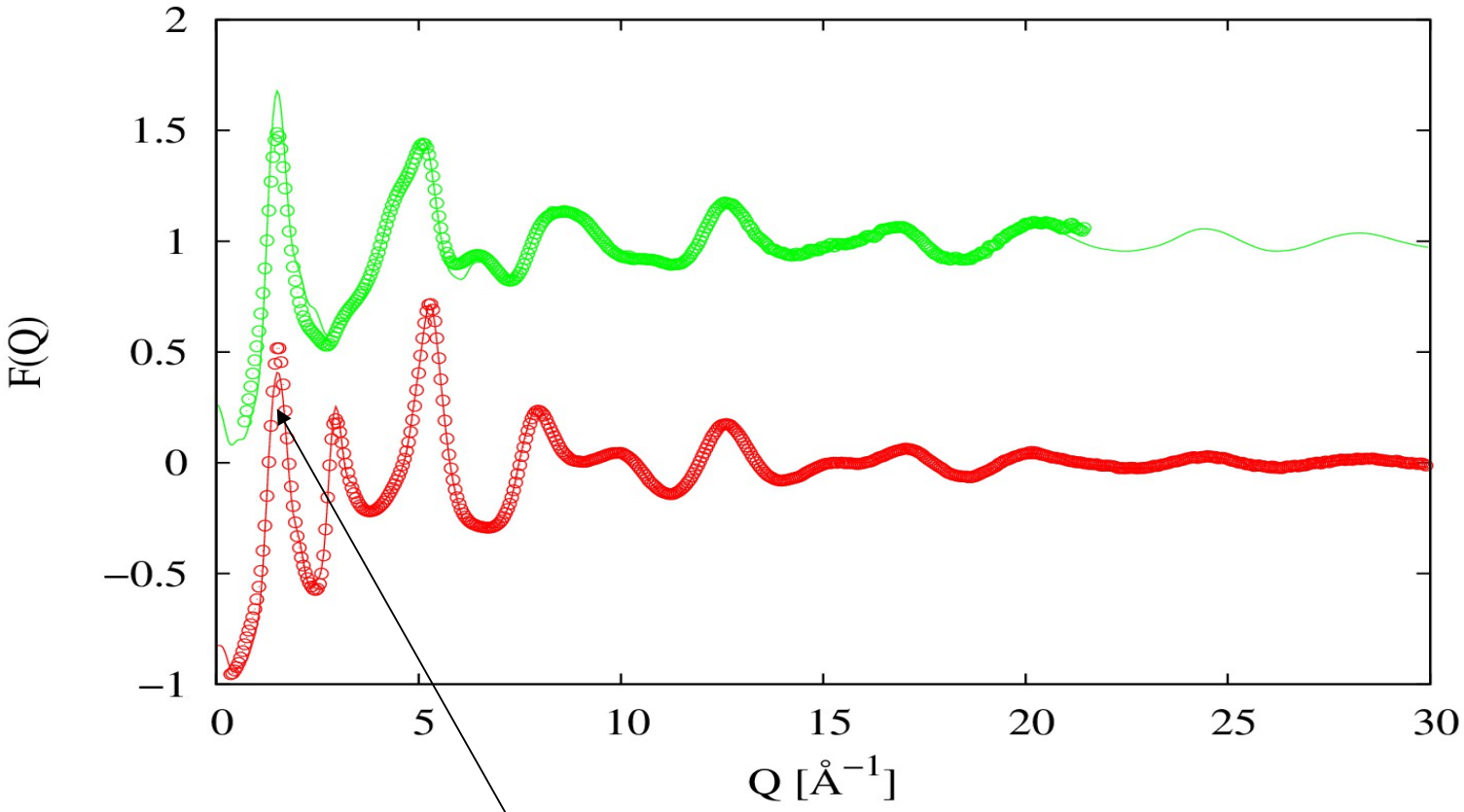


Compare with amorphous Si



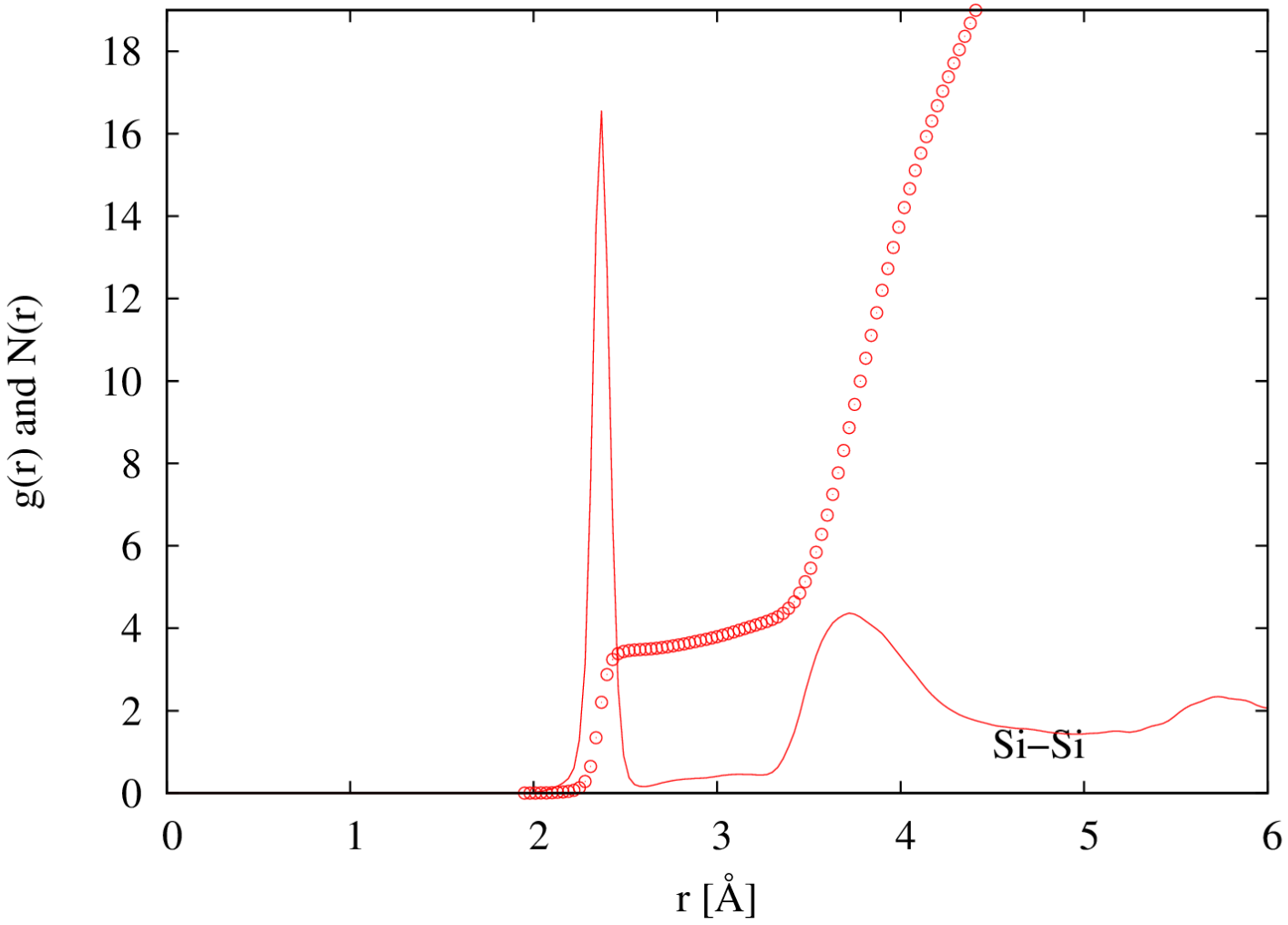
FSDP is absent!

Amorphous SiO_2

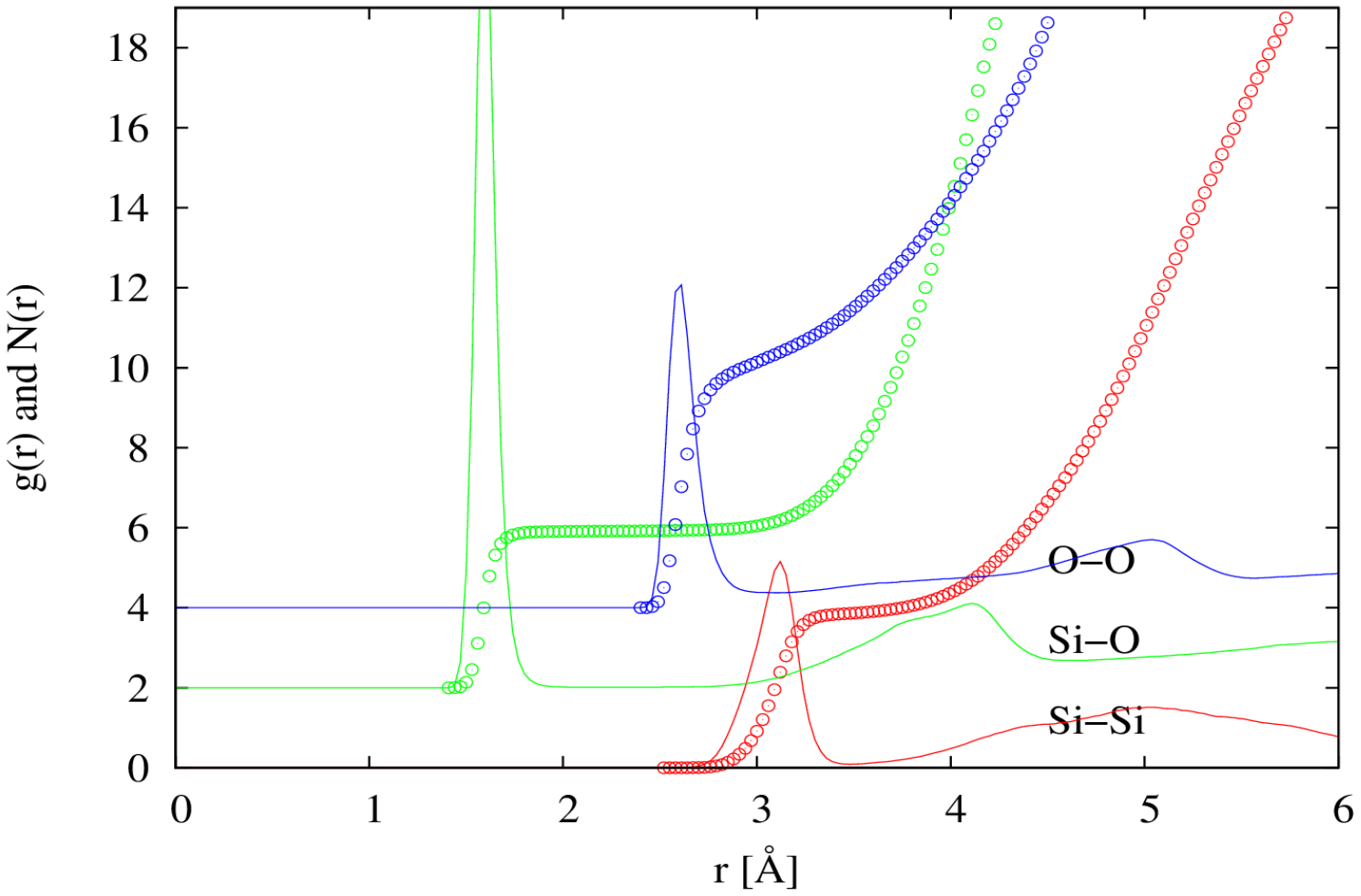


"First sharp diffraction peak" - FSDP

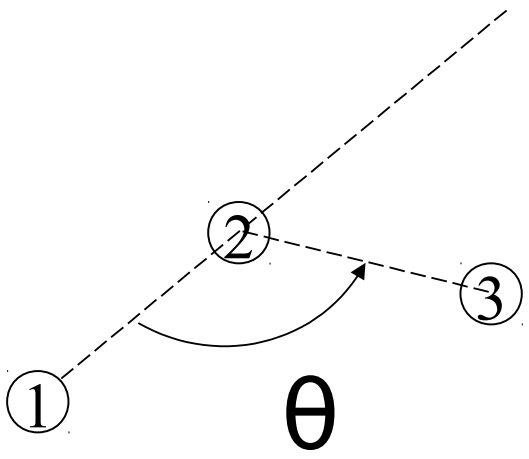
Coordination number- a-Si:

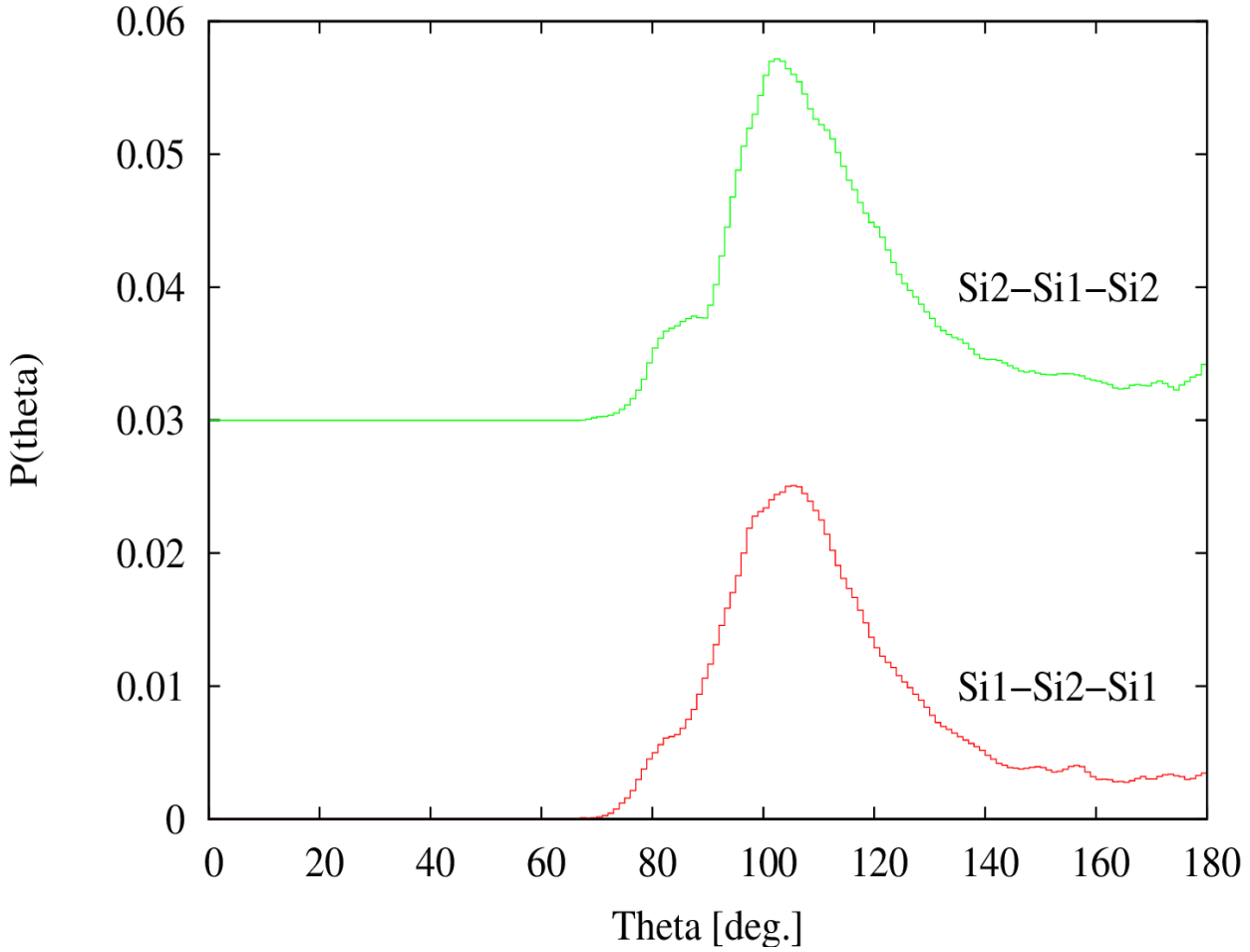


Coordination numbers – a-SiO_2:

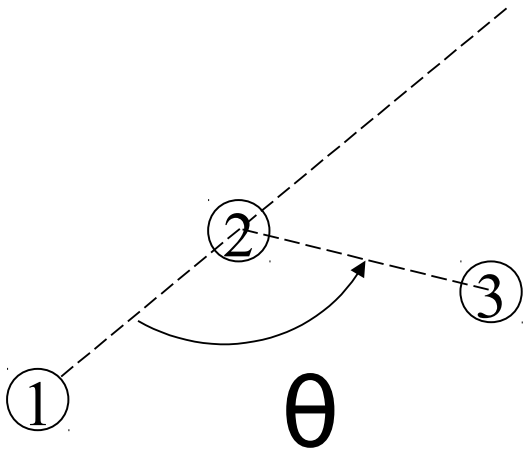


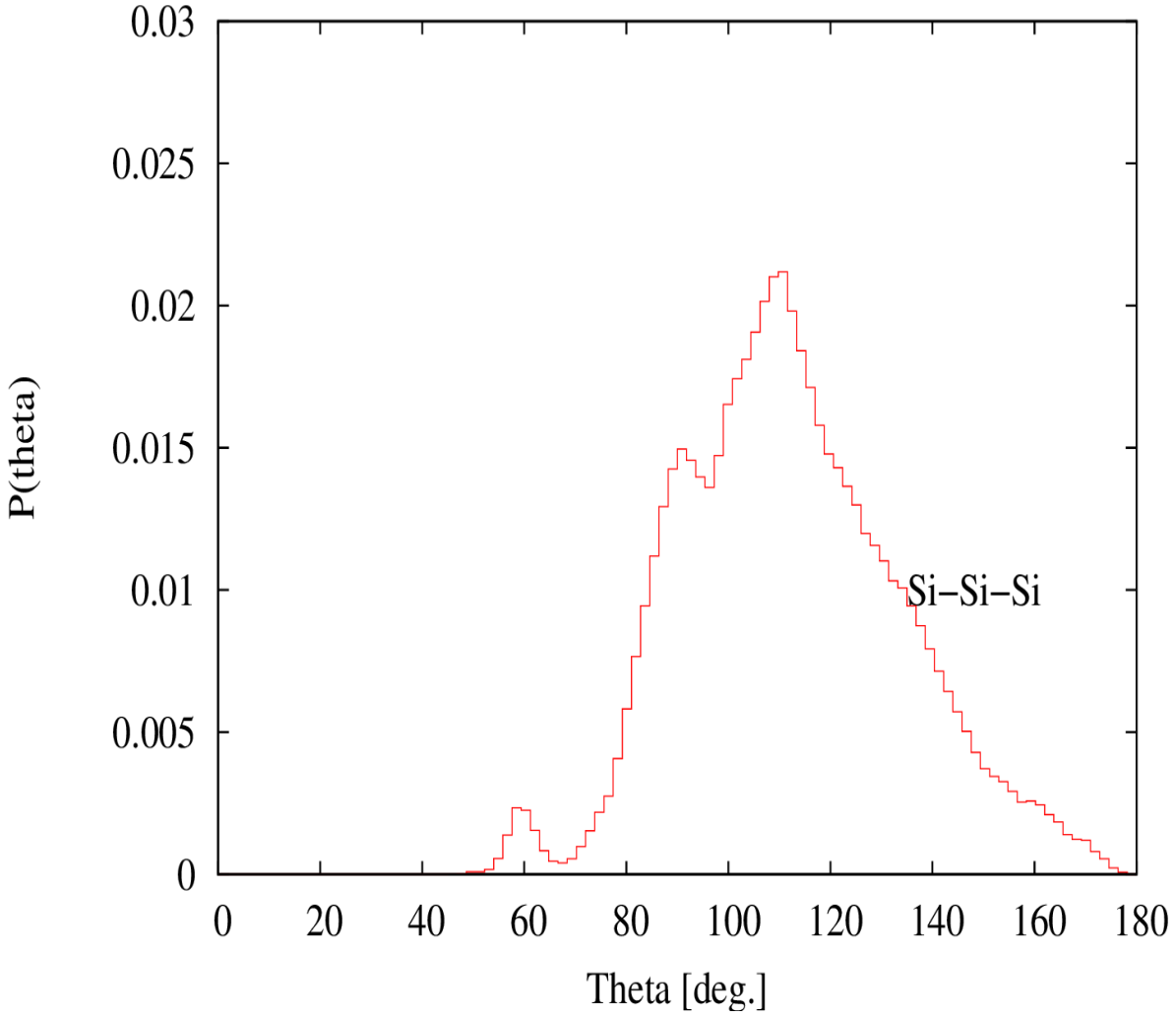
Triangle or "bond angle" distributions, a-Si:





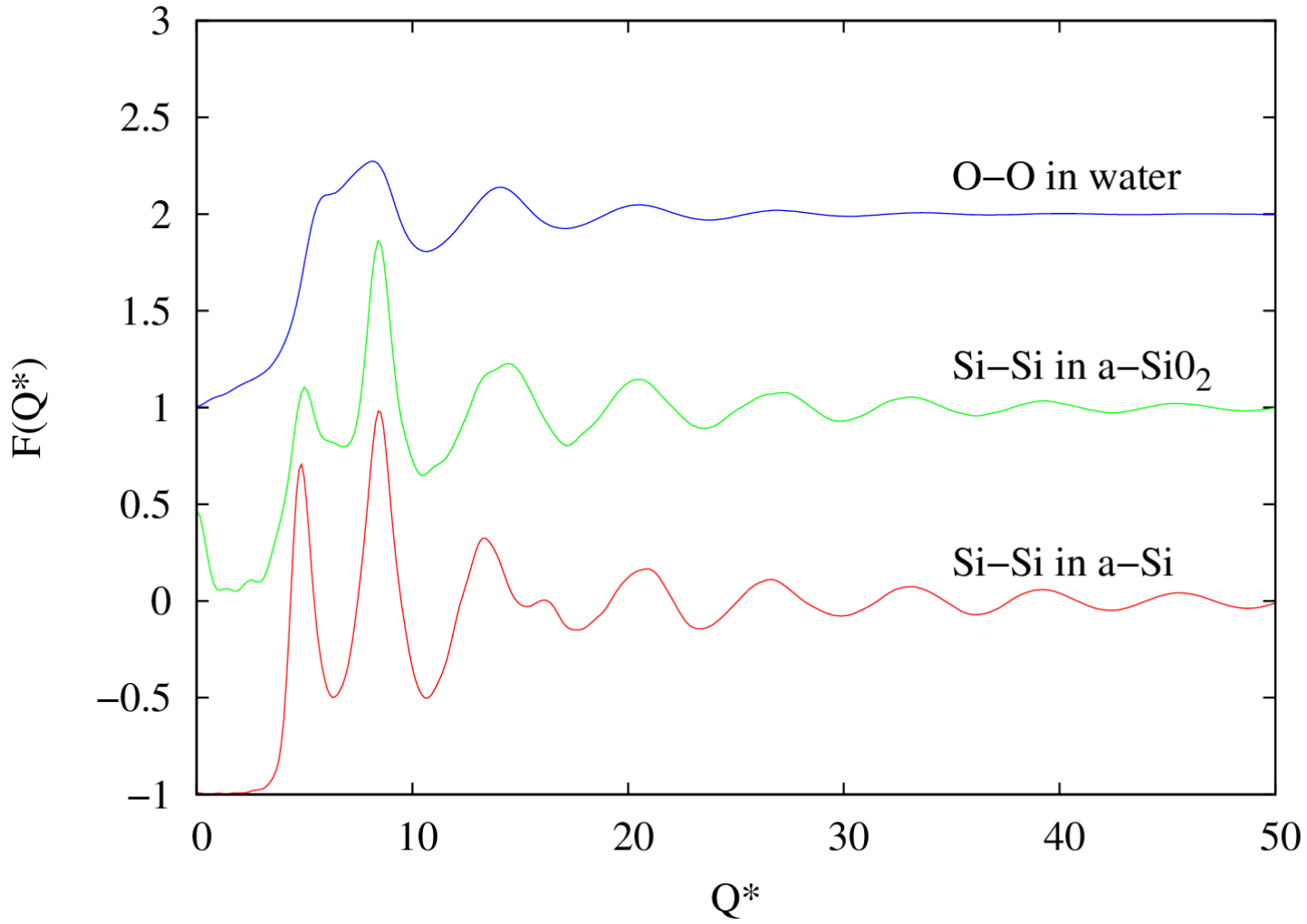
Triangle or "bond angle" distributions, a-SiO_2:



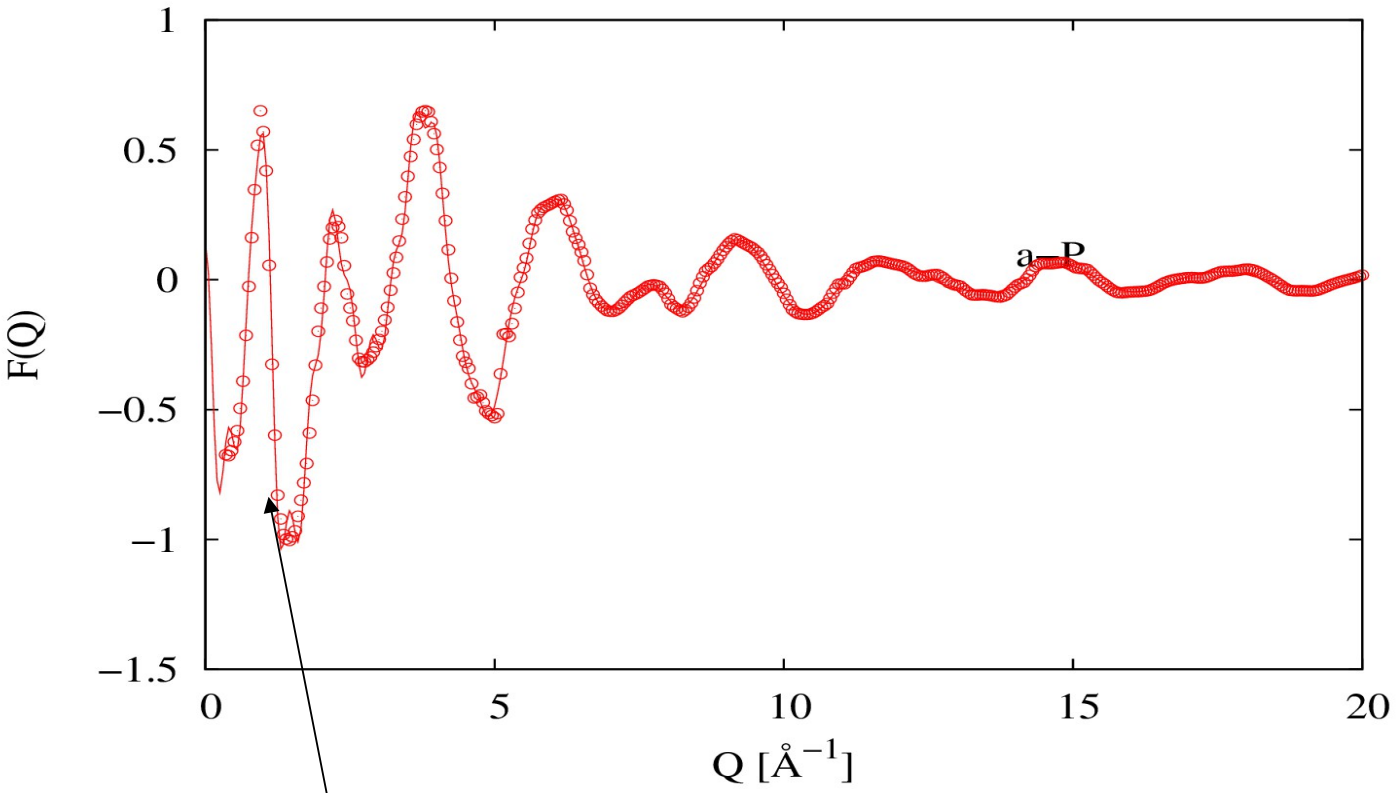


Compare structure factors…

(renormalise Q to near-neighbour distance)



A puzzle: a-(red)P



FSDP is present!

Summary (1)

- Disorder is intrinsic to our existence, and occurs over a very wide range of length scales.
- We quantify disorder at the atomic level via the pair correlation function. For molecules this is the *orientational* PCF, which contains more information than the radial distribution functions, $g(r)$.
- Structure factors measured in diffraction experiments derive from the site-site radial distribution functions.

Summary (2)

- Computer simulation is used to generate a model of the scattering system.
- Diffraction data are introduced either
  - via χ^2 (RMC),

or

  - via an empirical potential, (EPSR).
- Simulated ensembles are used to calculate a number of distribution functions not accessible directly from the experiment.

Summary (3)

- Tetrahedrally bonded glasses and liquids show structural similarities.
- Relevance/role of the “FSDP” is unclear.
- We can only really study these properties by forming structural models consistent with the data.

Thank you for your attention!