

# **Structure of Disordered Materials:**

*Finding and refining a structural  
model*

*Alan Soper*

*Disordered Materials Group*

*ISIS*

# *Summary of this lecture*

- Computer simulation as a tool to model disordered materials
- Molecular systems:
  - Spatial Density Function, bond angle distributions, Orientational Pair Correlation Function
- 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...

# *Total Scattering at ISIS*

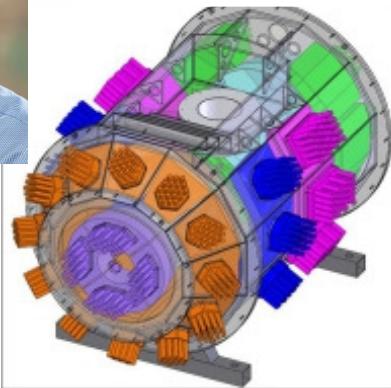
Daniel Bowron,  
Group Leader  
Disordered  
Materials

## GEM

Alex Hannon  
Dave Keen



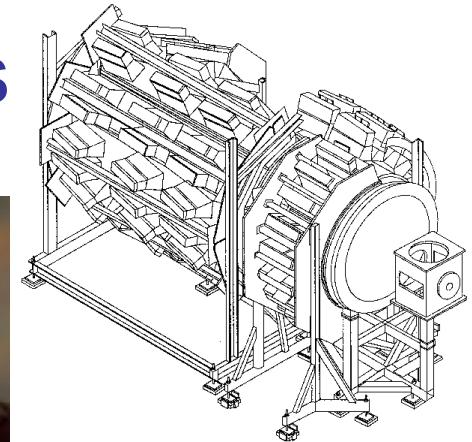
## POLARIS



(Sabrina Goertner)  
Silvia Imberti



## SANDALS



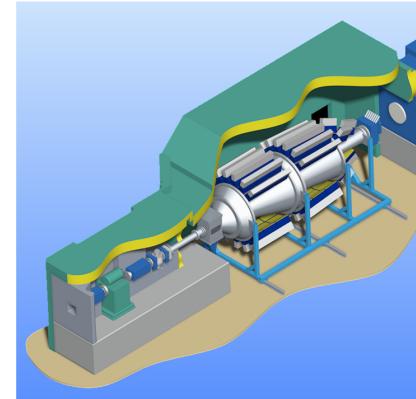
## XRD



Helen  
Playford

## NIMROD

Tristan Youngs  
Tom Headen



# *The liquid structure factor:*

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

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

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

Atomic fraction of component “ $\alpha$ ”

The atom scattering factor or “form factor”

# *“Rietveld refinement” of liquid structure: use Monte Carlo computer simulation*

- 1.Using the specified 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,  $\Delta U$ .
- 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.

# *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*

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

- $M$  measured datasets,  $N$  partial structure factors: (Usually  $M < N$ )

- Assign a “feedback” factor  $f$  for the data:

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

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

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

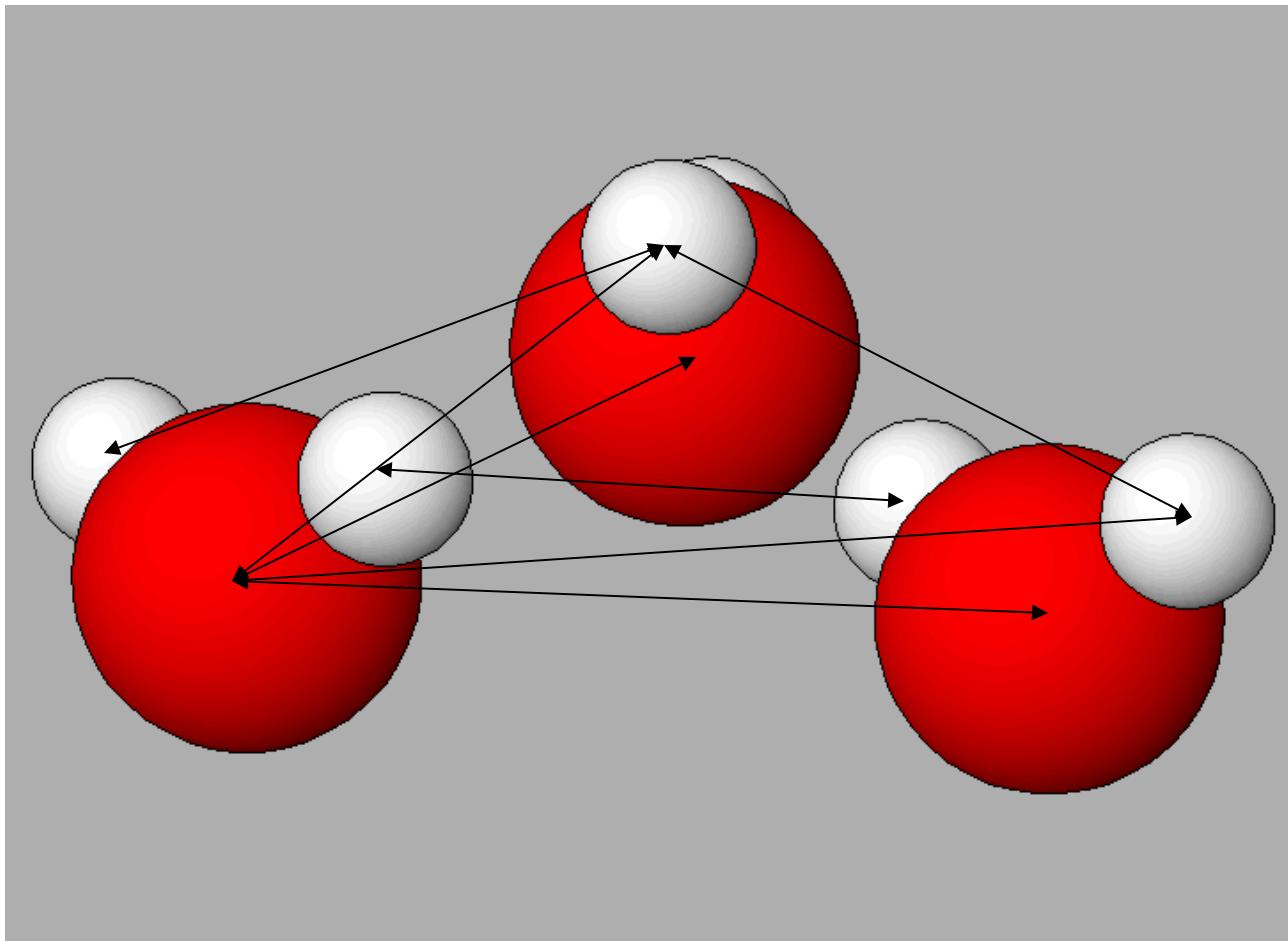
- Form inversion of  $w'_{ij}$ ,  $1 \leq i \leq M + N, 1 \leq j \leq N$

# Refining the potential: $M$ datasets, $N$ partial structure factors

$$F_{i(=1,M+N)}(Q) = \begin{array}{c|c} \text{Data} & \left[ \begin{array}{ccccccc} fw_{11} & fw_{12} & \cdots & & \cdots & fw_{IN} \\ fw_{21} & fw_{22} & \cdots & & \cdots & fw_{2N} \\ \cdots & \cdots & & & \cdots & \cdots \\ \cdots & \cdots & & & \cdots & \cdots \\ fw_{M1} & fw_{M2} & & & & & fw_{MN} \\ (1-f) & 0.0 & 0.0 & \cdots & \cdots & 0.0 \\ 0.0 & (1-f) & 0.0 & \cdots & \cdots & \cdots & \cdots \\ 0.0 & 0.0 & (1-f) & \cdots & & & \\ \cdots & \cdots & \cdots & \cdots & & & \\ & & & & \cdots & & \\ & & & & \cdots & & \\ & & & & \cdots & & \\ \cdots & & & & (1-f) & 0.0 & 0.0 \\ \cdots & & & & 0.0 & (1-f) & 0.0 \\ 0.0 & & \cdots & & 0.0 & 0.0 & (1-f) \end{array} \right] \\ \hline \text{Simulation} & \times \end{array} S_1 \\ S_2 \\ \cdots \\ S_N$$

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

*What do we measure if there are molecules present?*



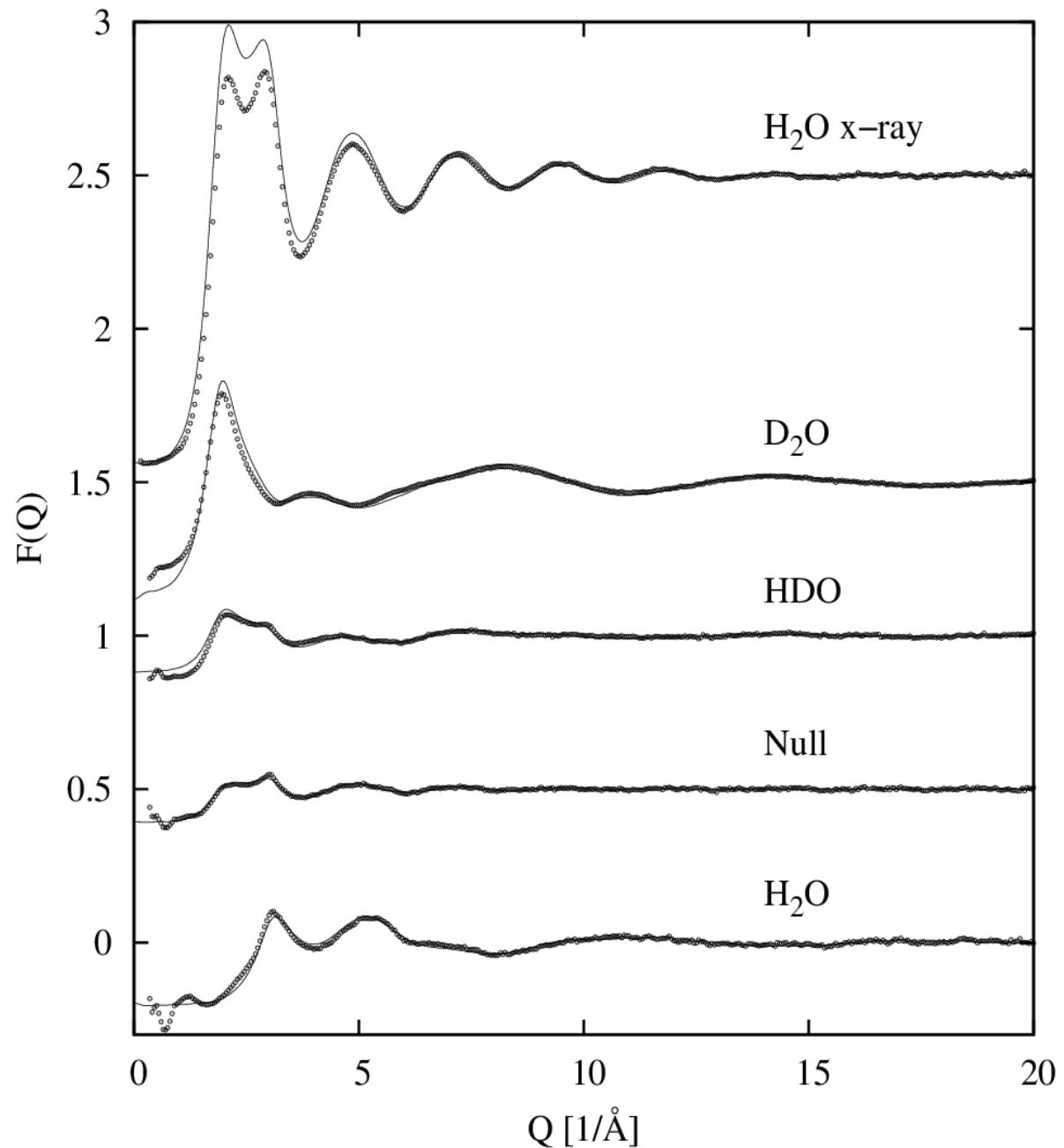
*However, two issues need to be addressed:-*

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

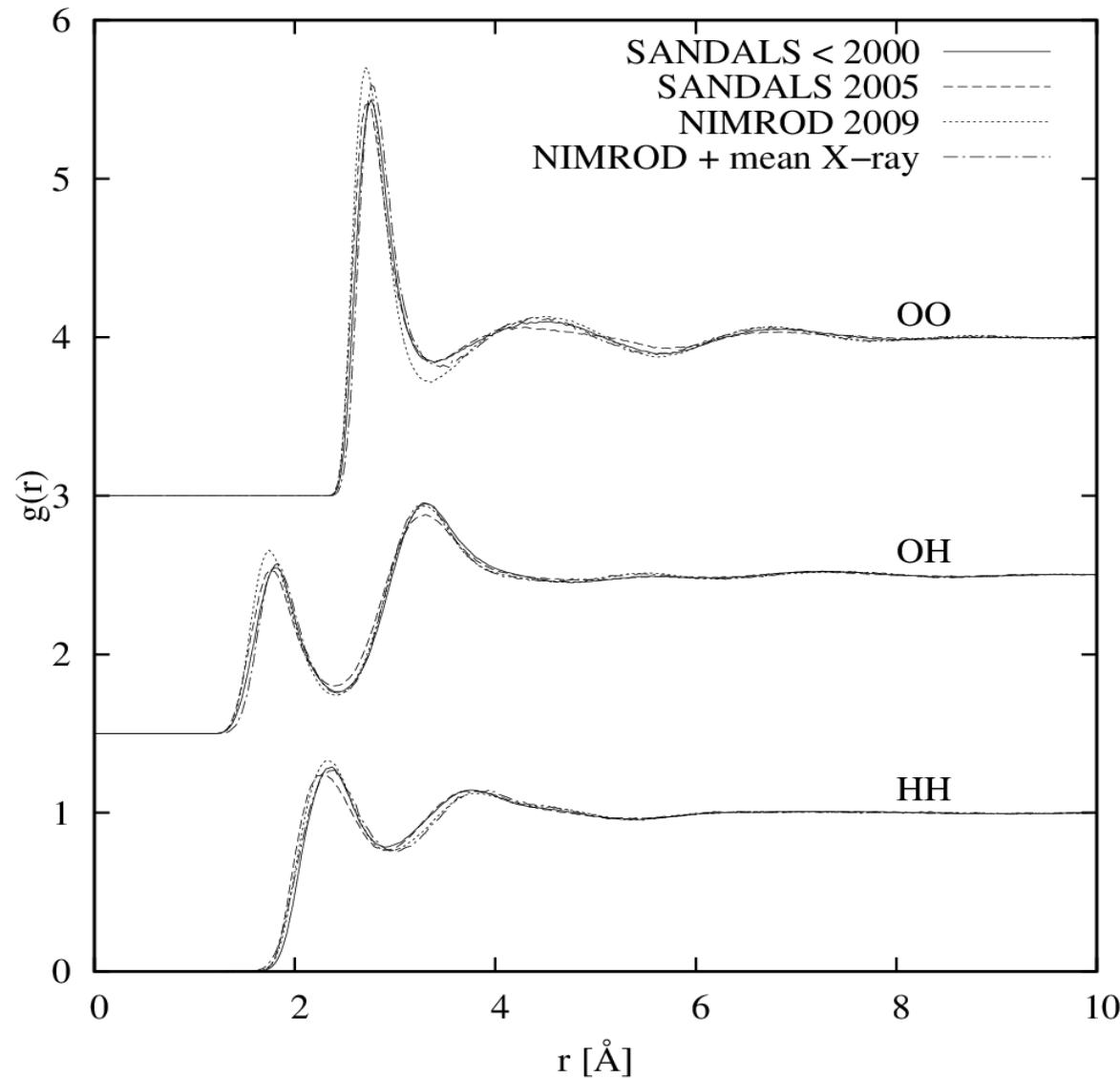
# *Structure refinement of liquid water*

# Water data

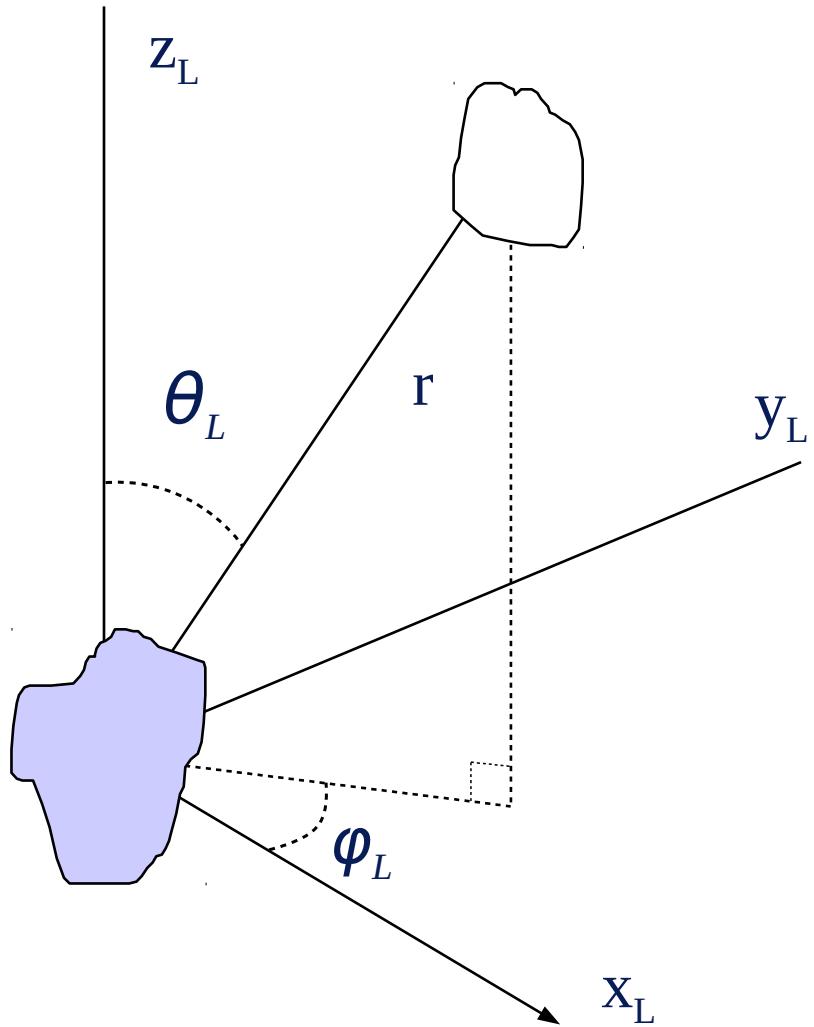
After  
structure  
refinement



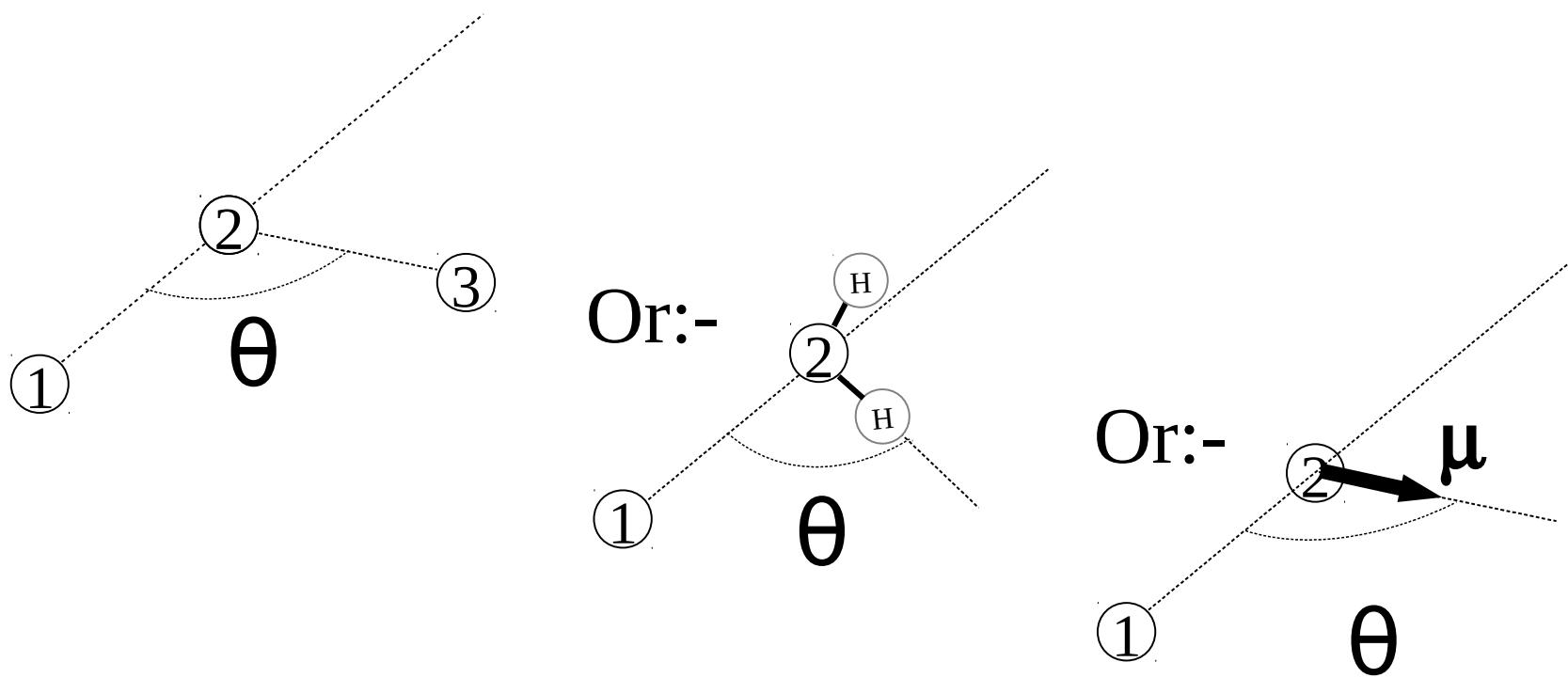
# *Water partial $g(r)$ 's*



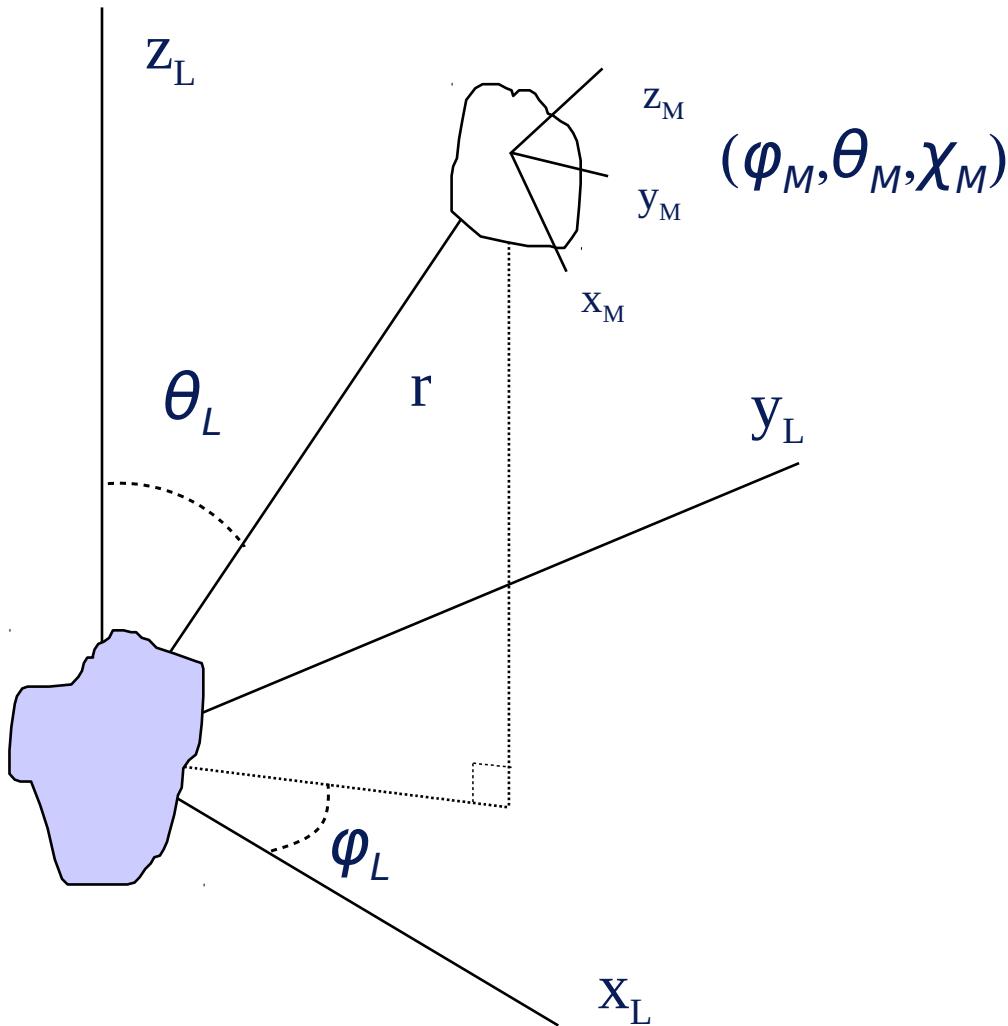
# *Beyond $g(r)$ : the spatial density function*



# *Bond angle distributions*

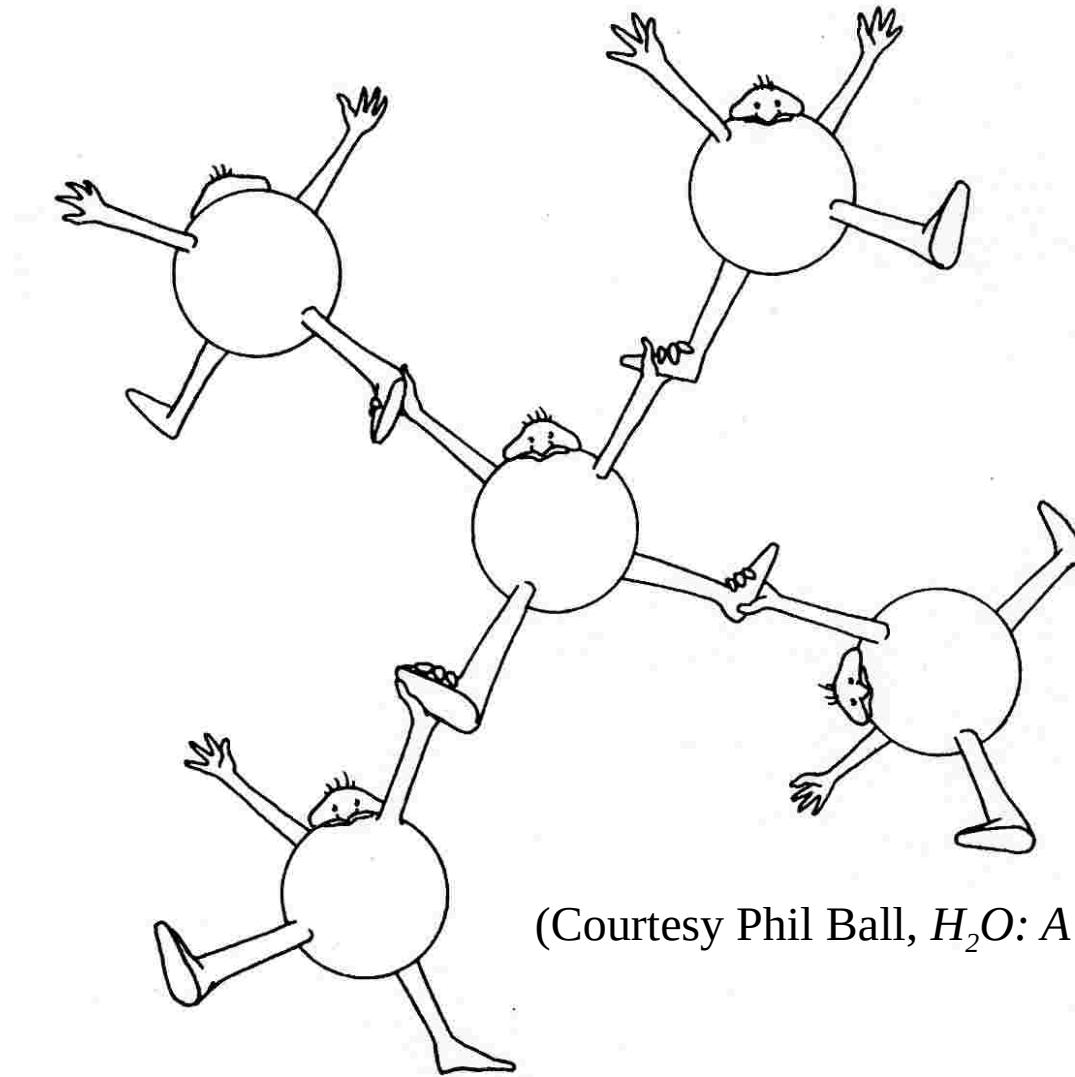


# *A step further: the orientational pair correlation function*



*The spatial density function of  
water...*

# *Water structure*



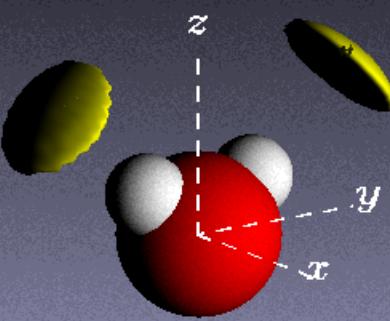
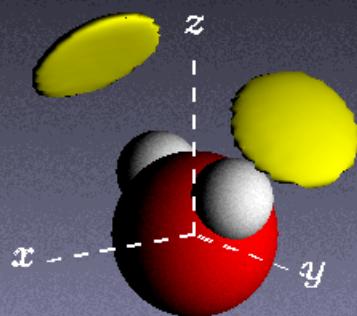
(Courtesy Phil Ball, *H<sub>2</sub>O: A Biography of Water*)

Choose distance range (0-5.7Å)

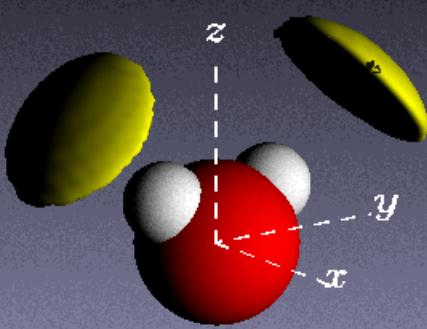
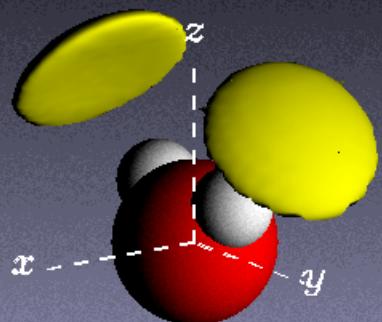
and a contour level

(% of all molecules in distance range)

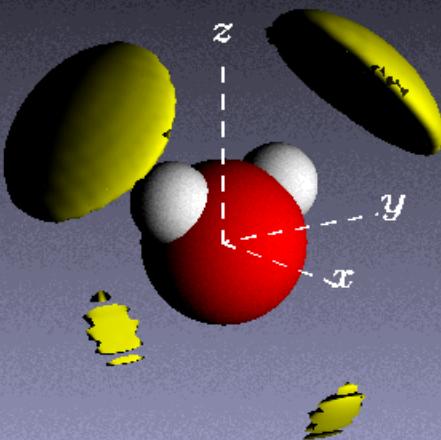
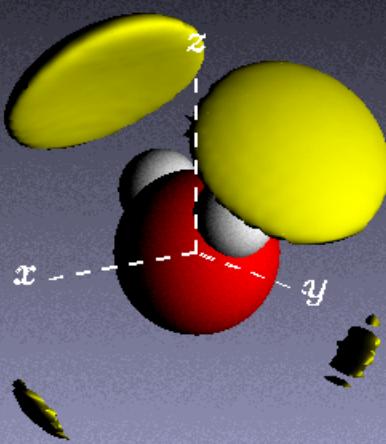
1%



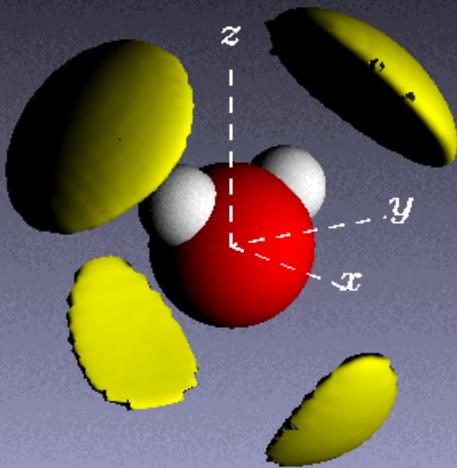
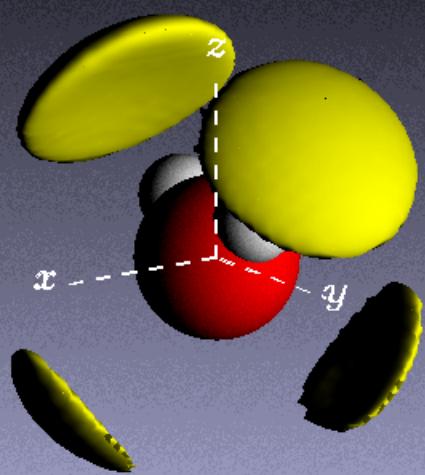
2%



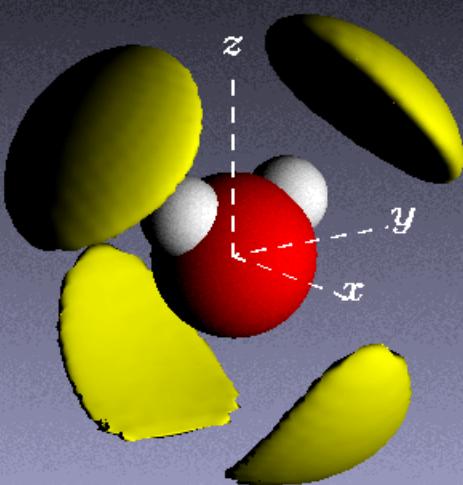
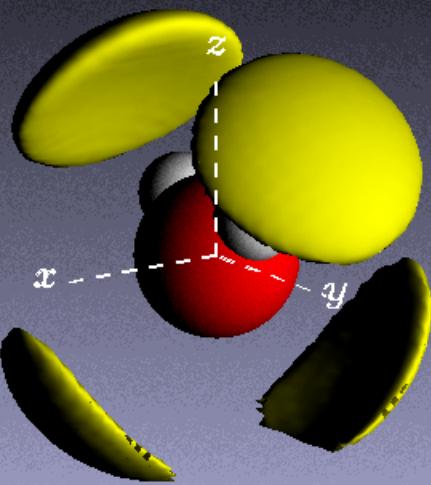
3%



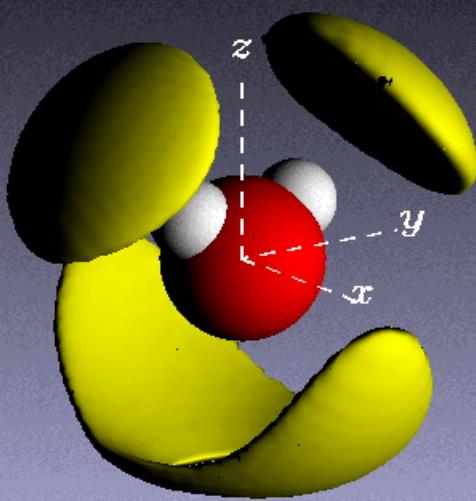
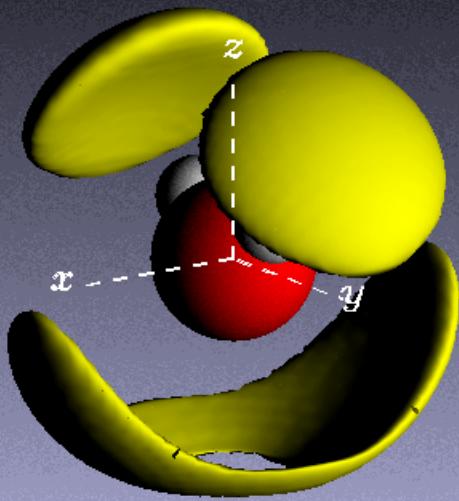
4%



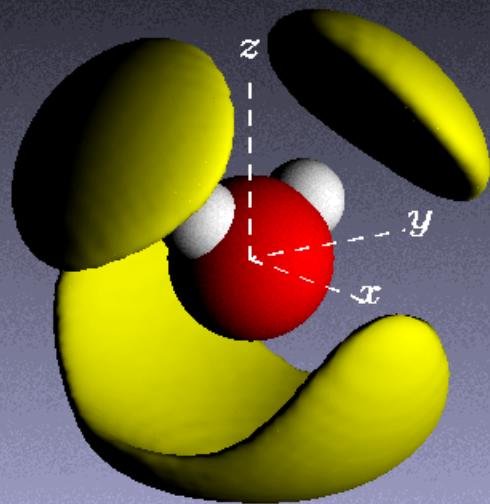
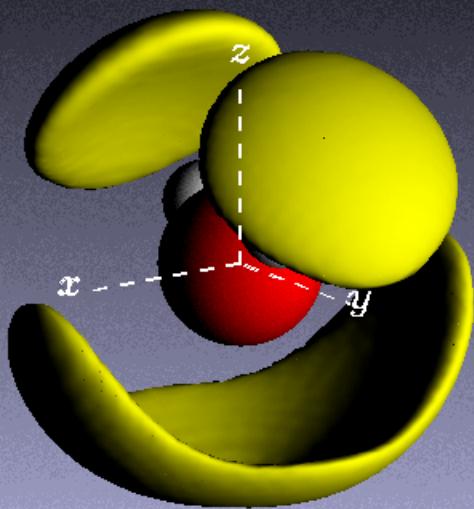
5%



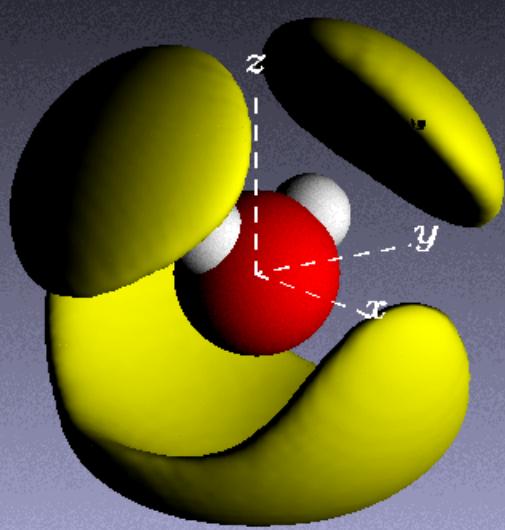
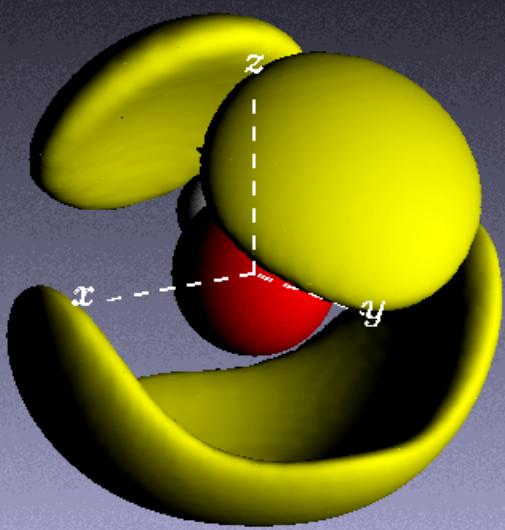
7%



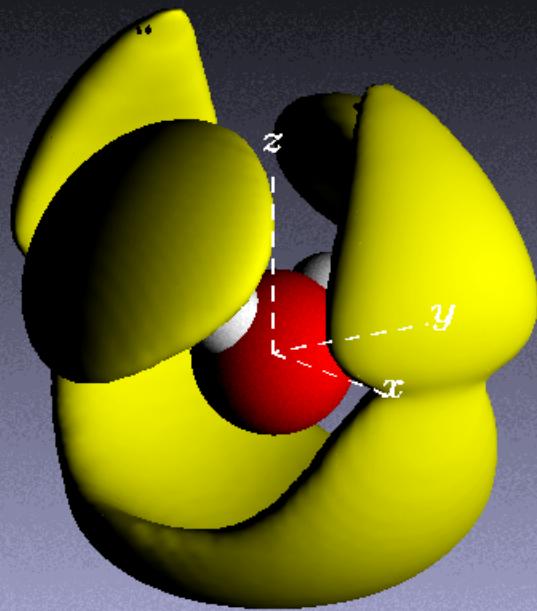
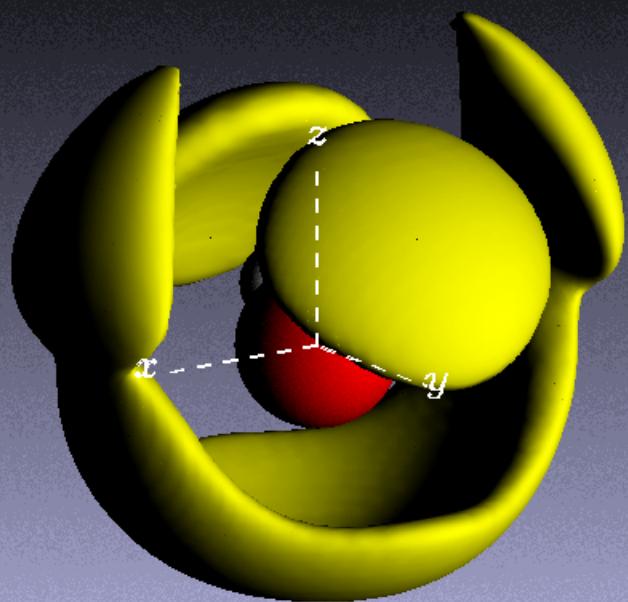
9%



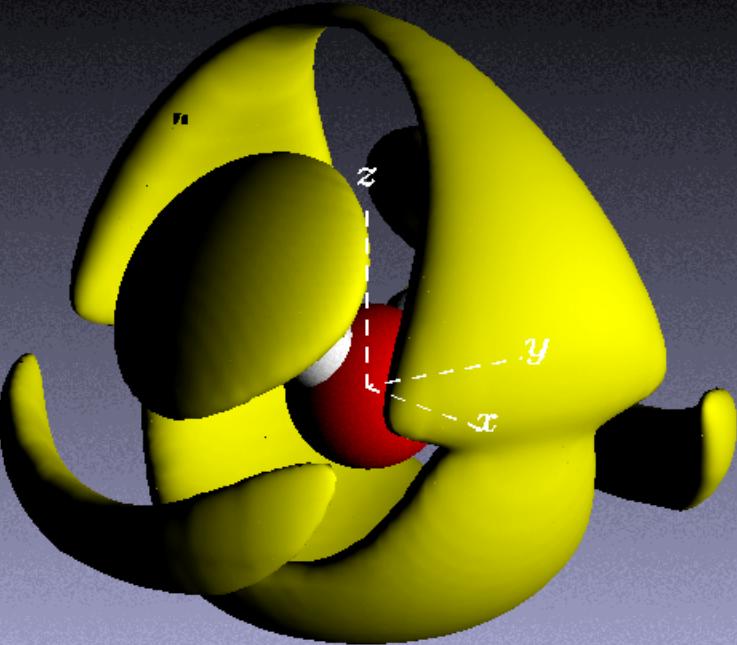
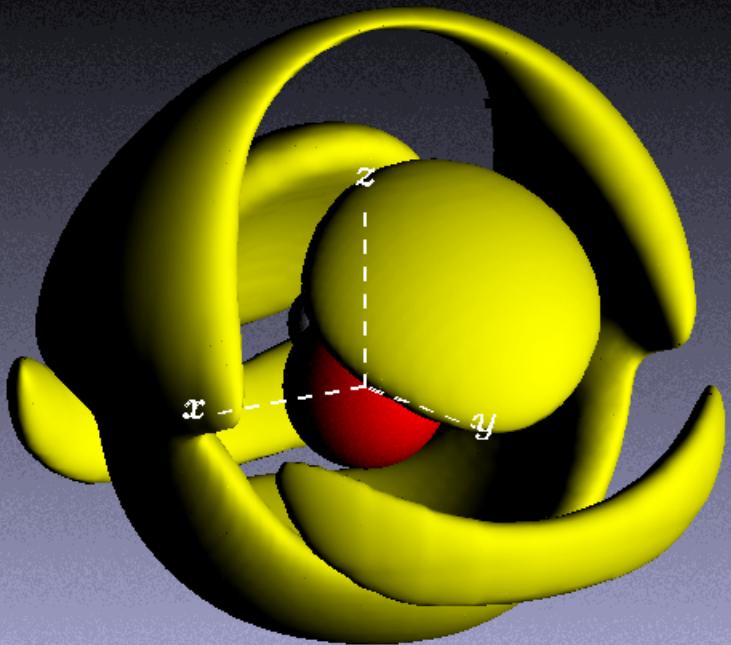
12%



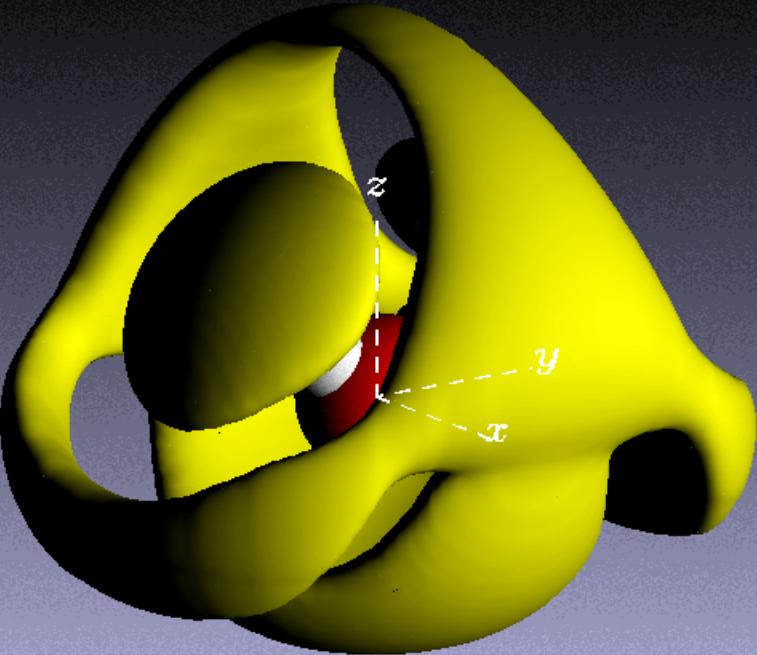
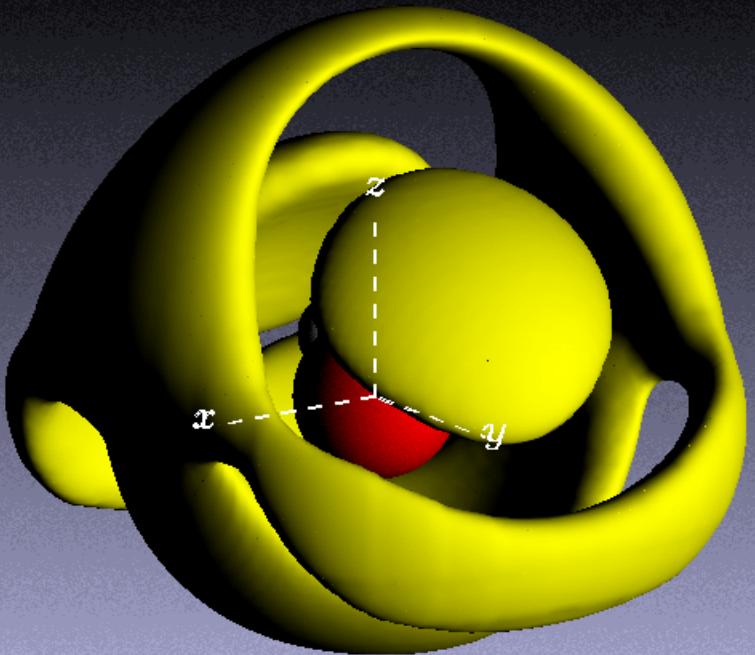
15%



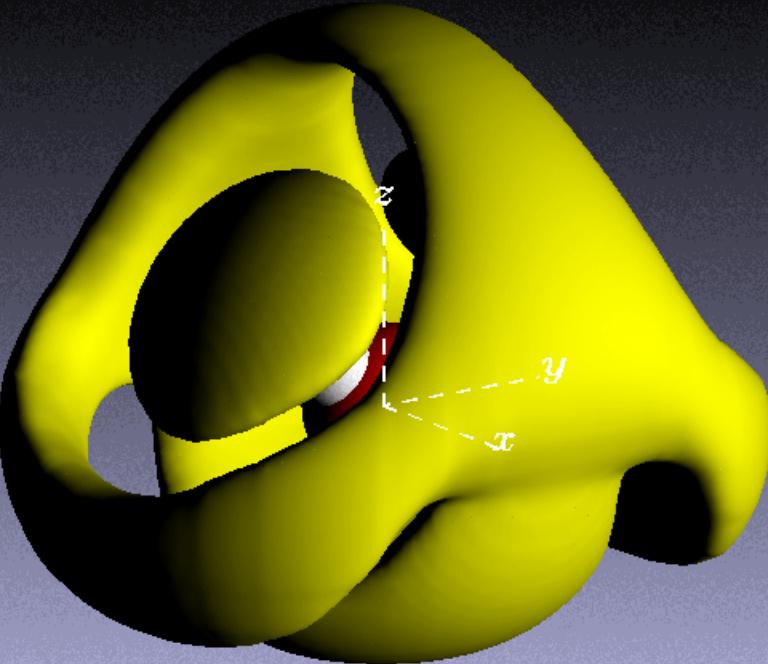
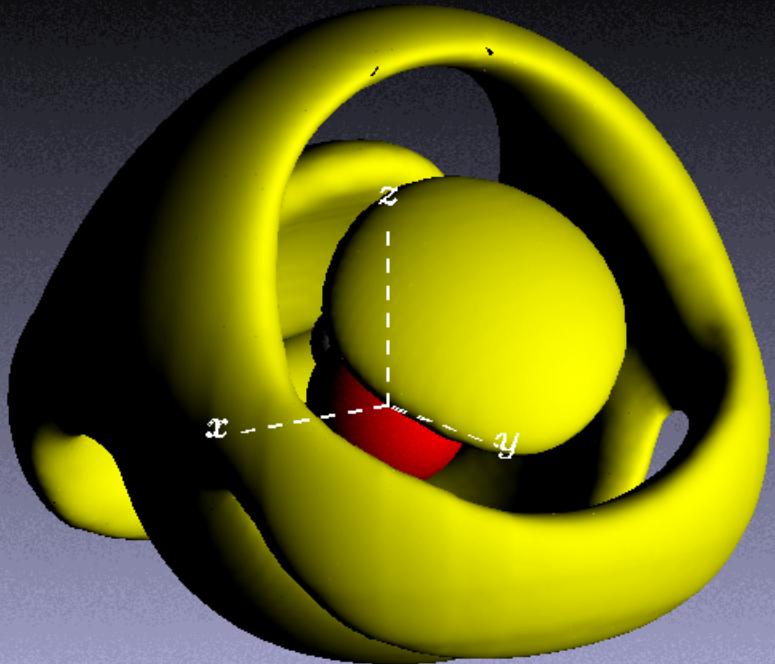
18%



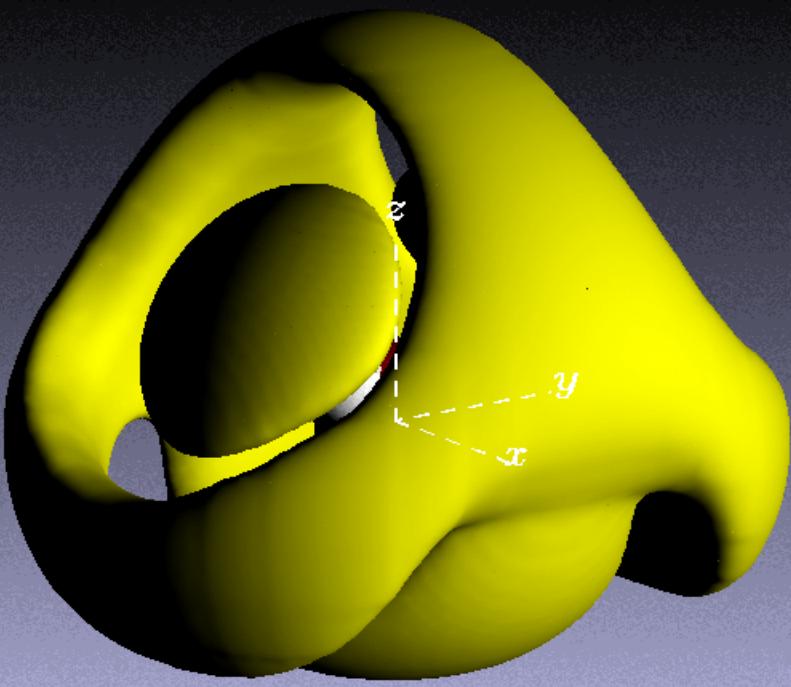
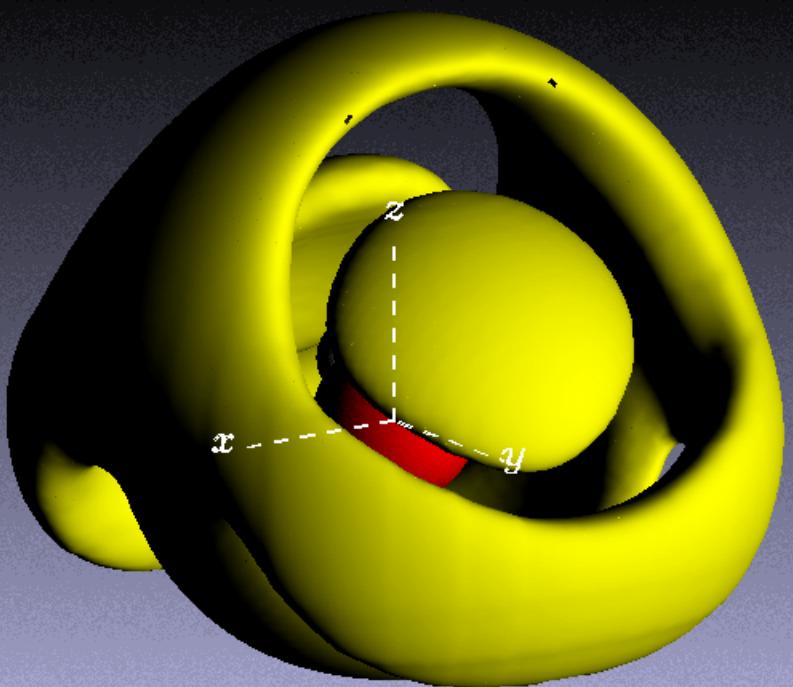
21%



25%

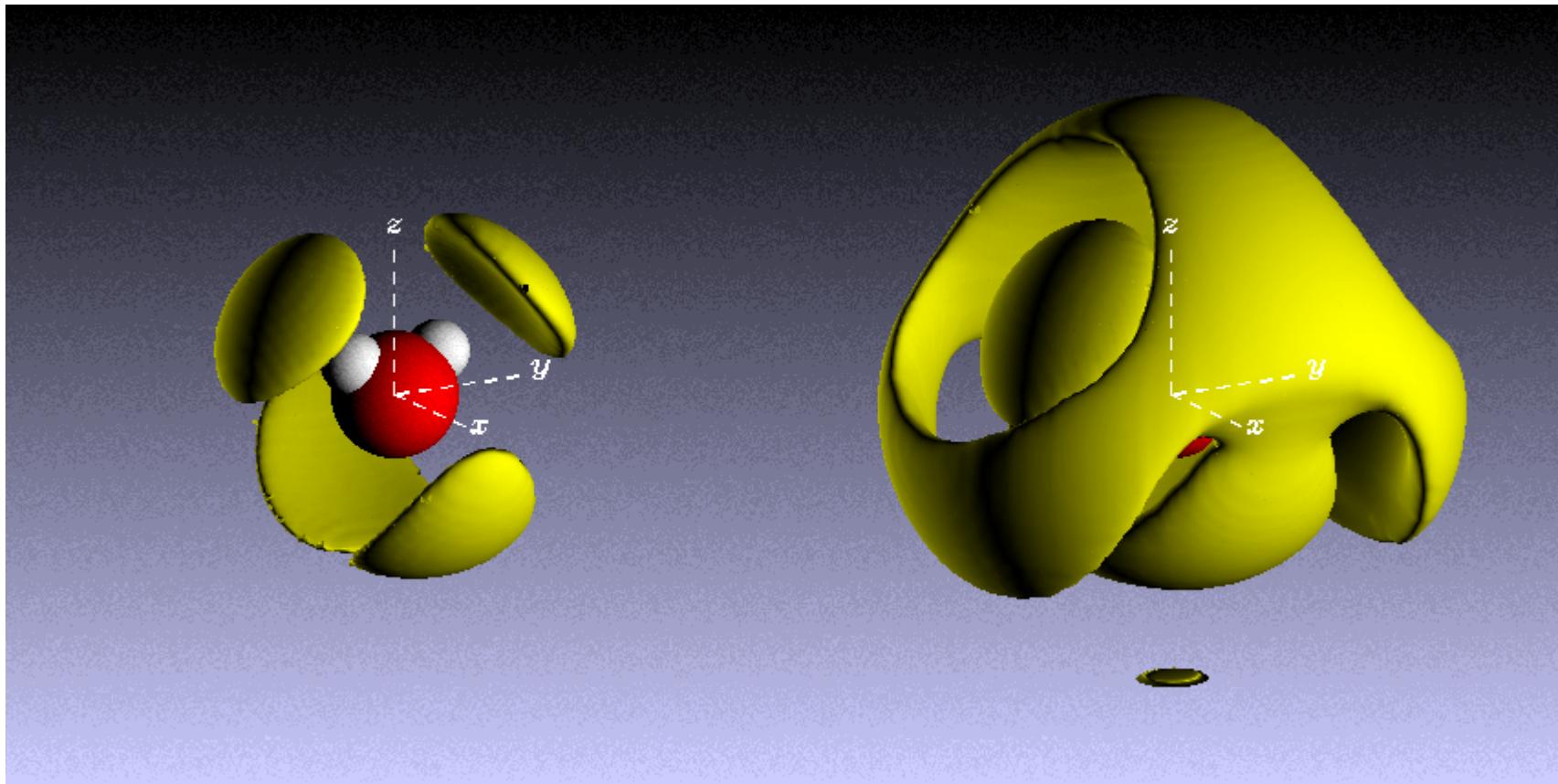


30%

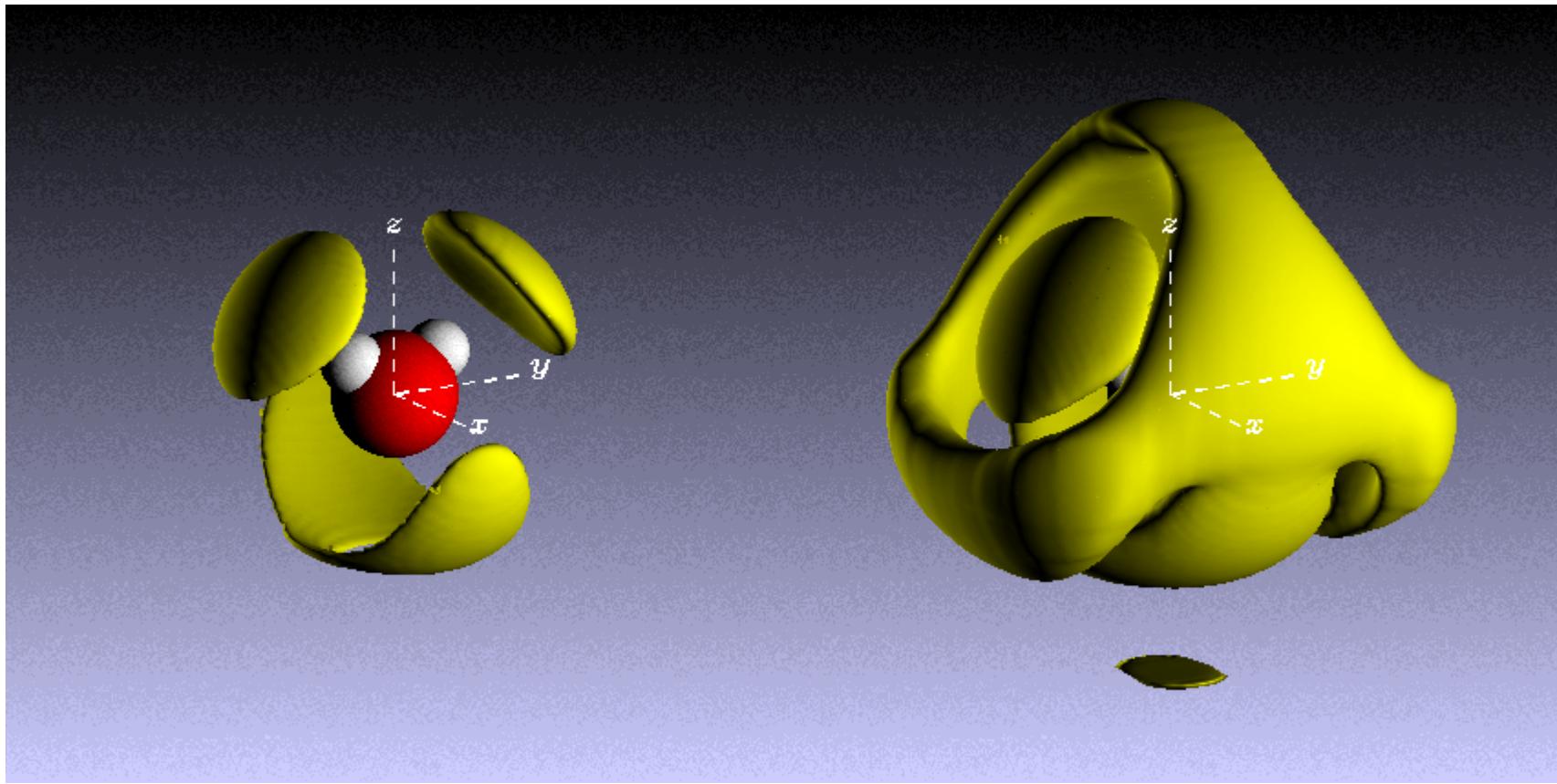


*Water under pressure*

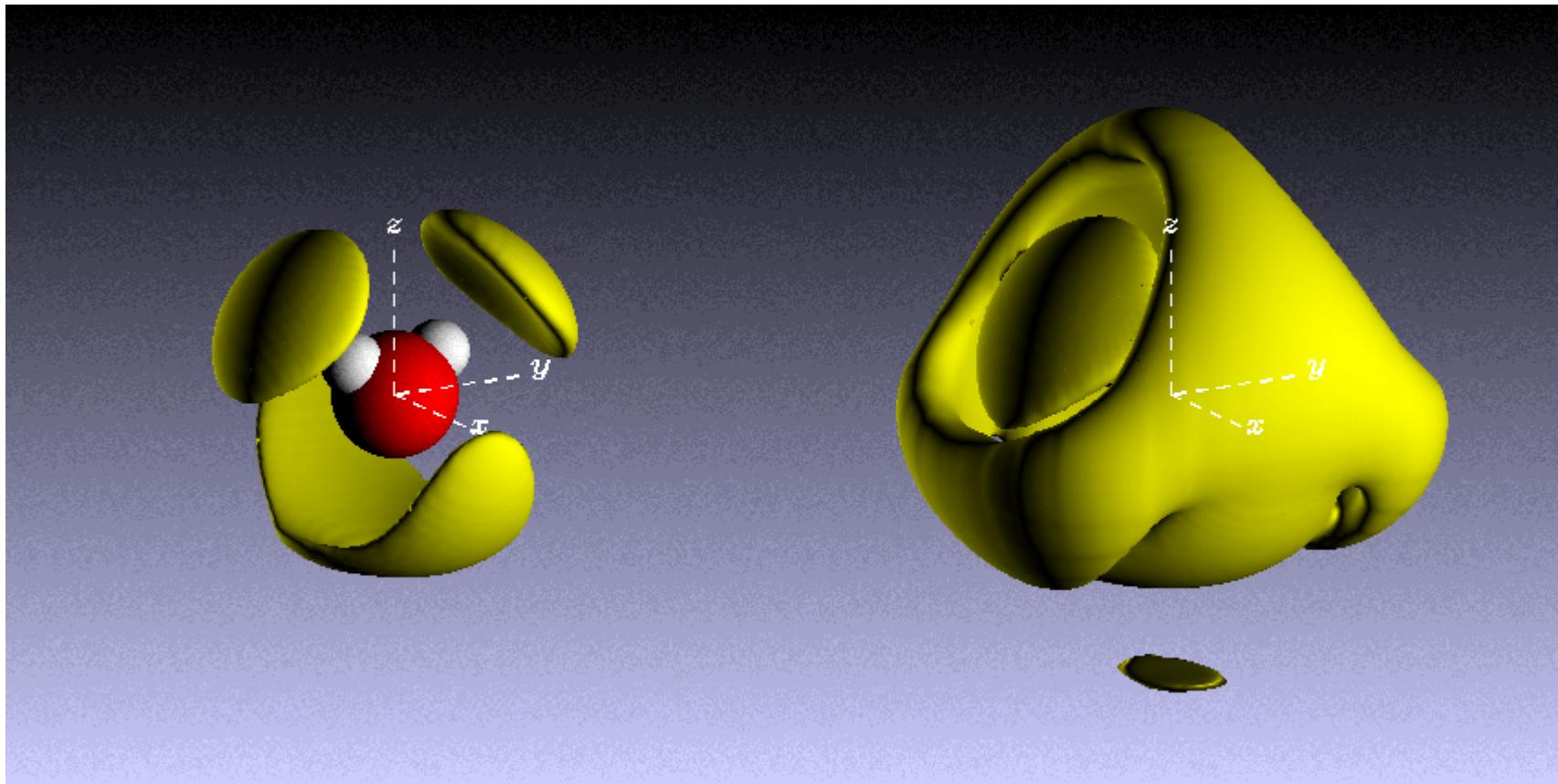
*Water at 268K, 0.26kbar*



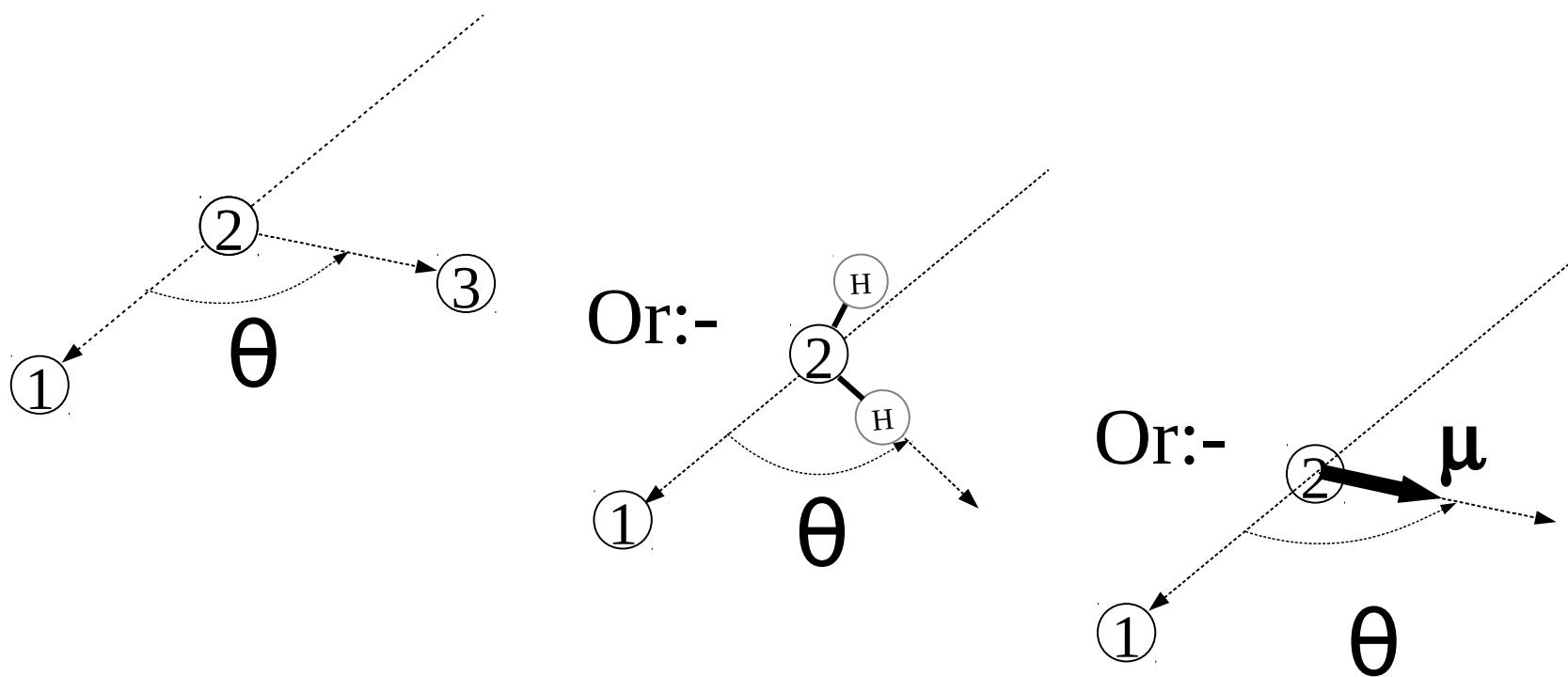
*Water at 268K, 2.09kbar*



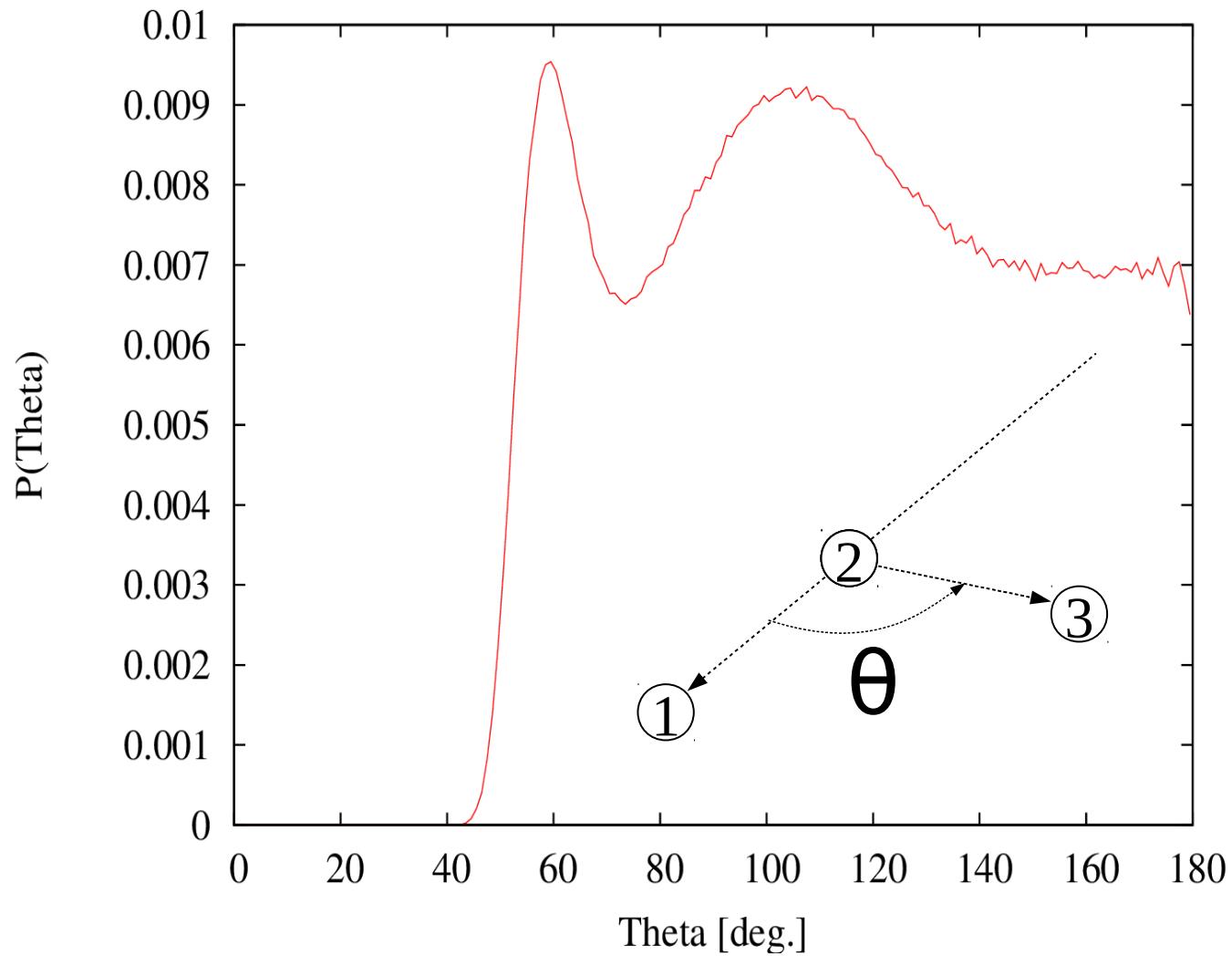
*Water at 268K, 4.00kbar*



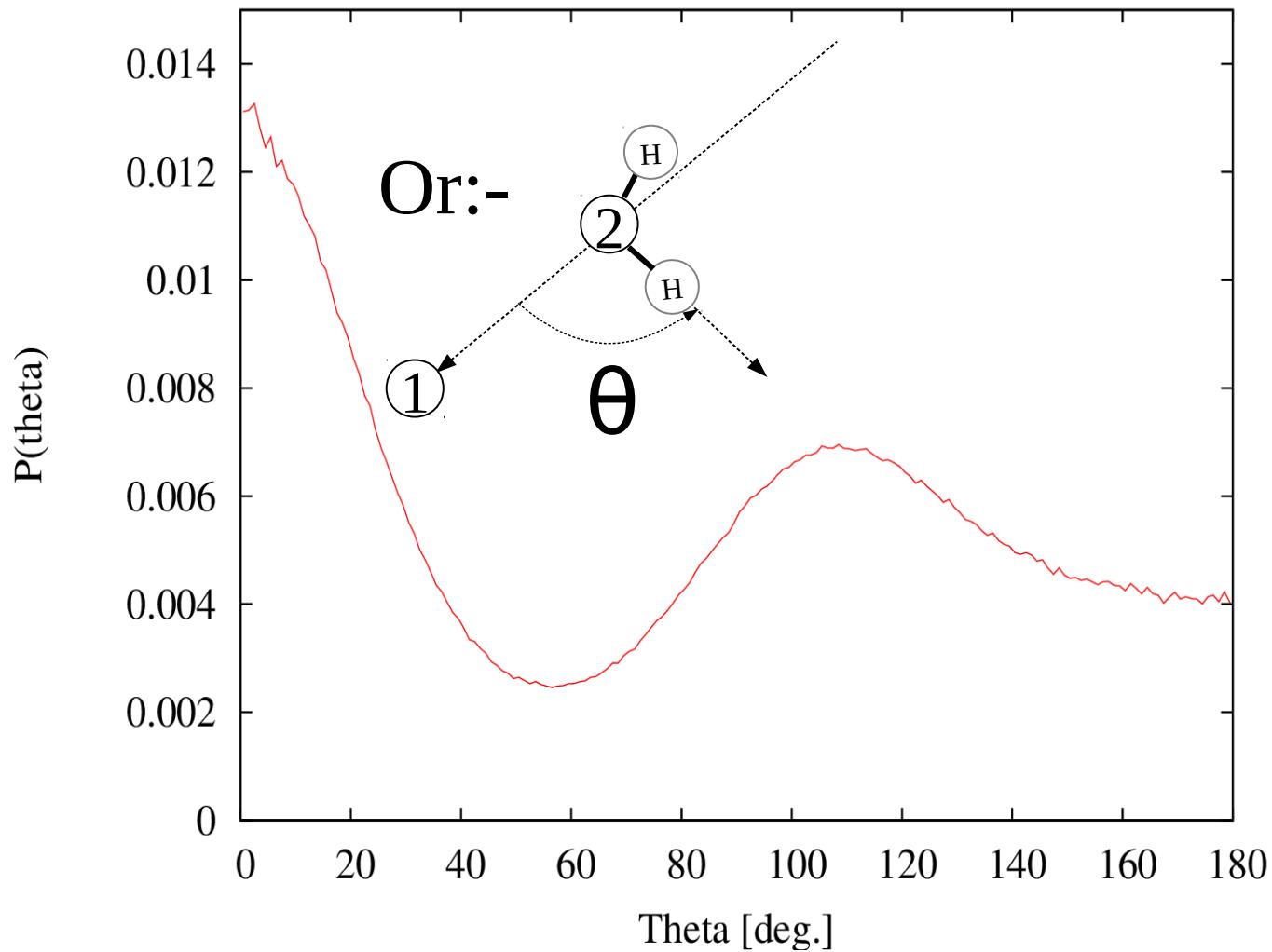
# *Bond angle distributions*



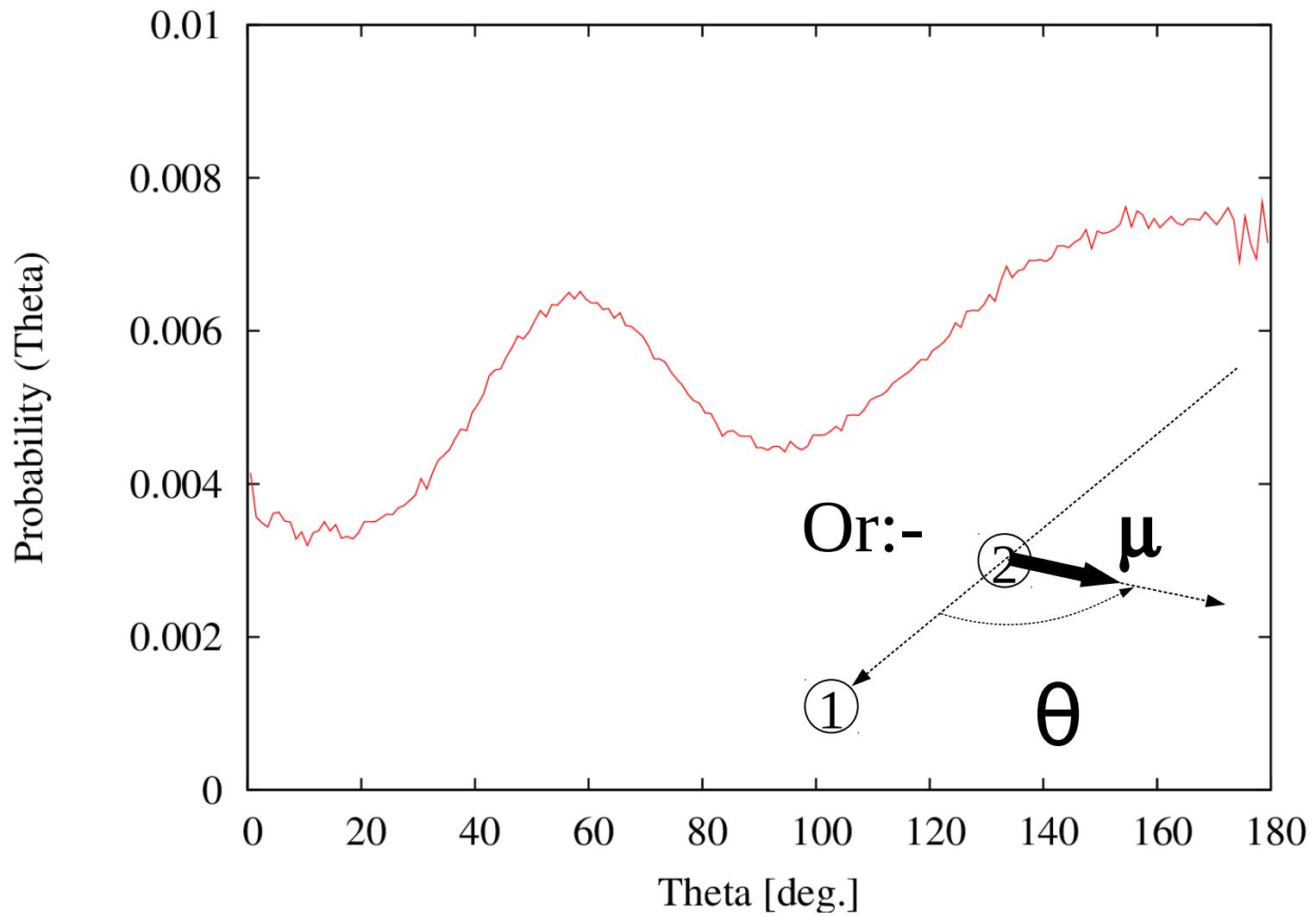
# *O-O-O angle distribution*



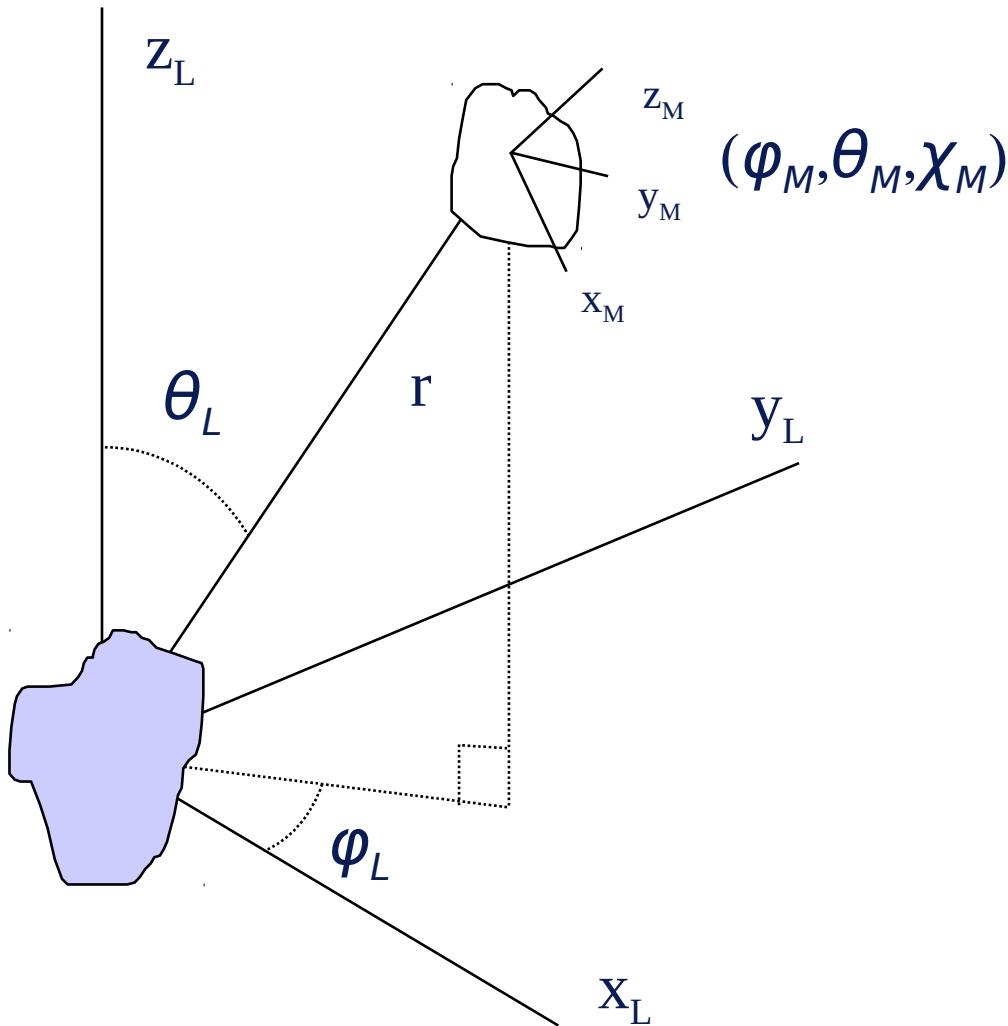
# *O-O-H angle distribution*

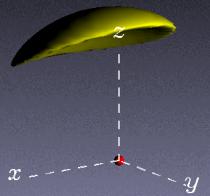


# *O- $\mu$ angle distribution*

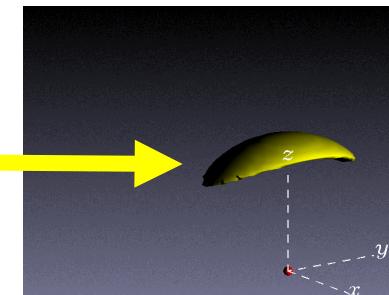
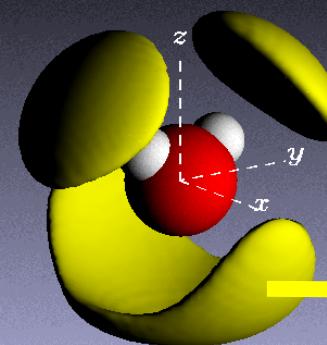
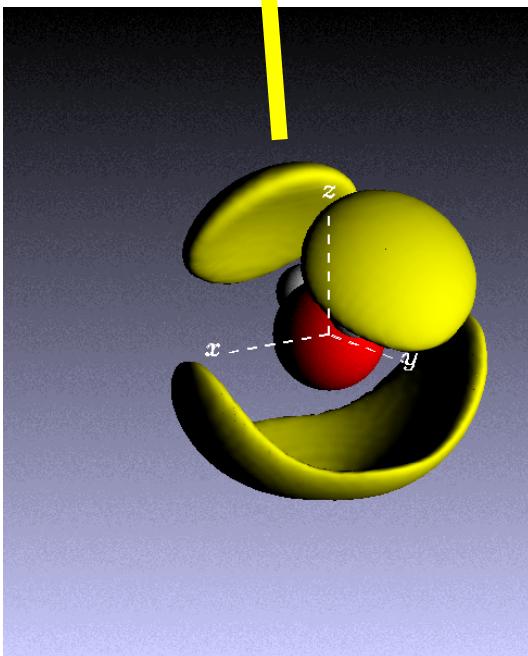


# *A step further: the orientational pair correlation function*





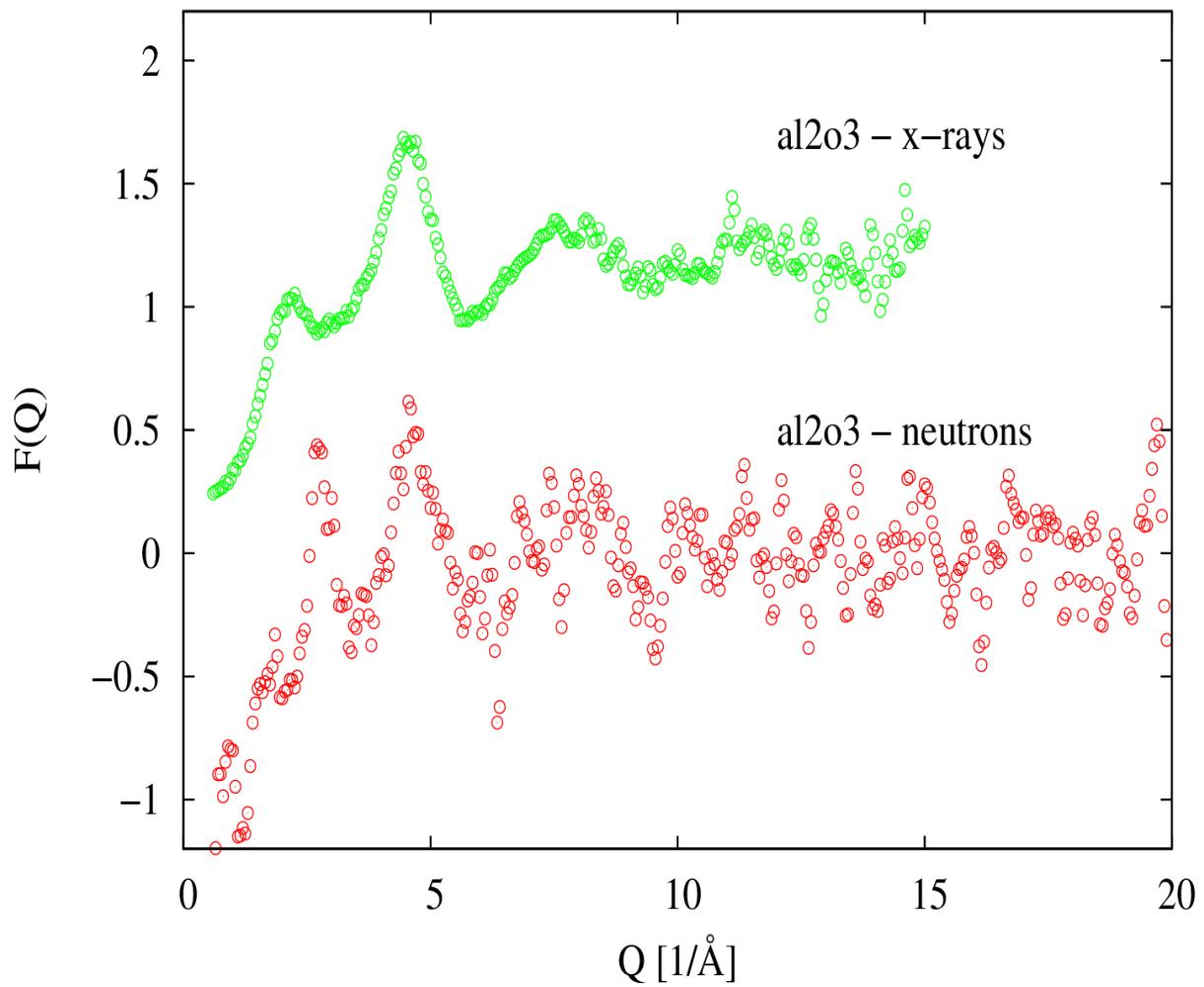
# Dipole orientations in water



*Another  
example:*

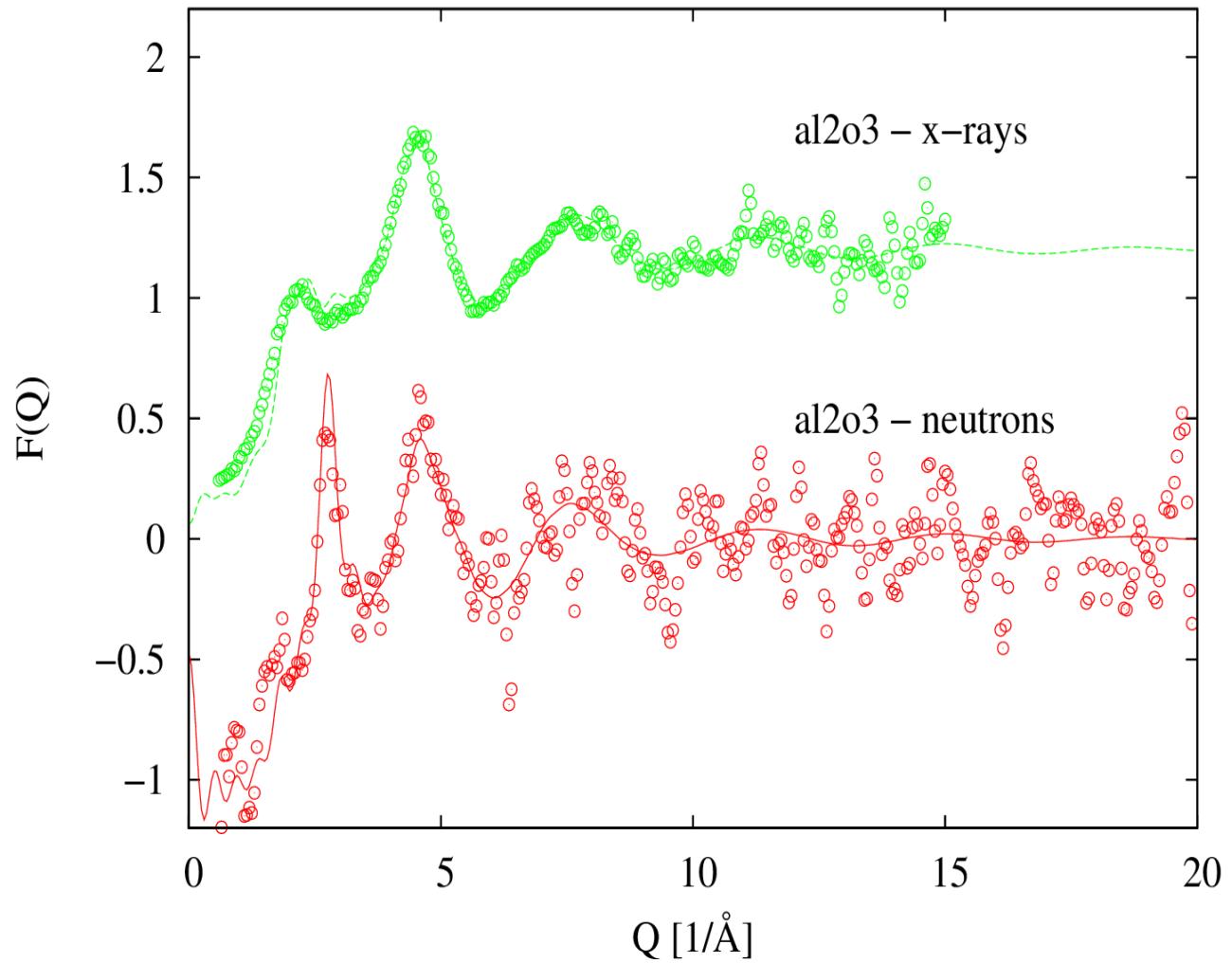
# *Molten $Al_2O_3$*

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

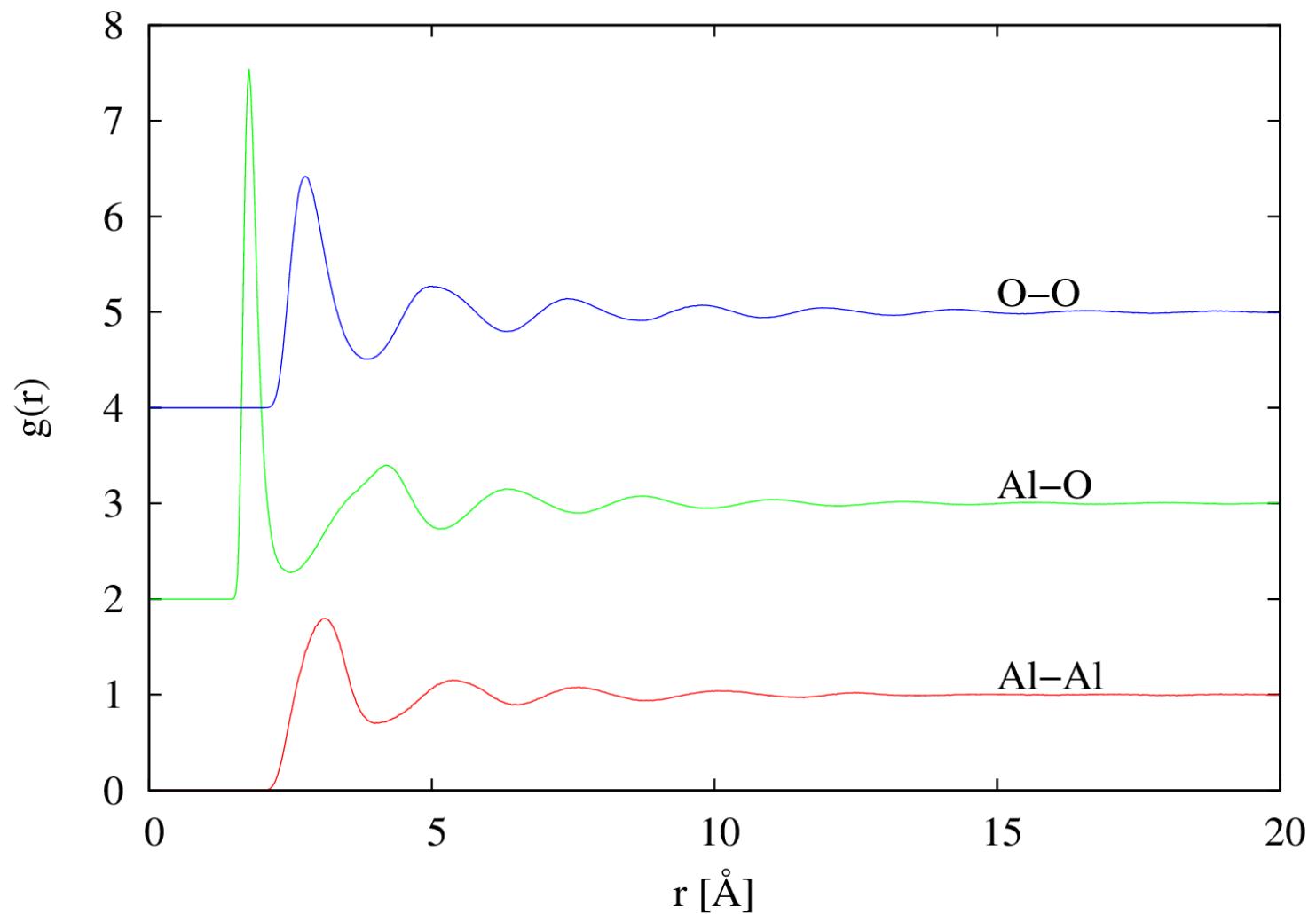


# *Molten Al<sub>2</sub>O<sub>3</sub>*

*Final  
fit  
after  
Empirical  
Potential  
Structure  
Refinement.*



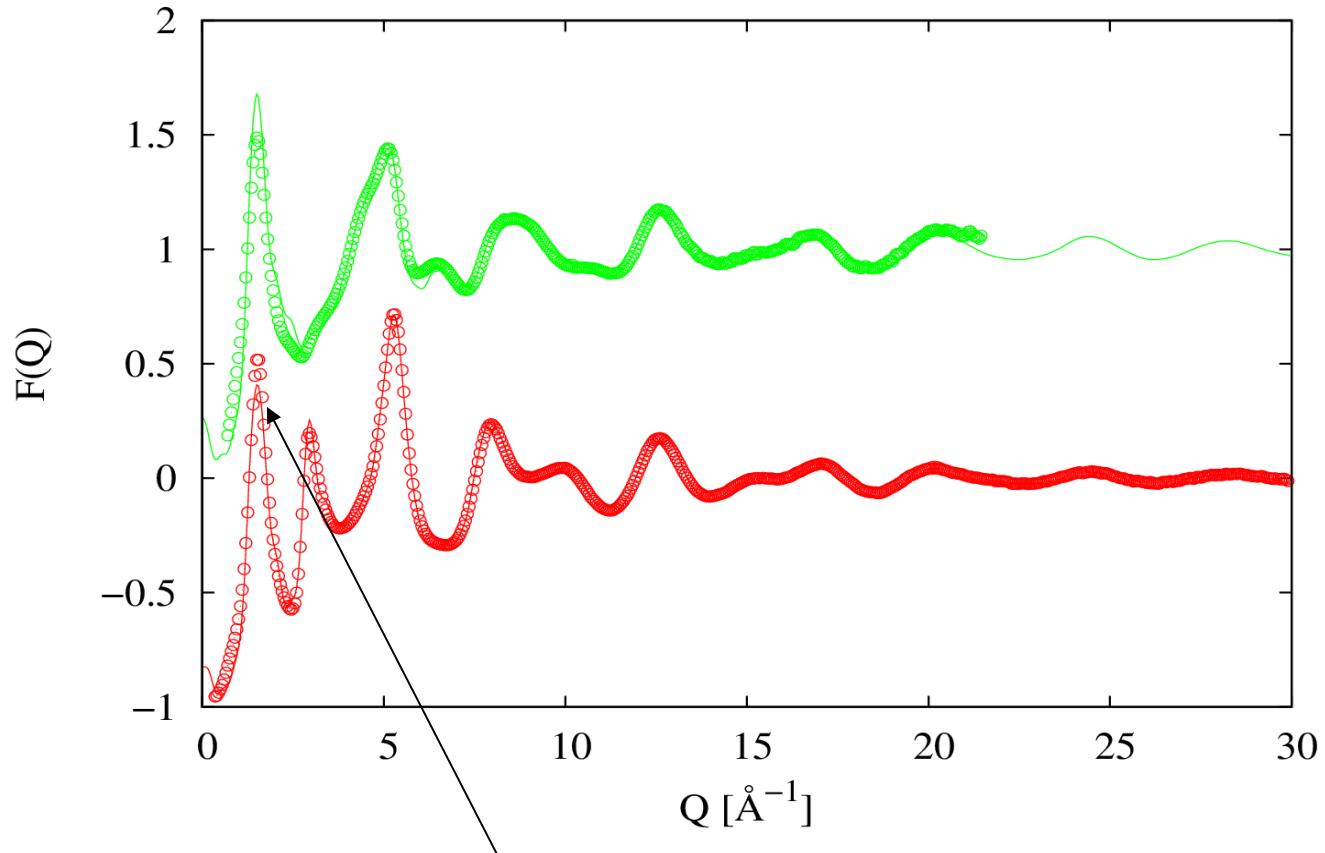
# *Partial $g(r)$ 's for $Al_2O_3$*



# *Tetrahedrally coordinated glasses and liquids*

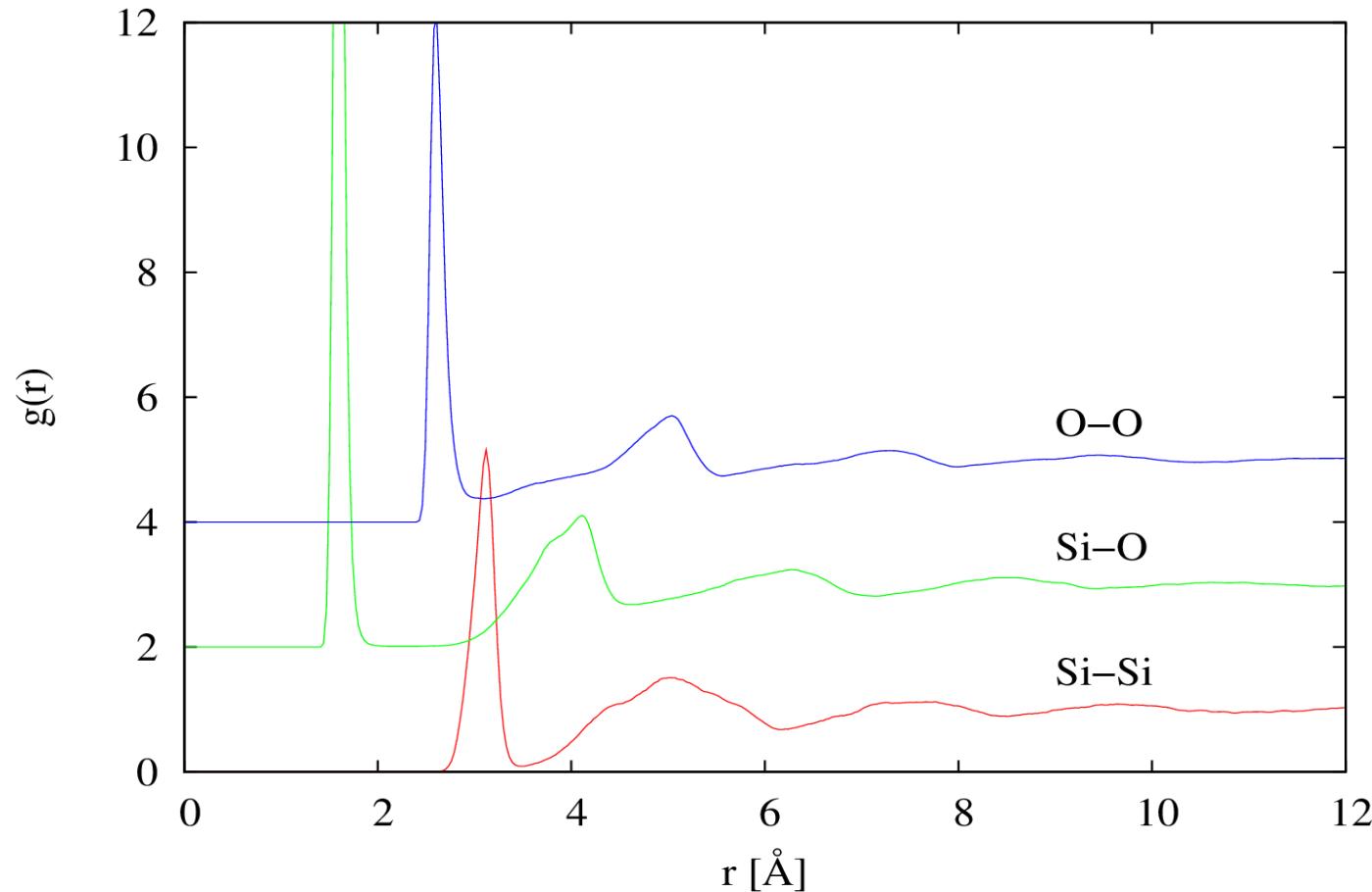
(water,  $a\text{-SiO}_2$ ,  $a\text{-Si}$ ,  $a\text{-Ge}$ )

# *Amorphous $SiO_2$*

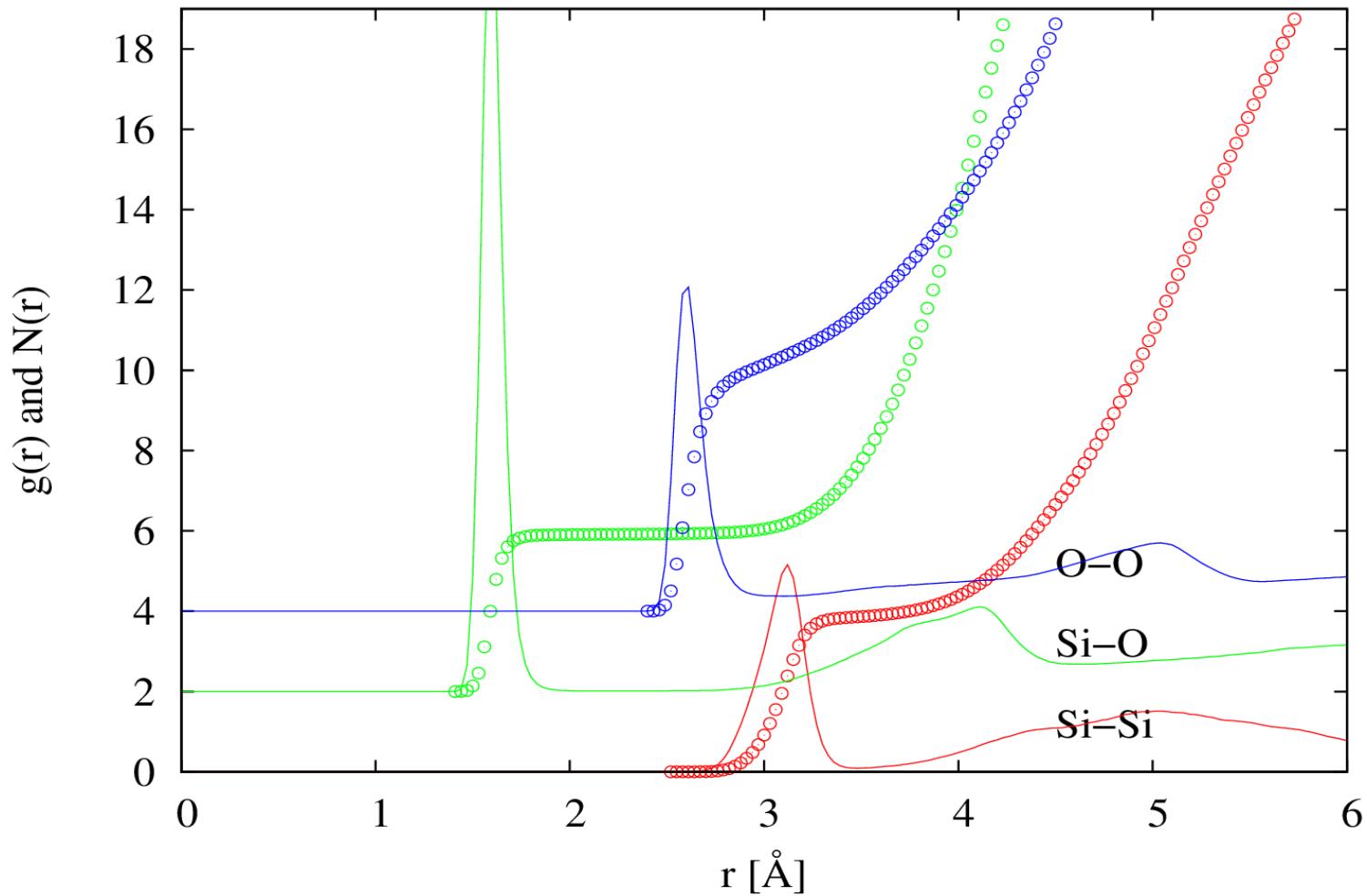


“First sharp diffraction peak” - FS $D$ P

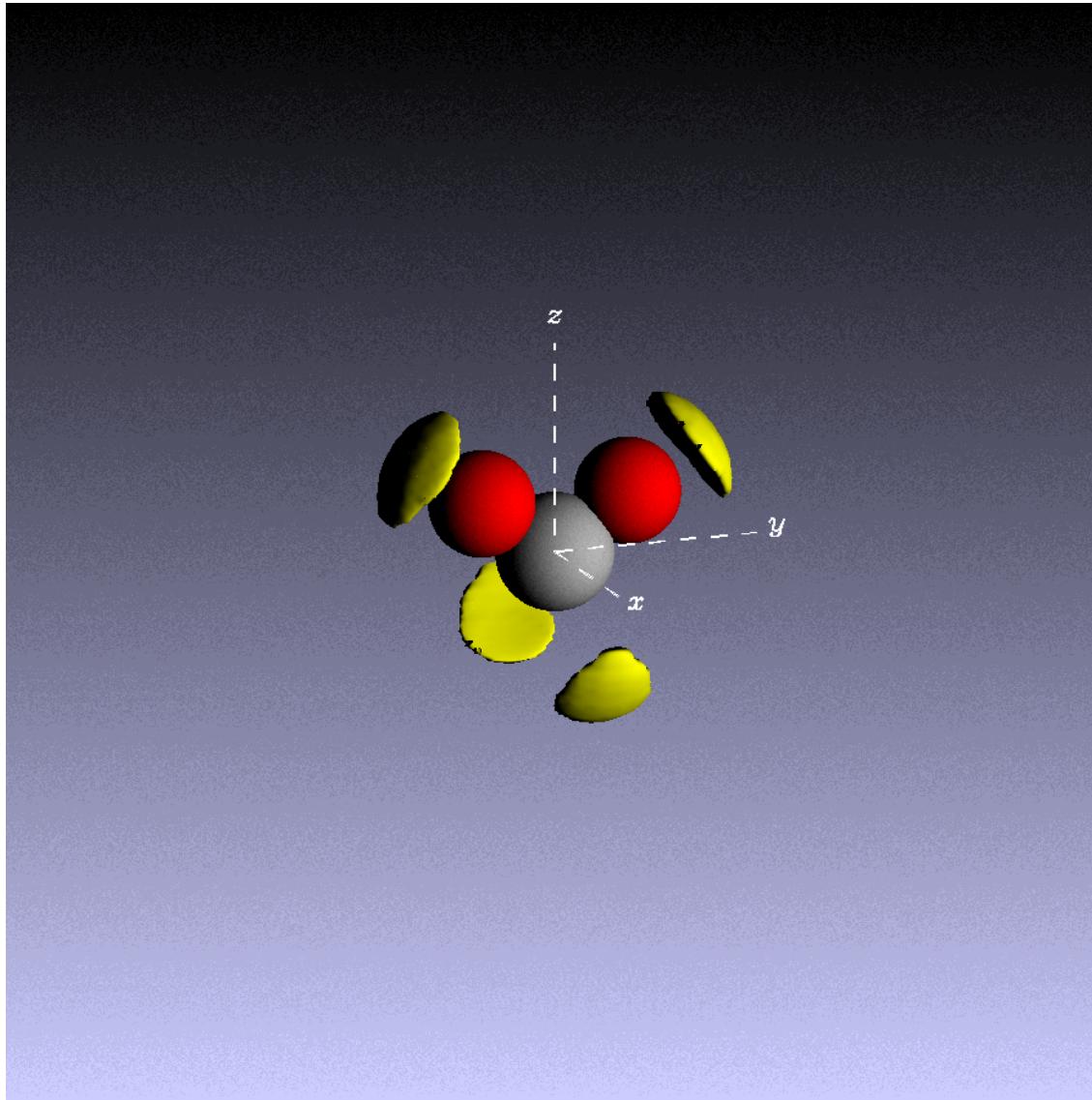
# *Radial distribution functions:*



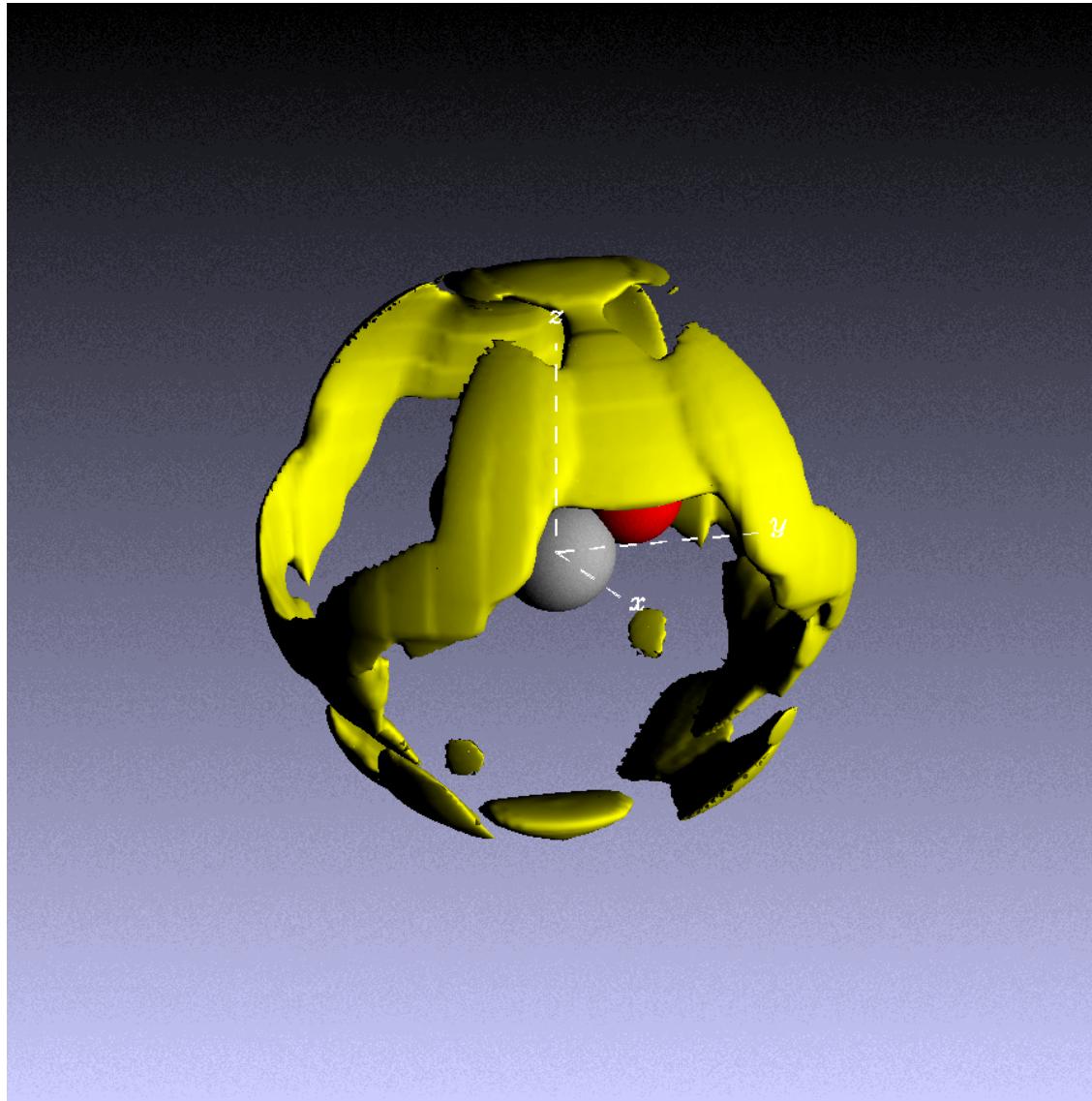
# *Coordination numbers:*



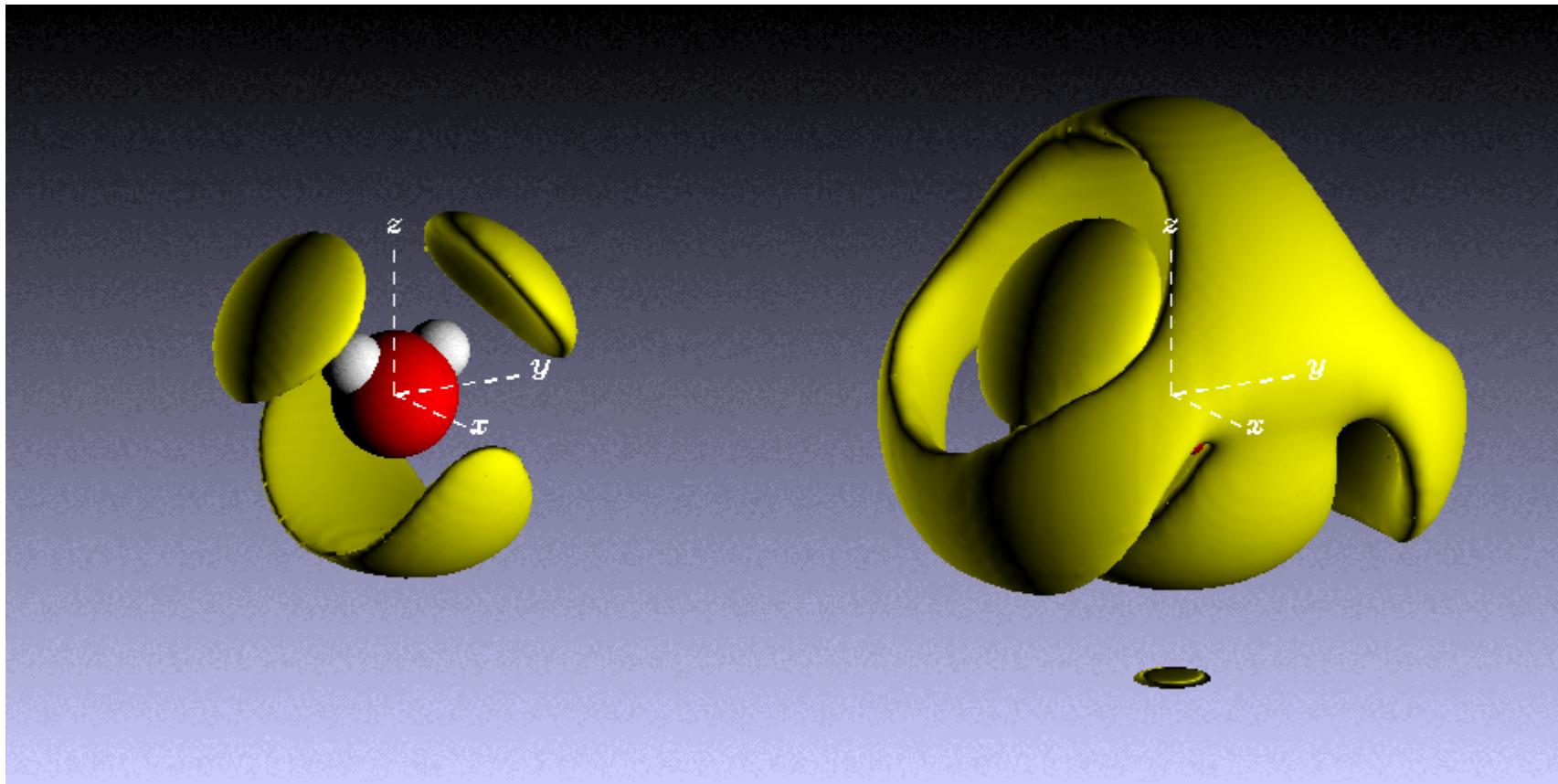
# *Spatial density function for a-SiO<sub>2</sub>:*



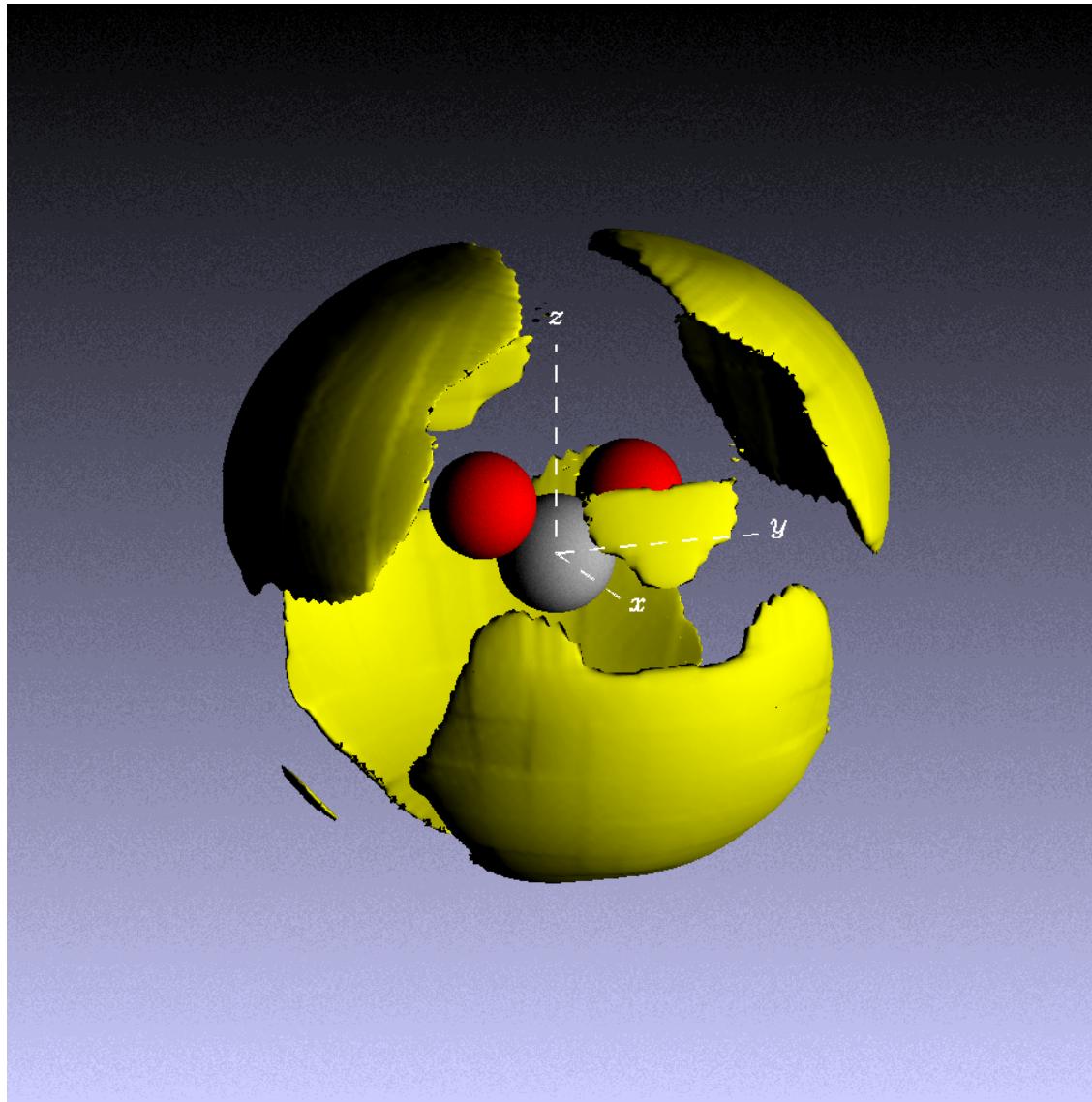
# *Spatial density function for $a\text{-SiO}_2$ :*



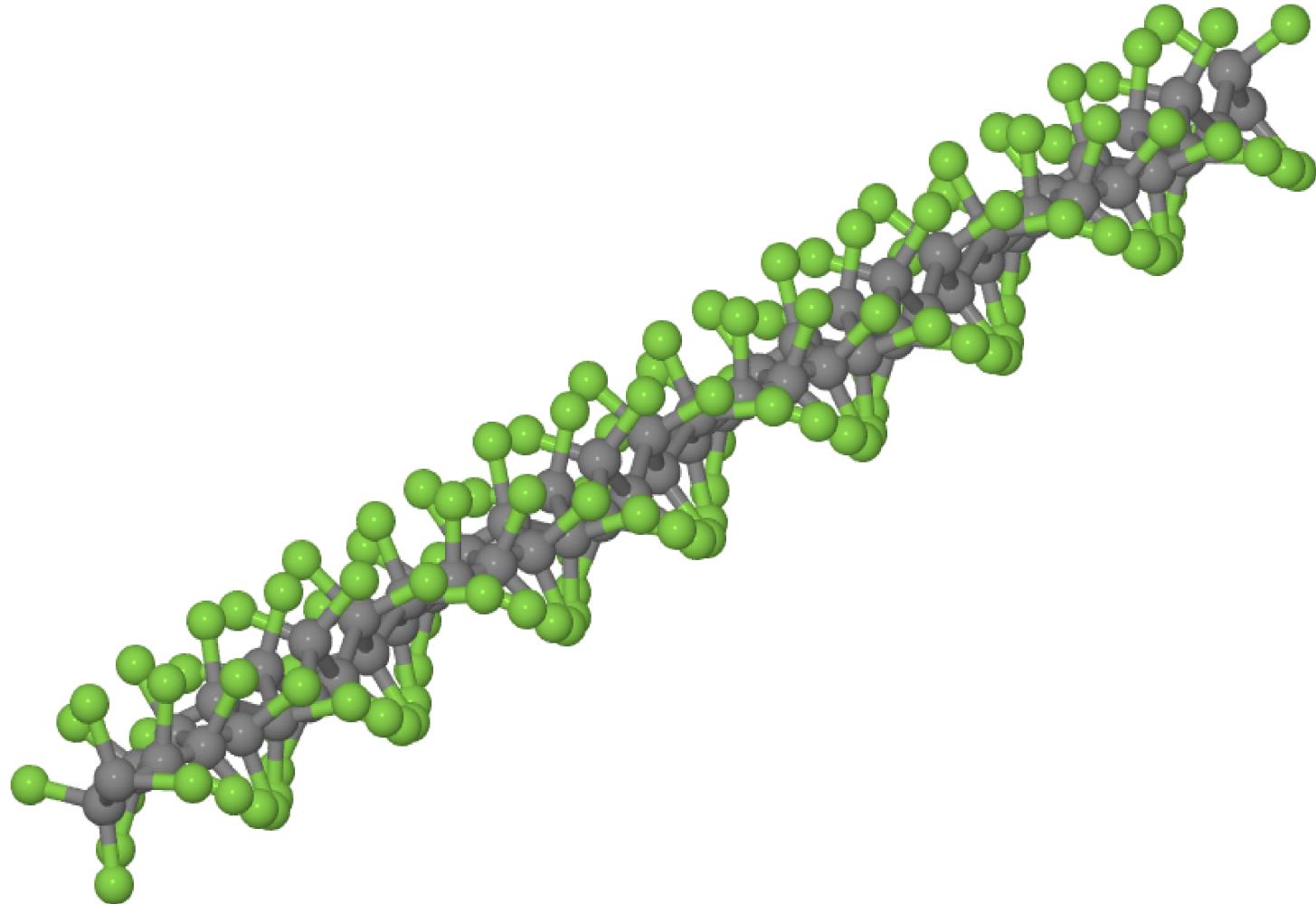
*Very analogous to water:*



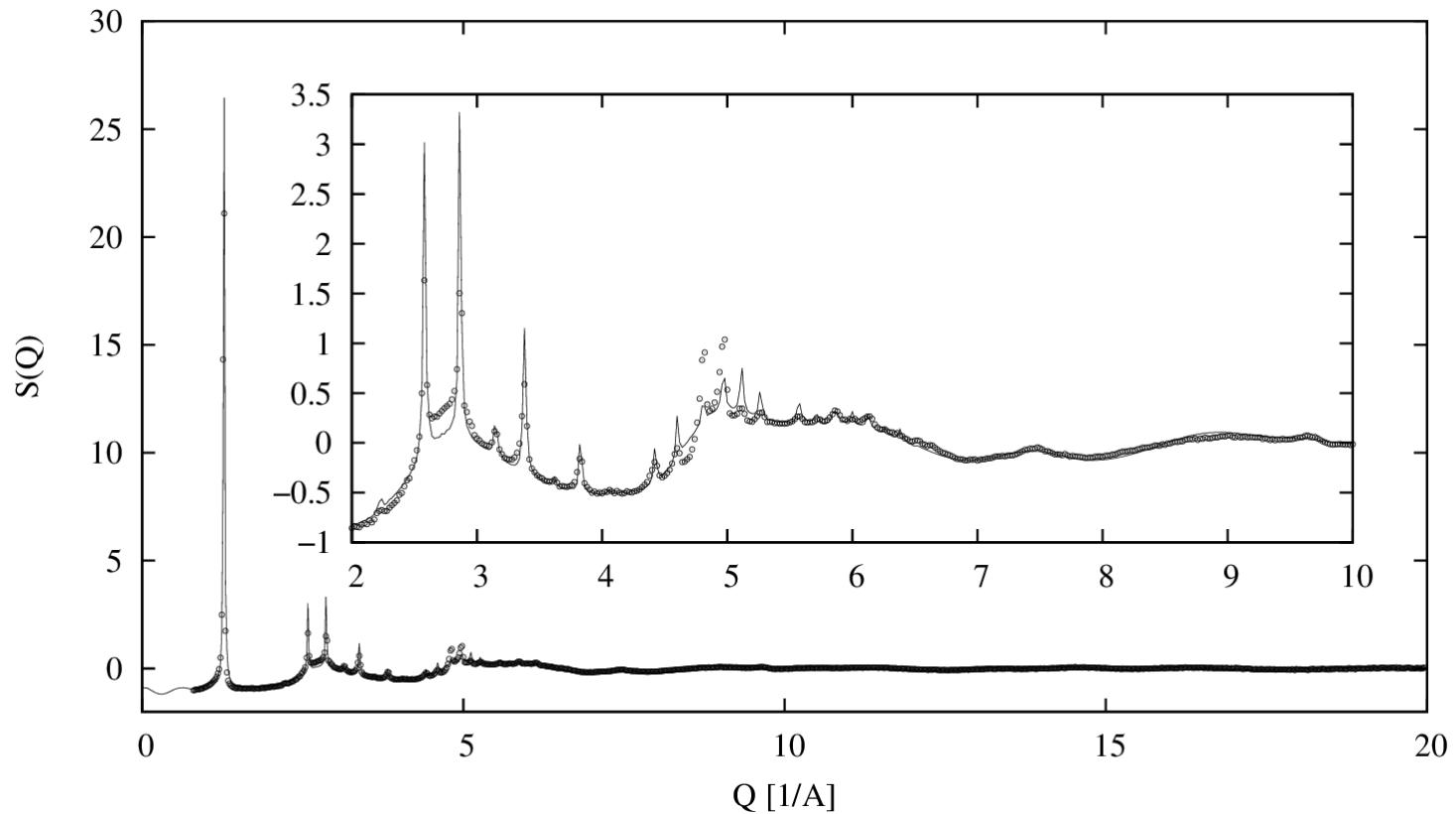
# *Spatial density function for $a\text{-SiO}_2$ :*



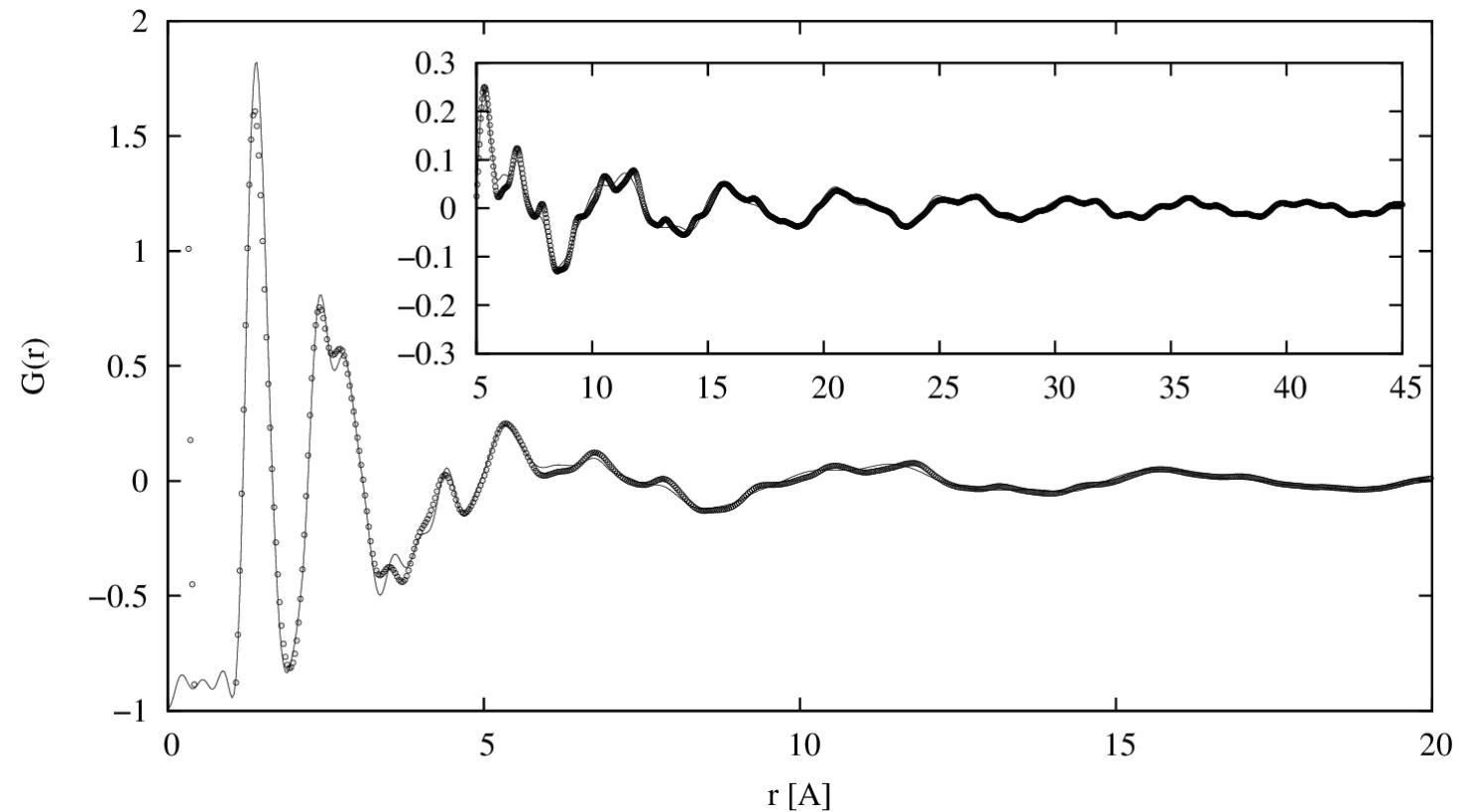
# *The structure of PTFE*



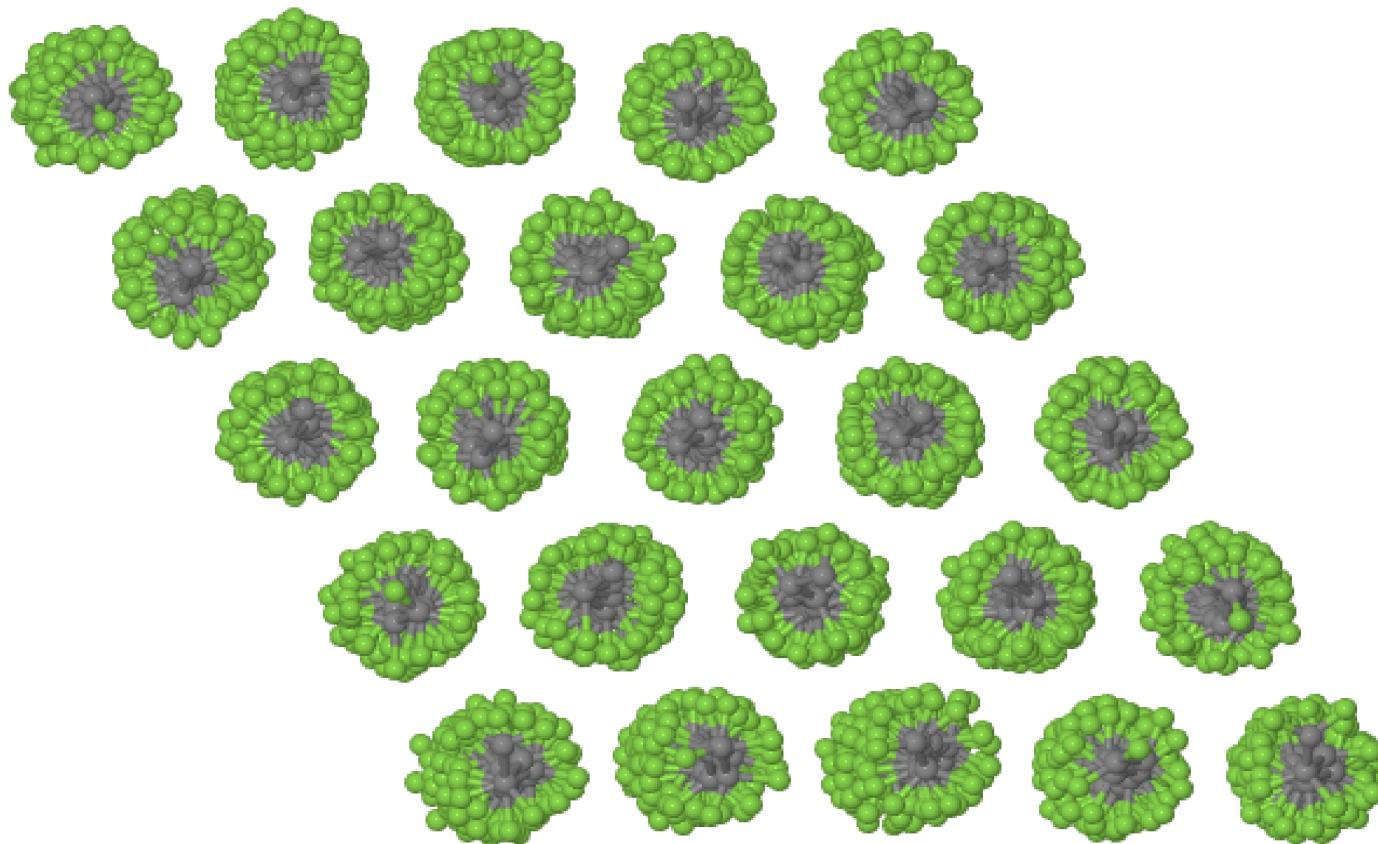
# *The structure of PTFE*



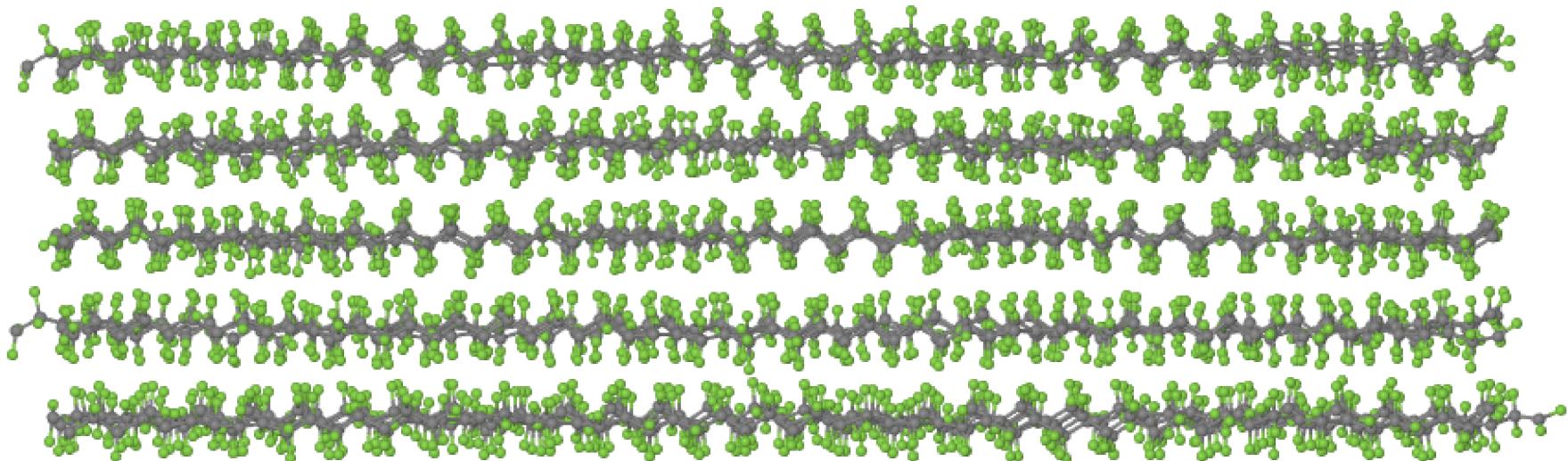
# *The structure of PTFE – $r$ space*



# *PTFE – end on view*

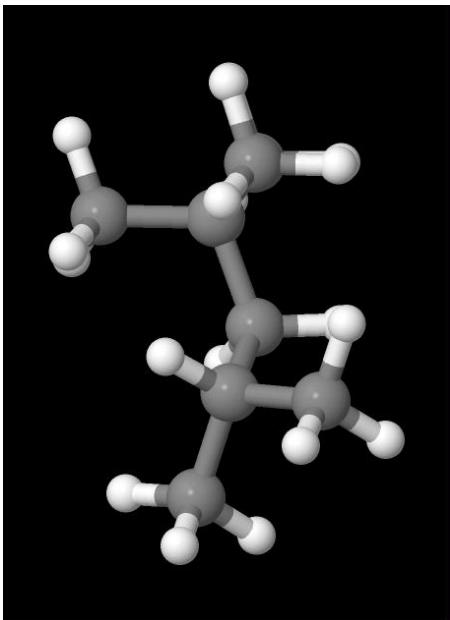


# *PTFE – side view*

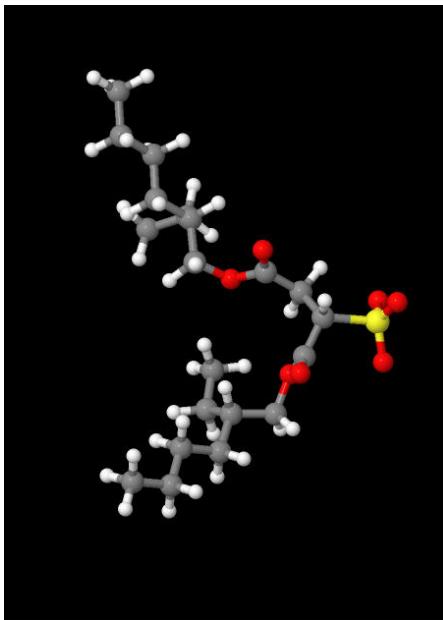


# *AOT reverse micelle*

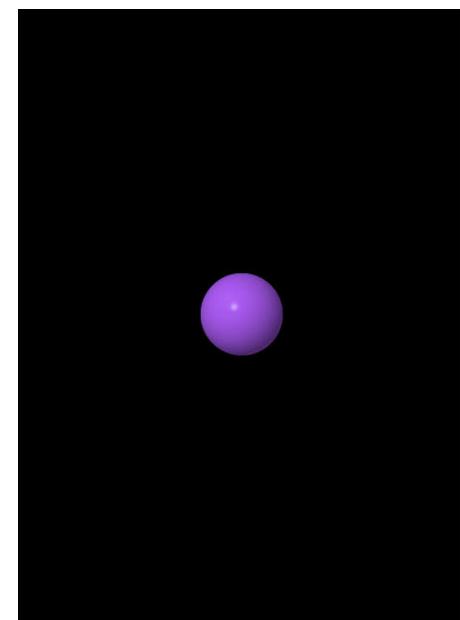
6 Isooctane :



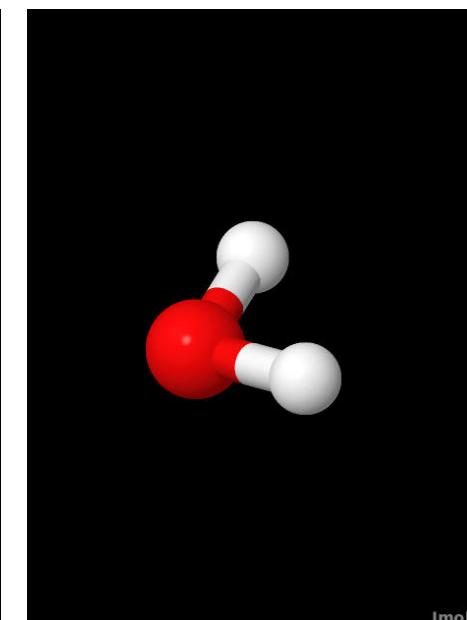
1 AOT :



1 Na :



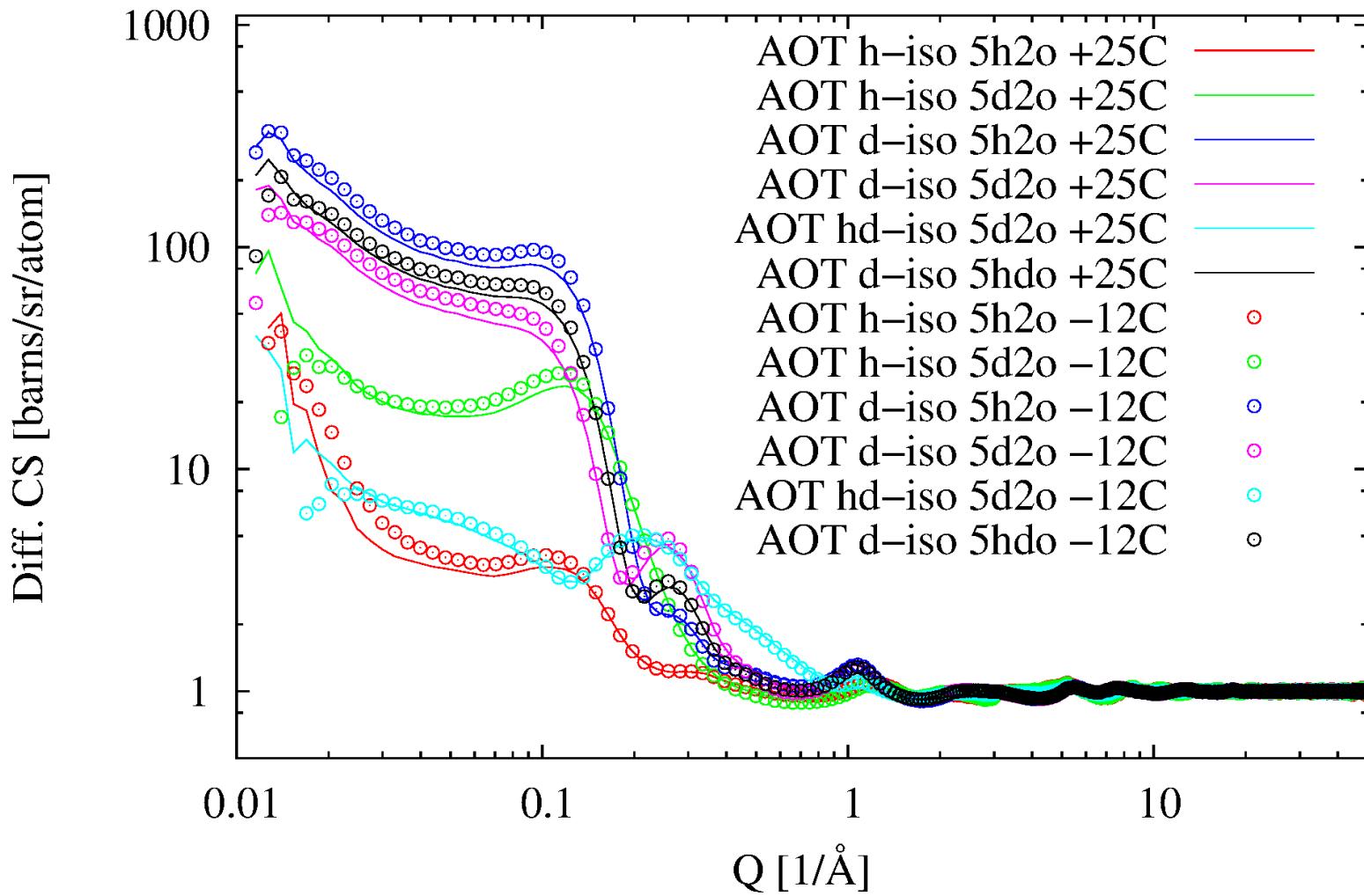
5 or 15 H<sub>2</sub>O



- 6 data sets: H:H:H, H:H:D, D:H:H, DHD,  
M:H:D, and D:H:M (iso:AOT:water, M=H+D)
- Acknowledgement: Karen Edler, Bath, U.K.

# *Neutron total scattering data*

NIMROD data



# *Deficiencies of atomistic analysis*

- Missing one order of magnitude of length scale
- Correlations out to at least 20 nm (depends on  $Q_{\min}$ );
- Learn nothing about micelle-micelle correlation
- Need box  $\sim 10 \times$  larger;
- Need  $\sim 1000 \times$  more atoms.

# *Coarse Grain EPSR simulation of AOT Reverse Micelle*

- 208 (6:1:5) or 63 (6:1:15) 'q' atoms to represent centre of micelles;
- 9600 iso-octane spheres, each representing 8 iso-octane molecules;
- 3200 AOT spheres, each representing 4 AOT molecules;
- 50 Na (neutral) spheres, each representing 256 Na atoms;
- 1000 or 3000 water spheres, each representing 64 water molecules;
- Total: 14,058 or 15,913 spheres – still not a small system
- Box size  $\sim$ 32.75 nm – minimum  $Q \sim 0.2 \text{ nm}^{-1}$ ;
- Maximum  $Q \sim 10 \text{ nm}^{-1}$ ;
- Equivalent to  $\sim 3.03 \times 10^6$  atoms.

# *Only weakly interacting...*

- Exponential repulsive force possible:

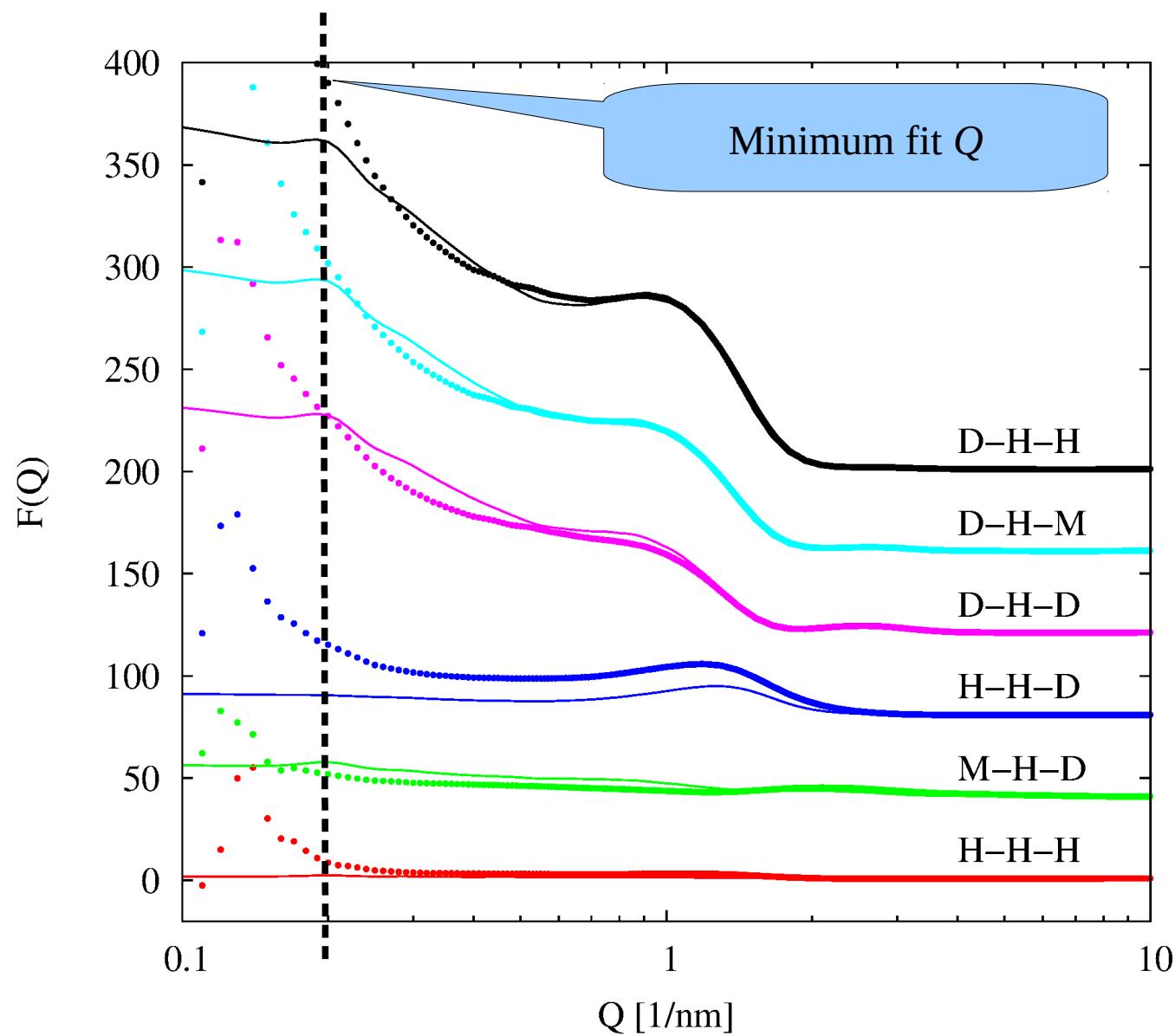
$$U_{\alpha\beta}^{(ref)}(r) = C_{\alpha\beta}^{(0)} \exp\left(\frac{1}{w_{\alpha\beta}^{(0)}}(r_{\alpha\beta}^{(0)} - r)\right)$$

- Container force - restricts maximum separation:

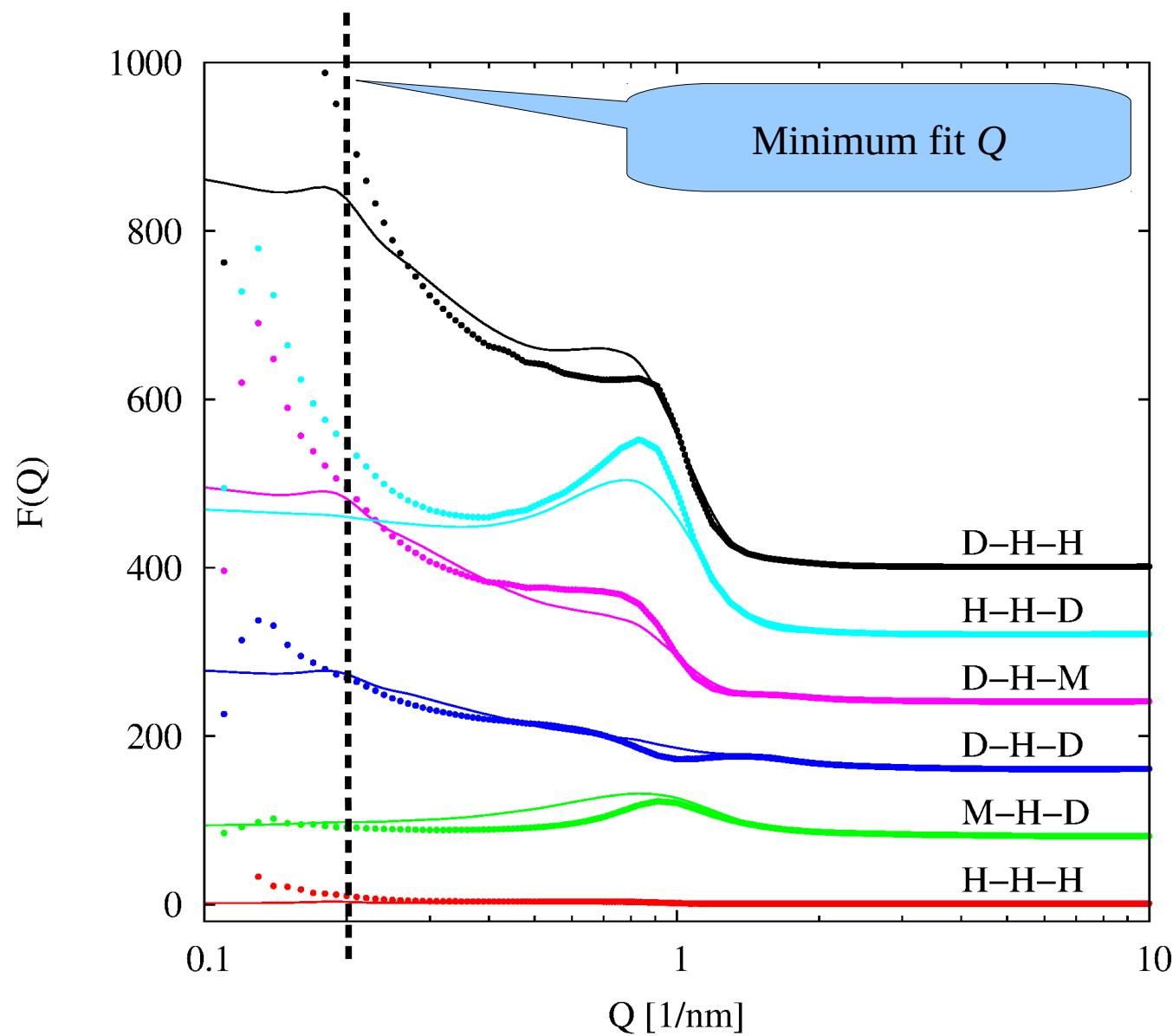
$$U_{\alpha\beta}^{(ref)}(r) = C_{\alpha\beta}^{(c)} \exp\left(\frac{1}{w_{\alpha\beta}^{(c)}}(r - r_{\alpha\beta}^{(c)})\right); \quad r_{\alpha\beta}^{(c)} < r - w_{\alpha\beta}^{(c)}$$

- Constrained AOT to 1.4 or 2.8 nm, and iso-octane to 2.0 or 3.4 nm, OUTSIDE micelle
- Constrained water to within 1.6 or 3.0 nm of centre of micelle (Q atom)

# *RM 6:1:5 data and CG-EPSR fit*

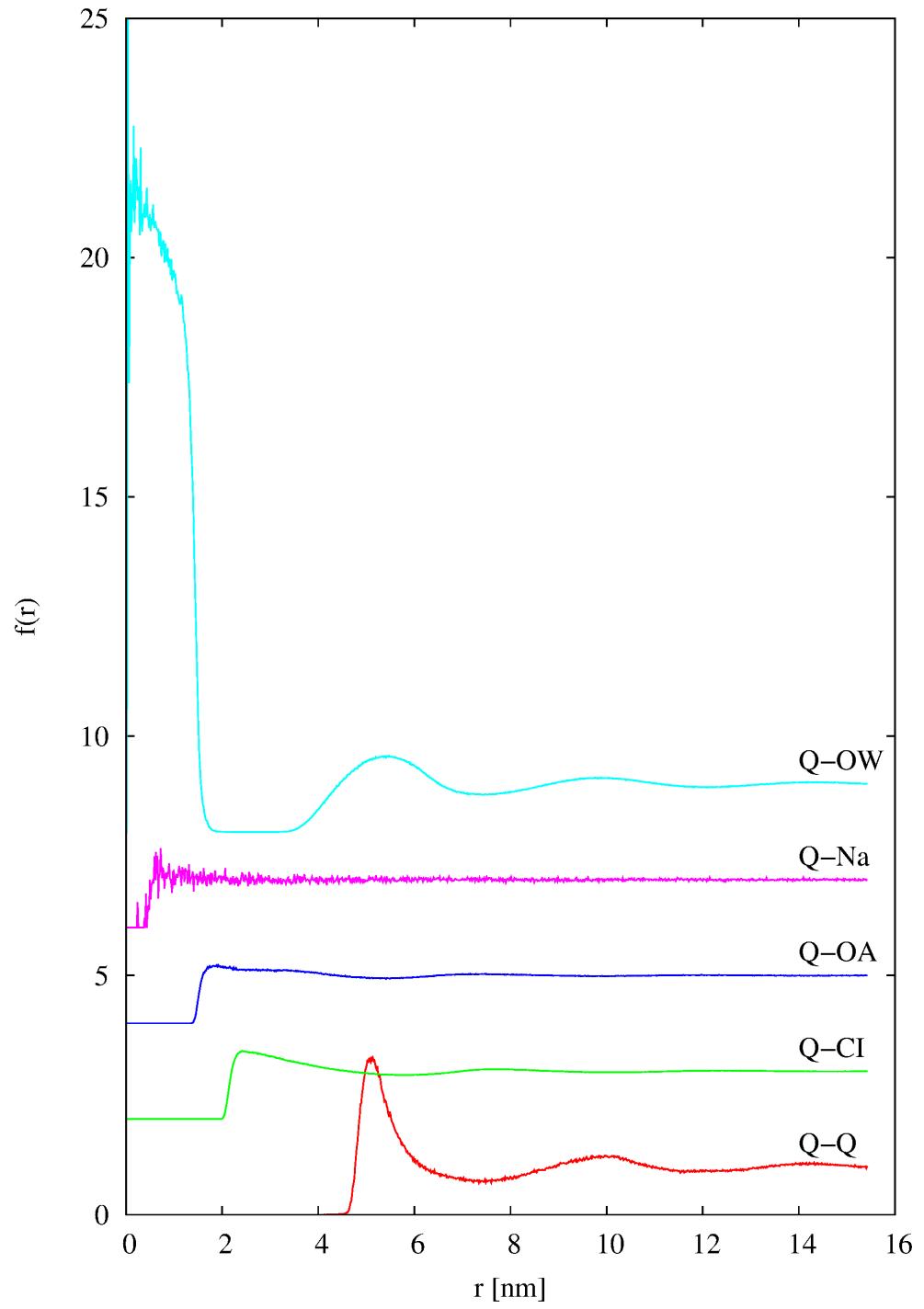


# *RM 6:1:15 data and CG-EPSR fit*



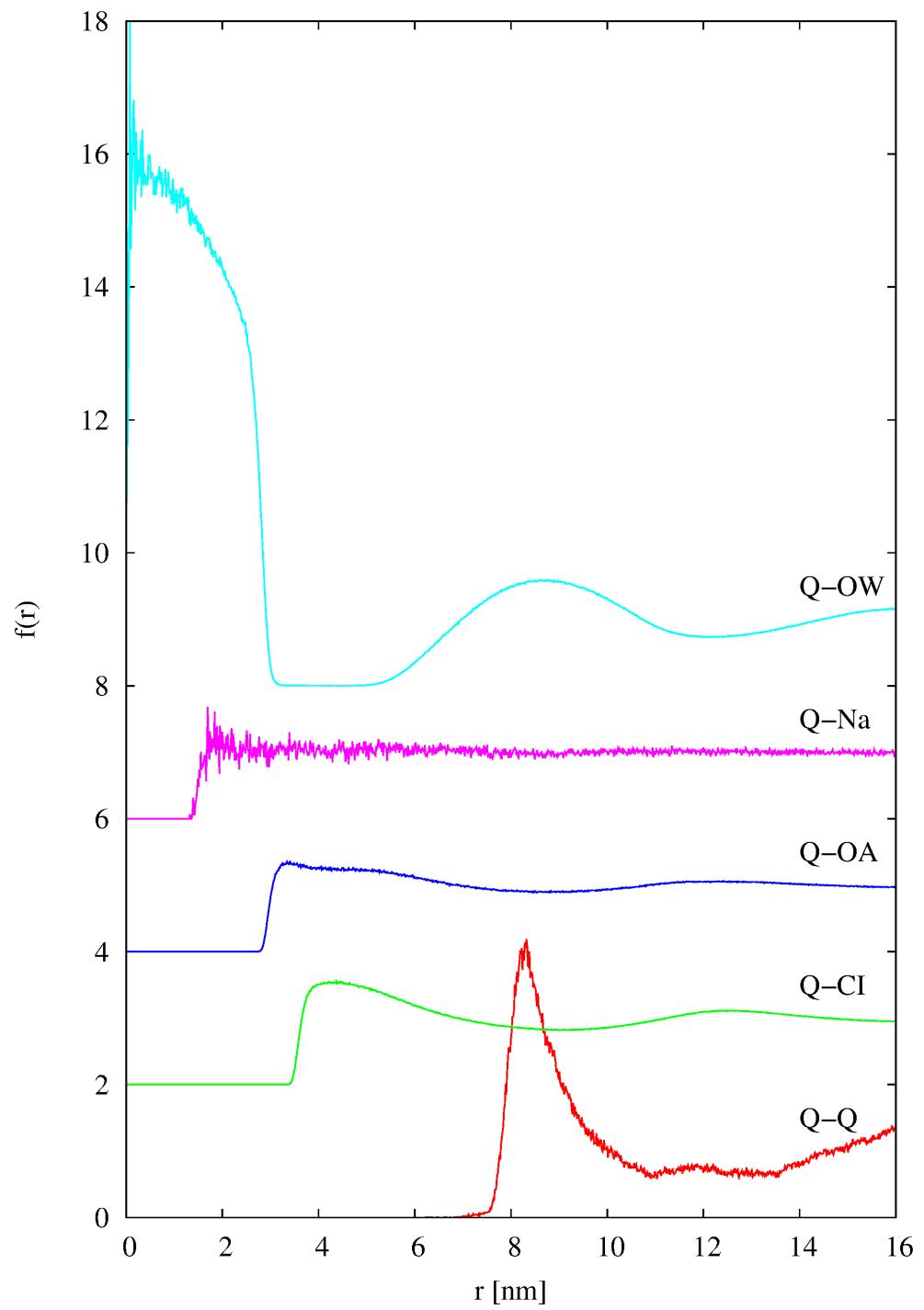
# *RM 6:1:5*

## *interfacial density distribution*

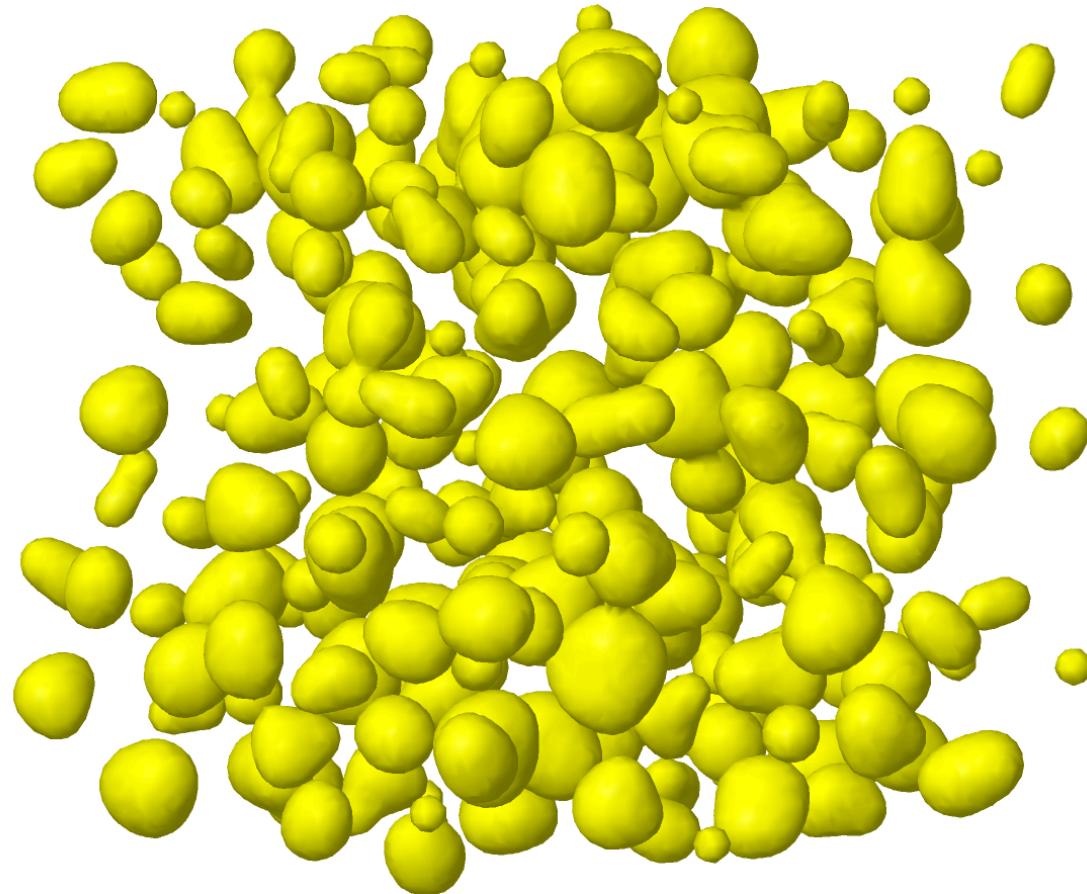


**RM 6:1:15**

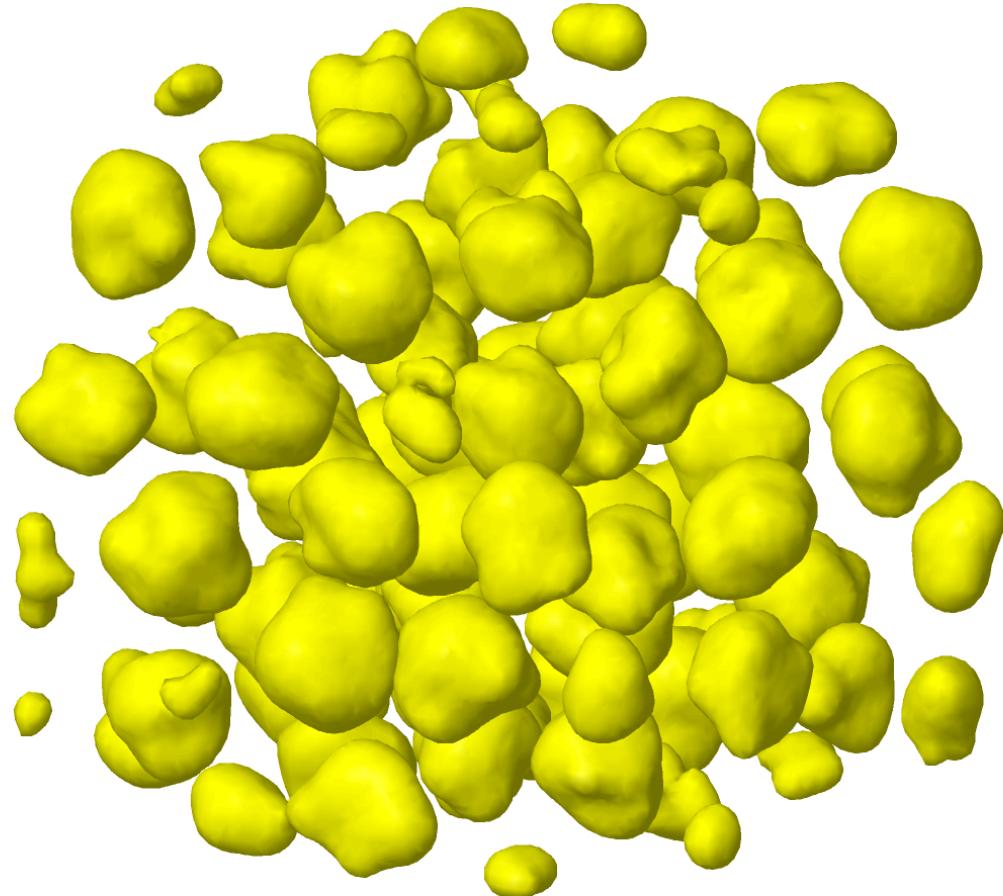
*interfacial  
density  
distribution*



# *RM 6:1:5 - water distribution*



# *RM 6:1:15 - water distribution*



# *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  $\chi^2$  (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)*

- Method is being used in increasingly complex, partially crystalline systems.
- Coarse-graining is being introduced to address larger scale structures.

Thank you for your attention!