

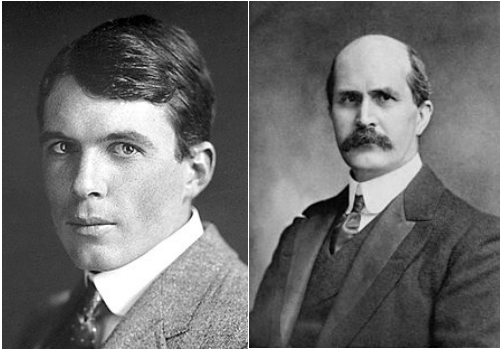
Wide Angle Scattering and Pair Distribution Functions

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The University of Manchester
@k_edkins

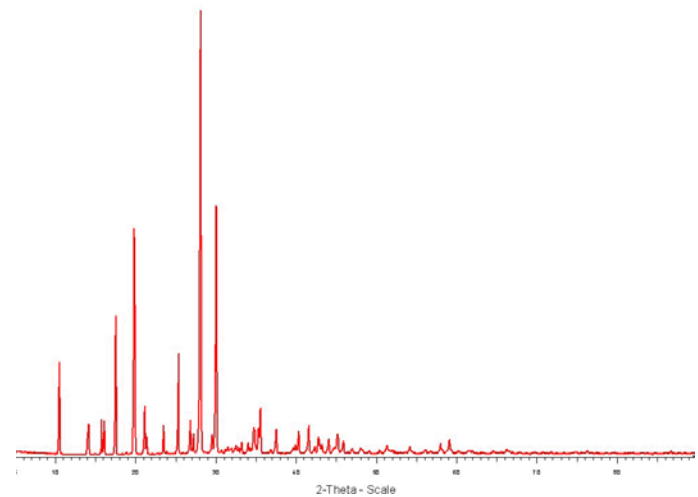
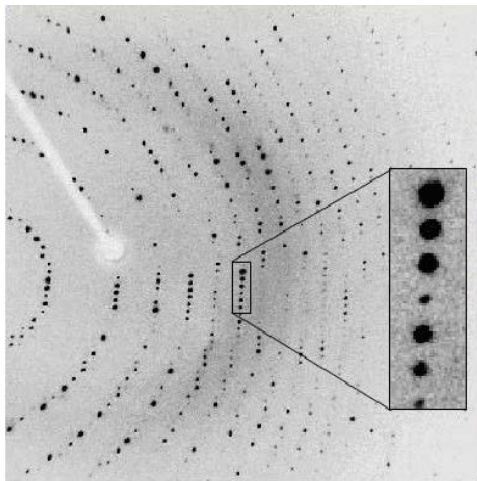
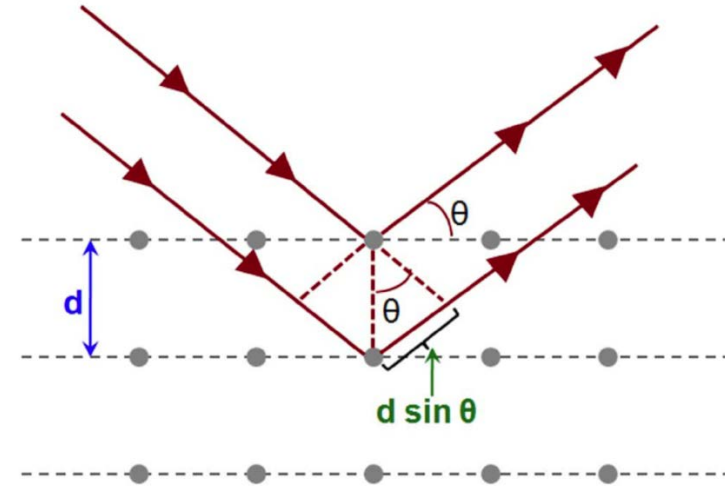
Overview

- Diffraction
 - What are the effects of increasing disorder?
- Small vs wide angle scattering
- Pair distribution function
- Examples

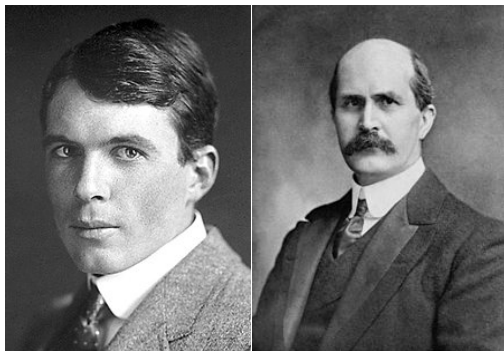
Diffraction



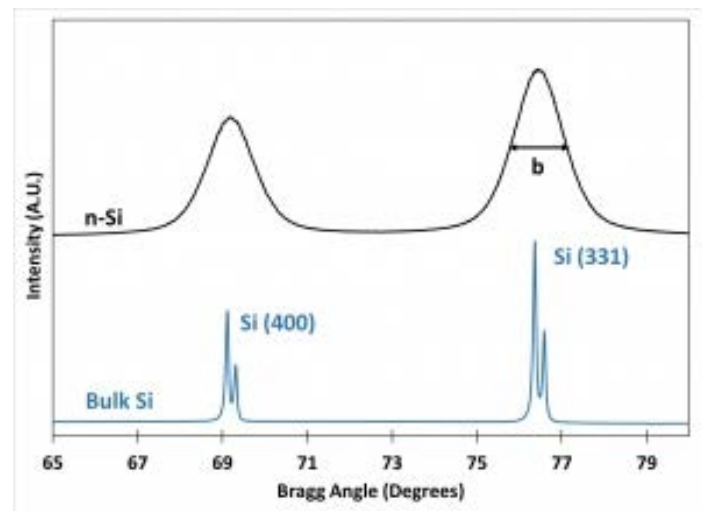
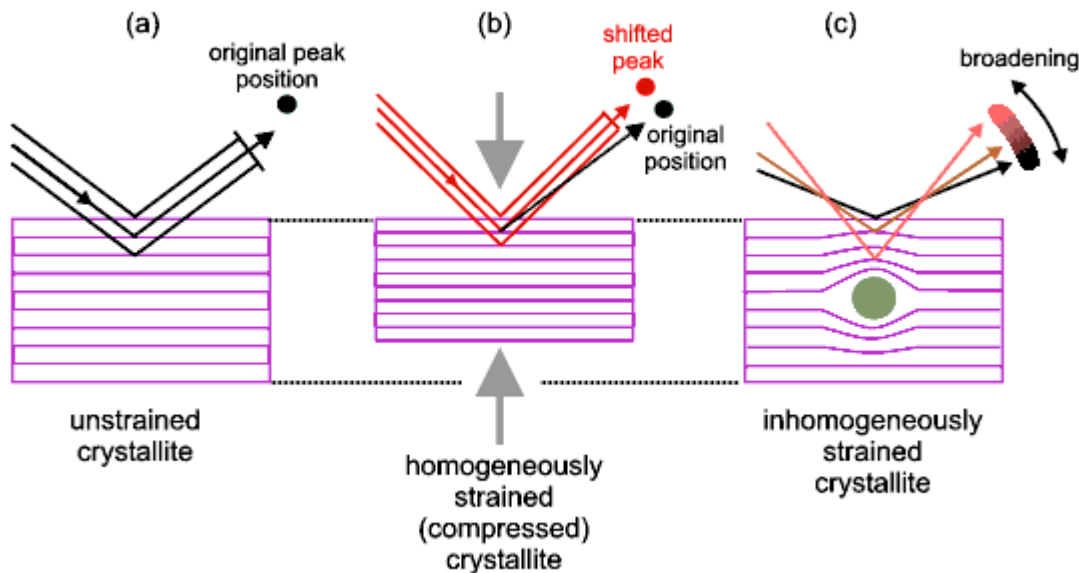
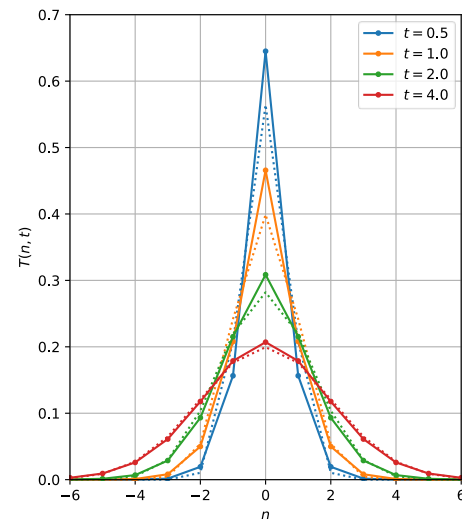
$$n\lambda = 2d \sin(\theta)$$



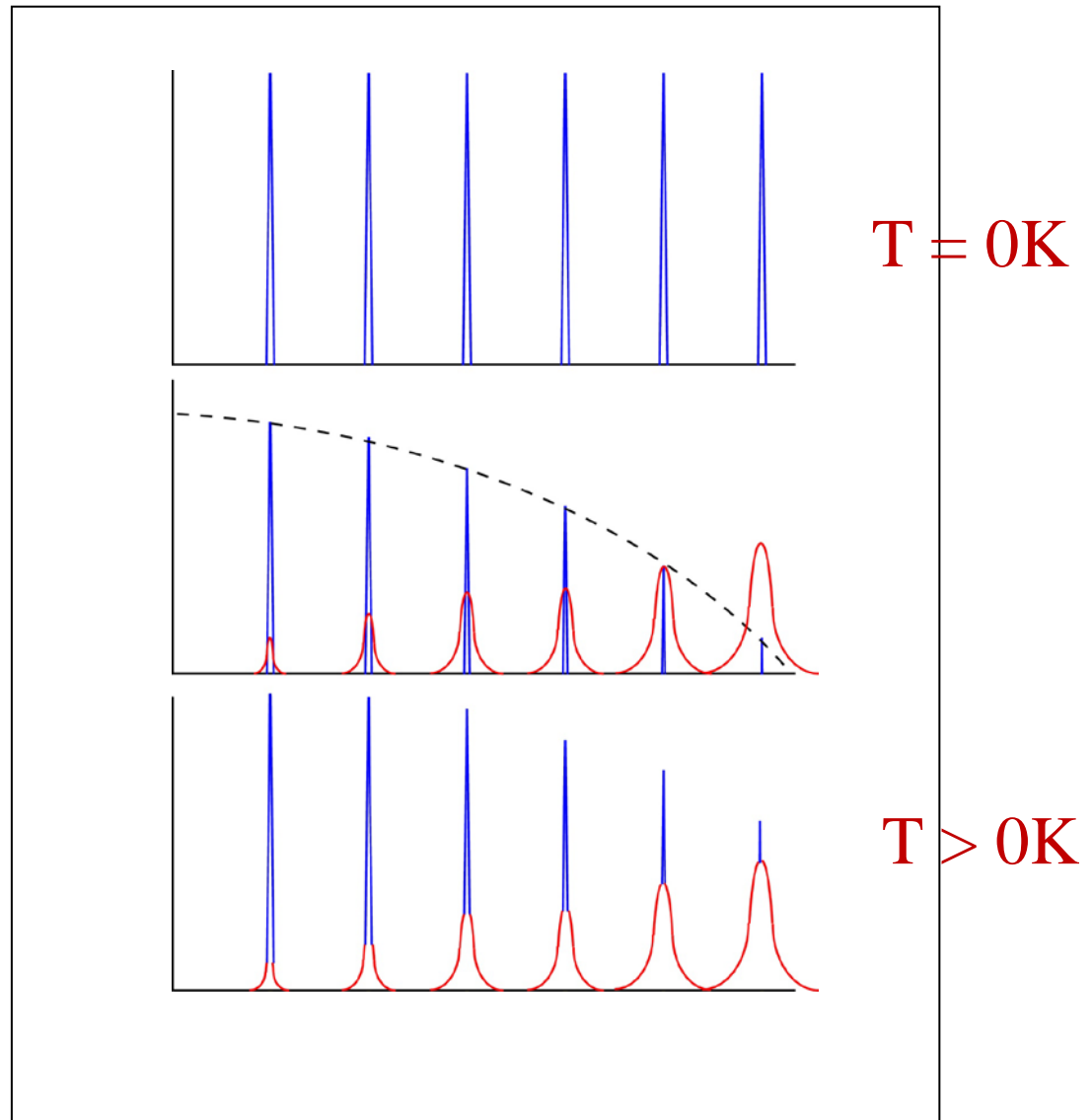
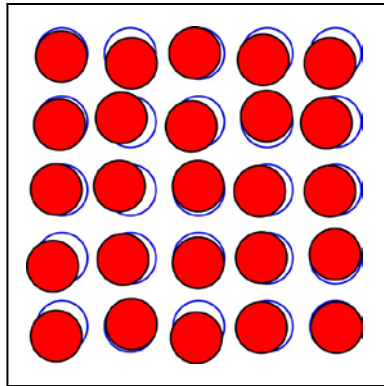
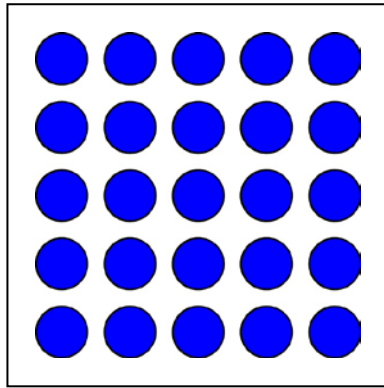
Diffraction



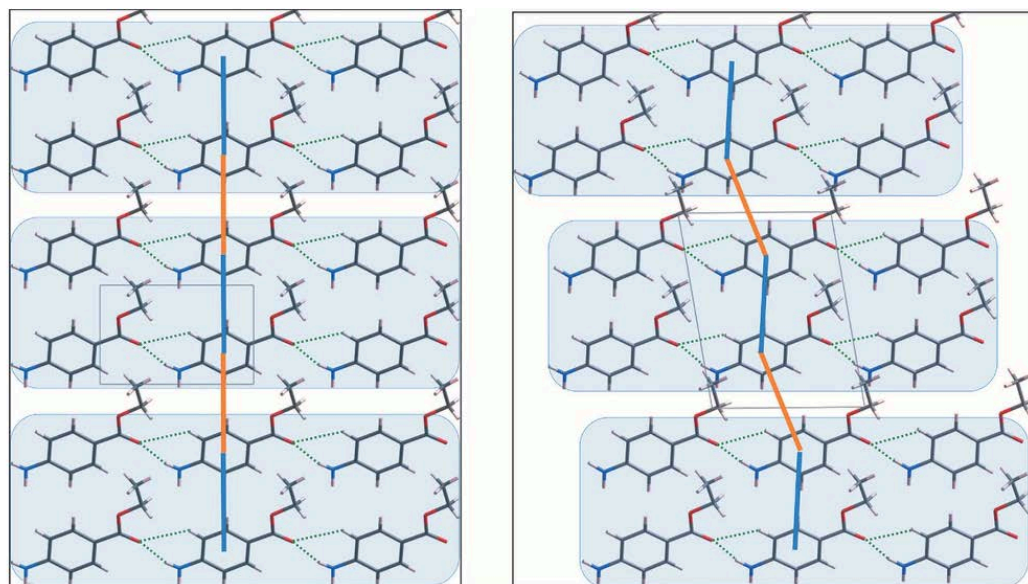
$$n\lambda = 2d \sin(\theta)$$



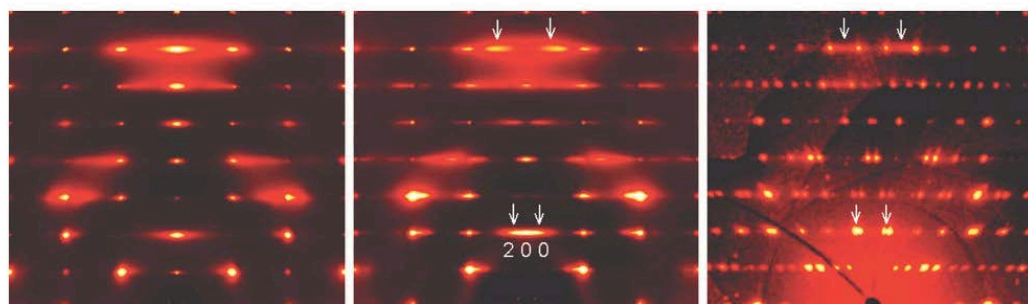
The effect of temperature



The effect of dislocation



(a)



I

II

III

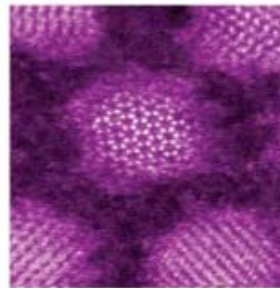
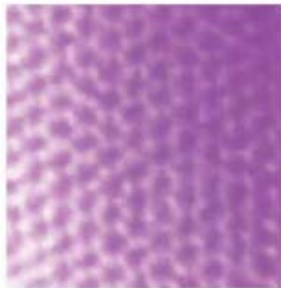
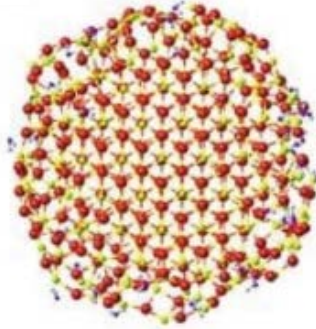
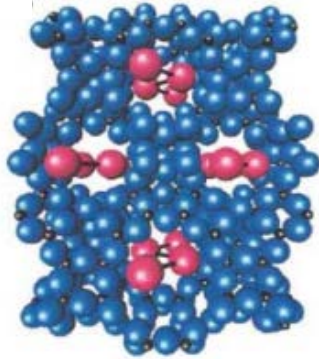
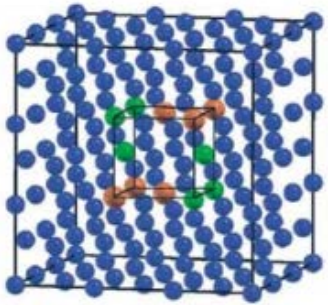
(b)

Single-crystal diffuse scattering studies on polymorphs of molecular crystals. I. The room-temperature polymorphs of the drug benzocaine.

E.J. Chan, T.R. Welberry, D.J. Goossens, A.P. Heerdegen, A. Beasley, P.J. Chupas

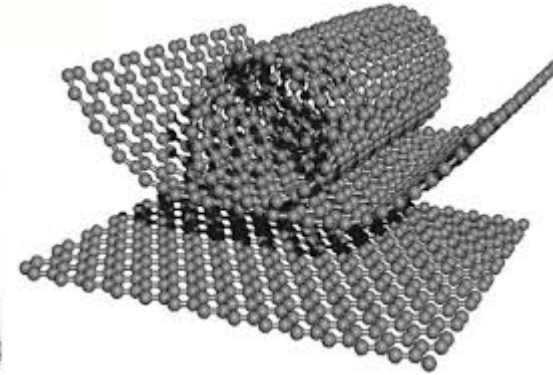
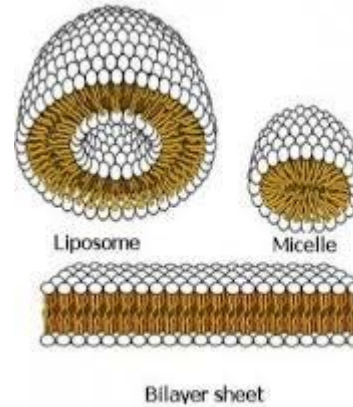
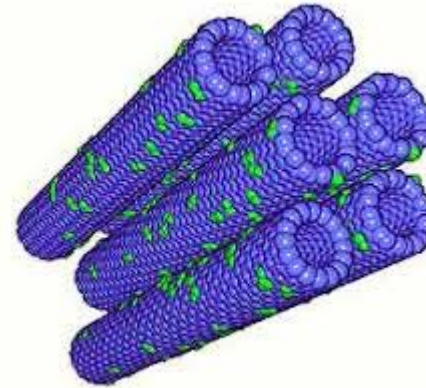
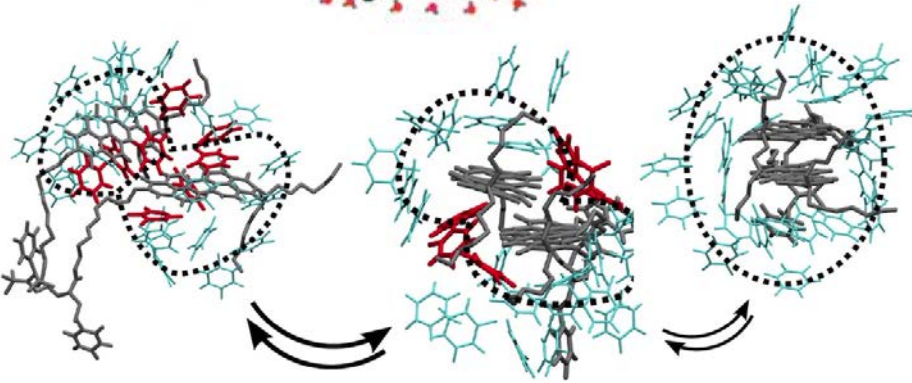
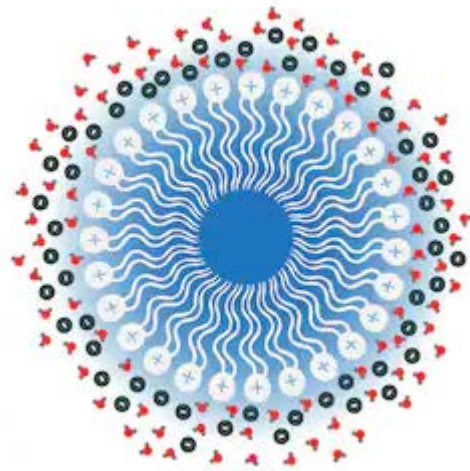
DOI:10.1107/S0108768109015857

Nanoscale structure



Wide vs small angle scattering

Wide Angle Scattering $< 10^{-9}$ m

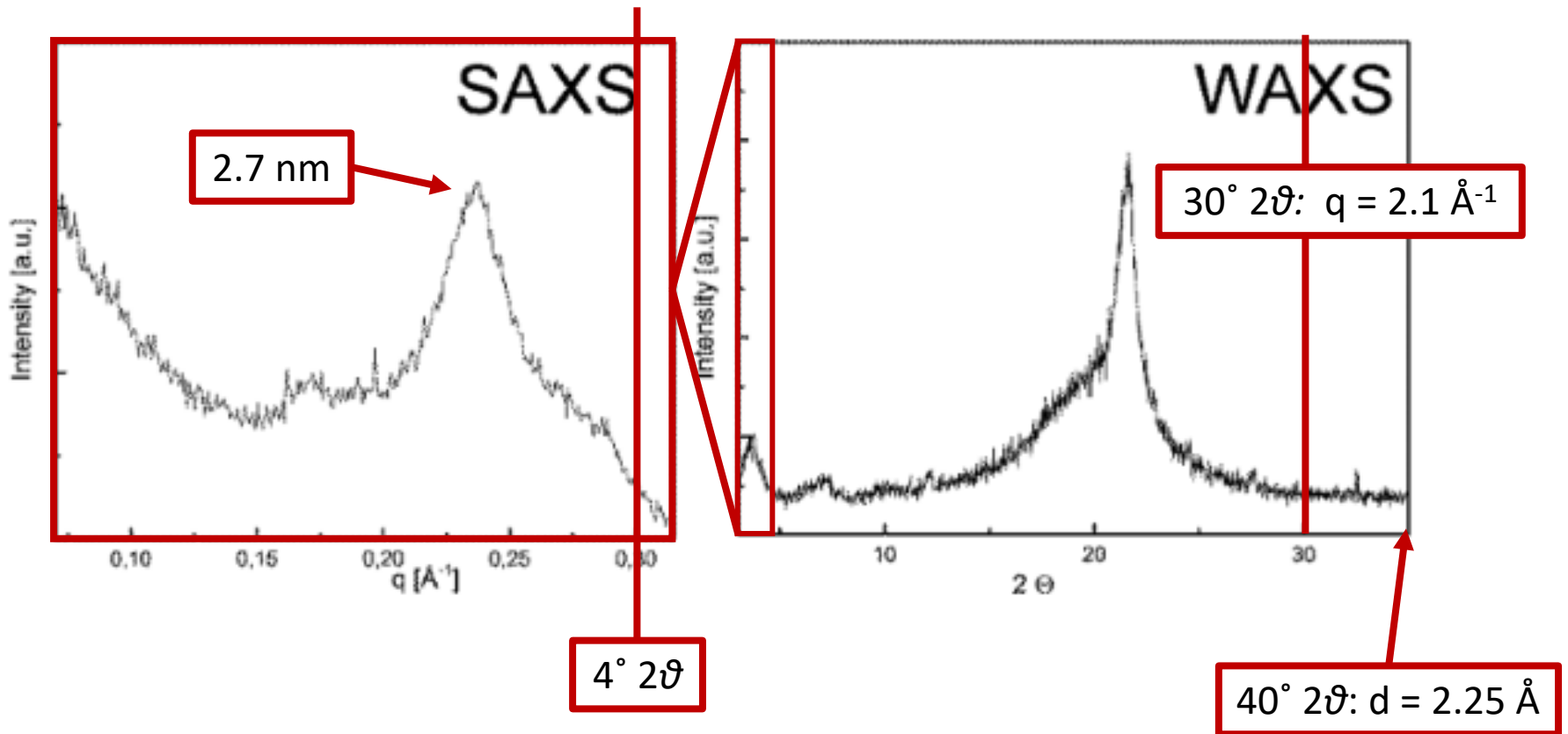


Small Angle Scattering $> 10^{-9}$ m

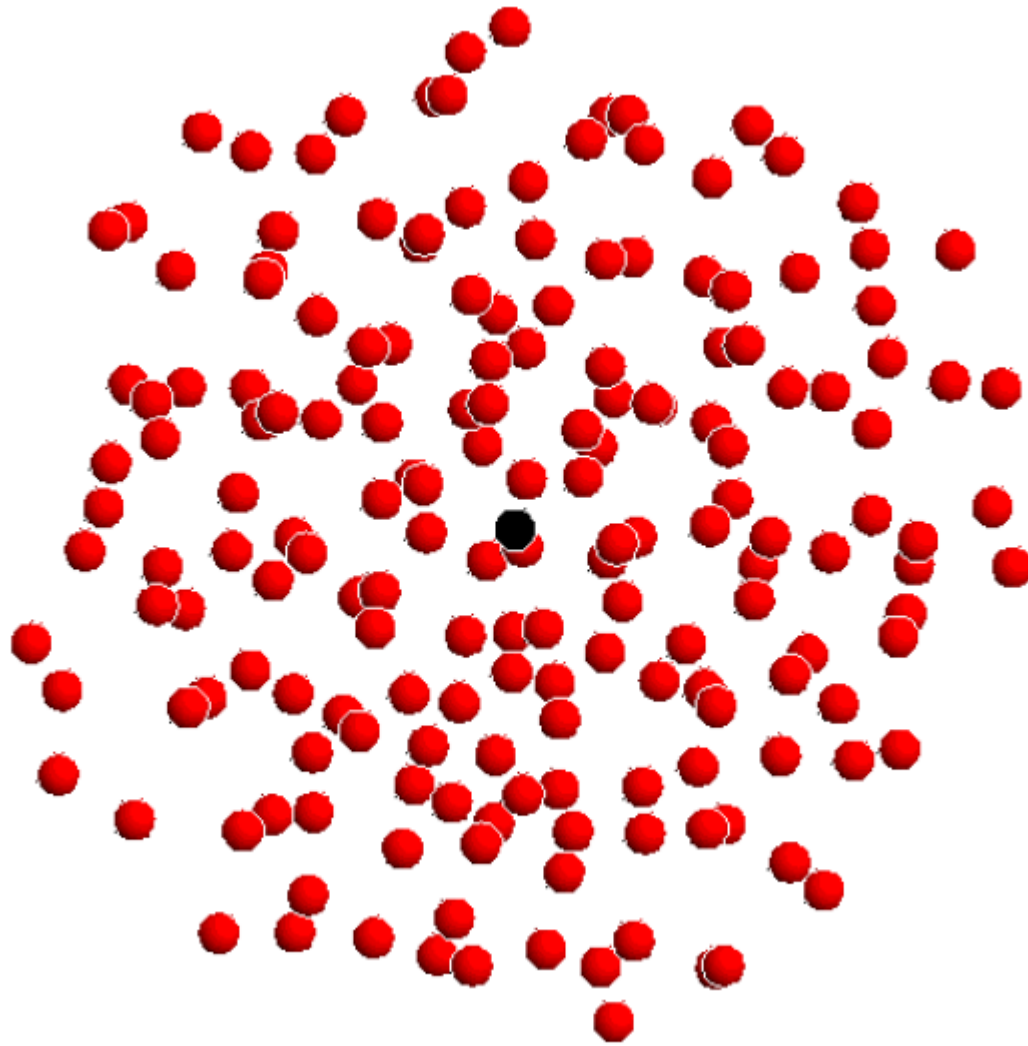
Wide vs small angle scattering

$$q = \frac{4\pi\sin(\theta)}{\lambda}$$

Amorphous poly(phosphoamidate), data acquired with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$)

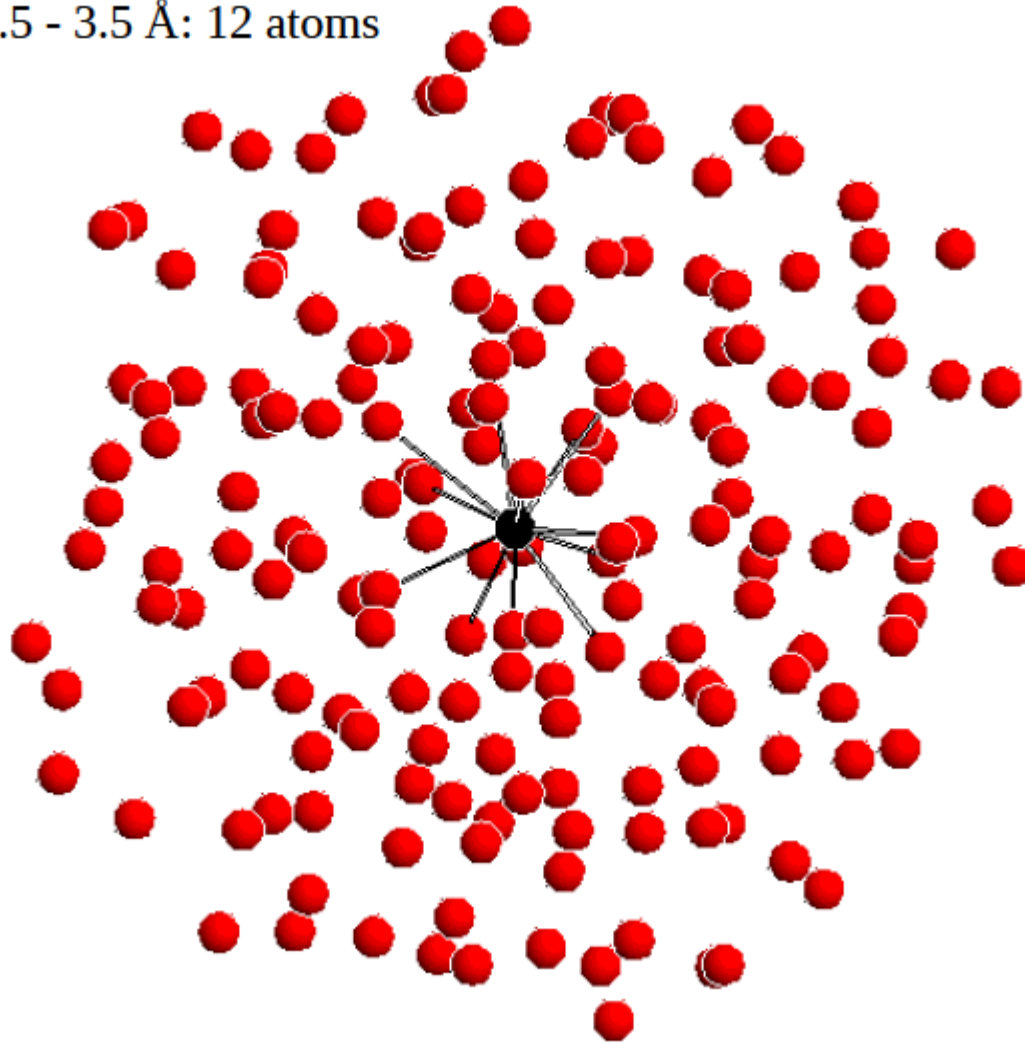


Pair distribution function



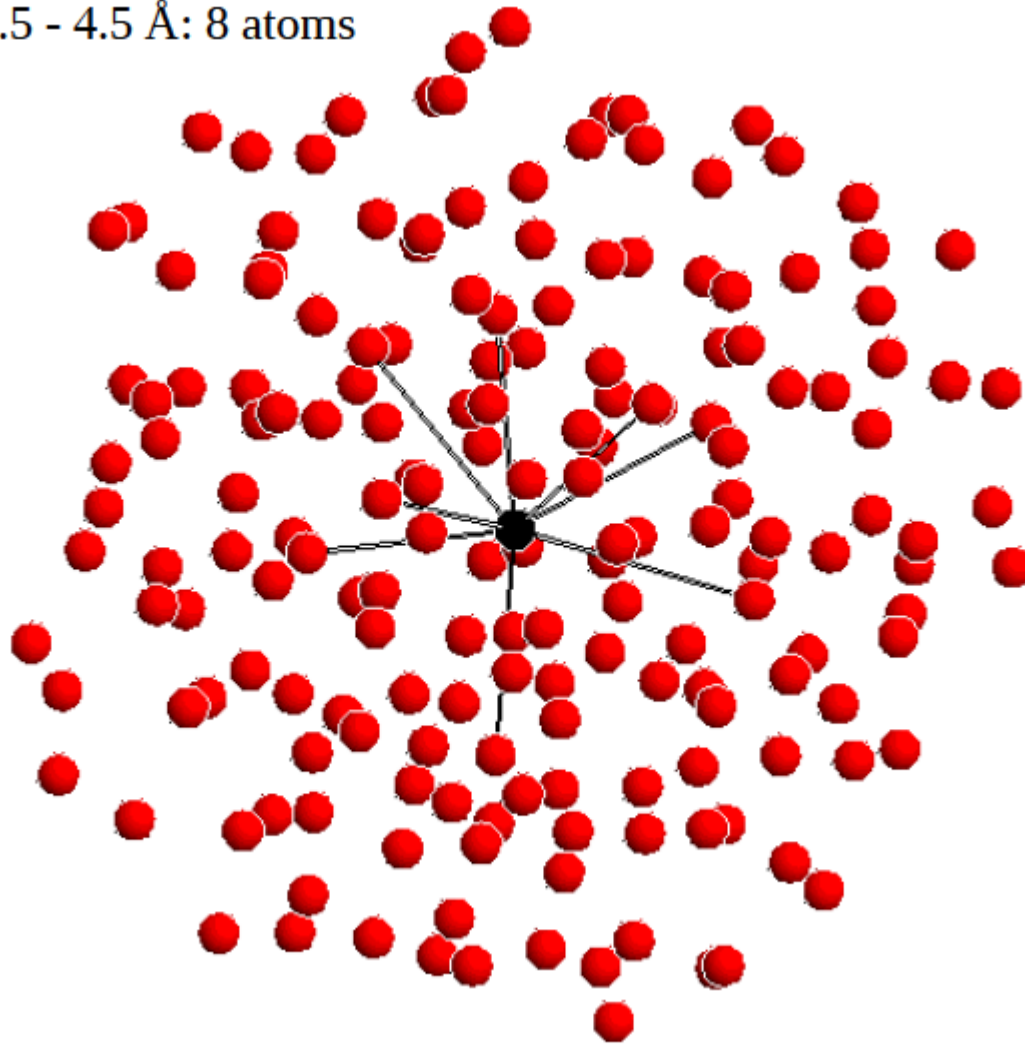
Pair distribution function

2.5 - 3.5 Å: 12 atoms



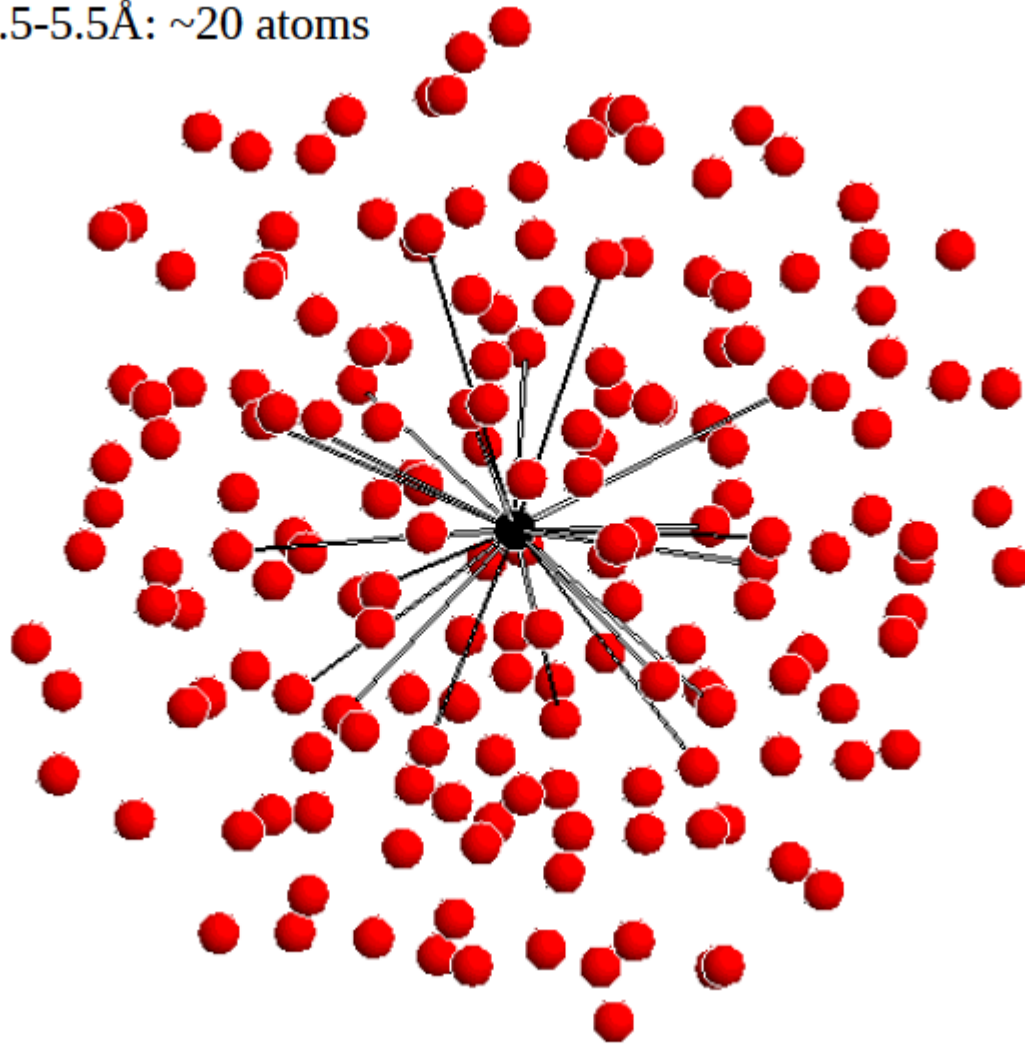
Pair distribution function

3.5 - 4.5 Å: 8 atoms



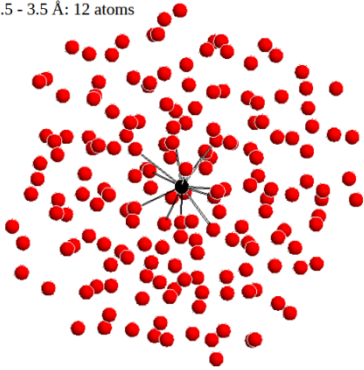
Pair distribution function

4.5-5.5Å: ~20 atoms

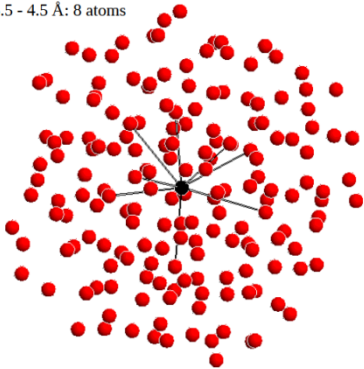


Pair distribution function

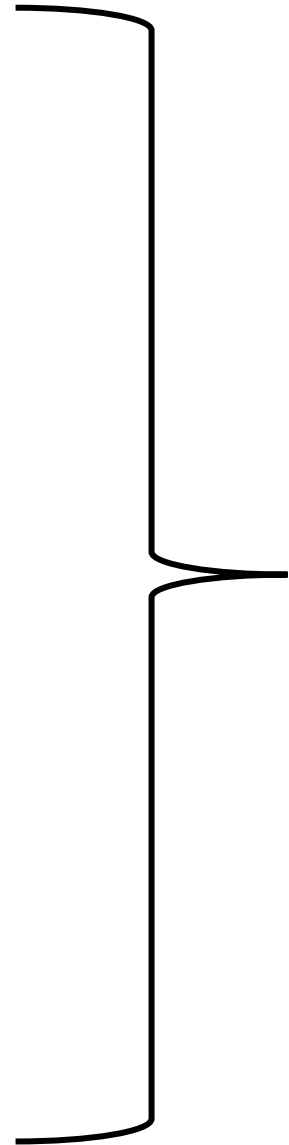
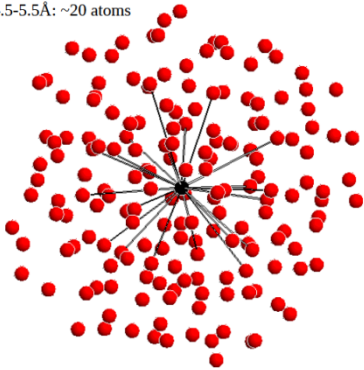
2.5 - 3.5 Å: 12 atoms



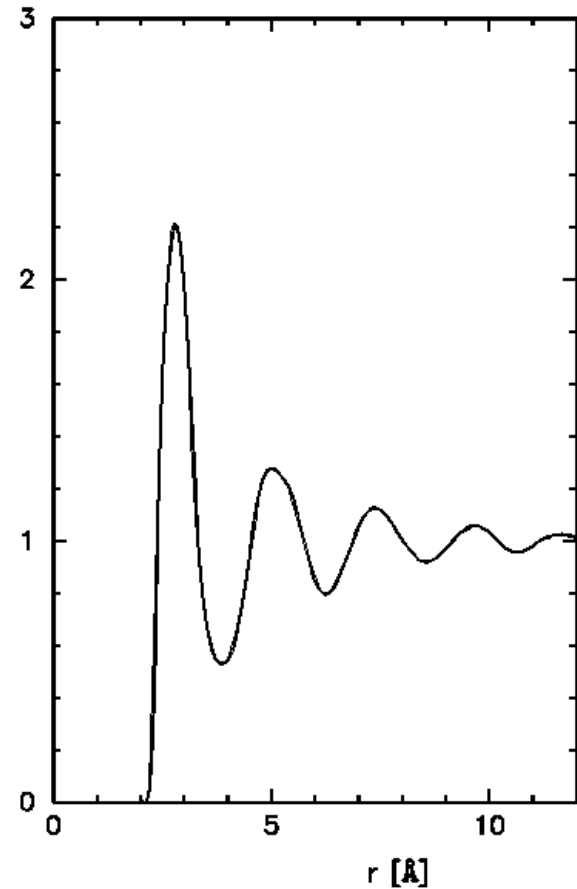
3.5 - 4.5 Å: 8 atoms



4.5-5.5Å: ~20 atoms

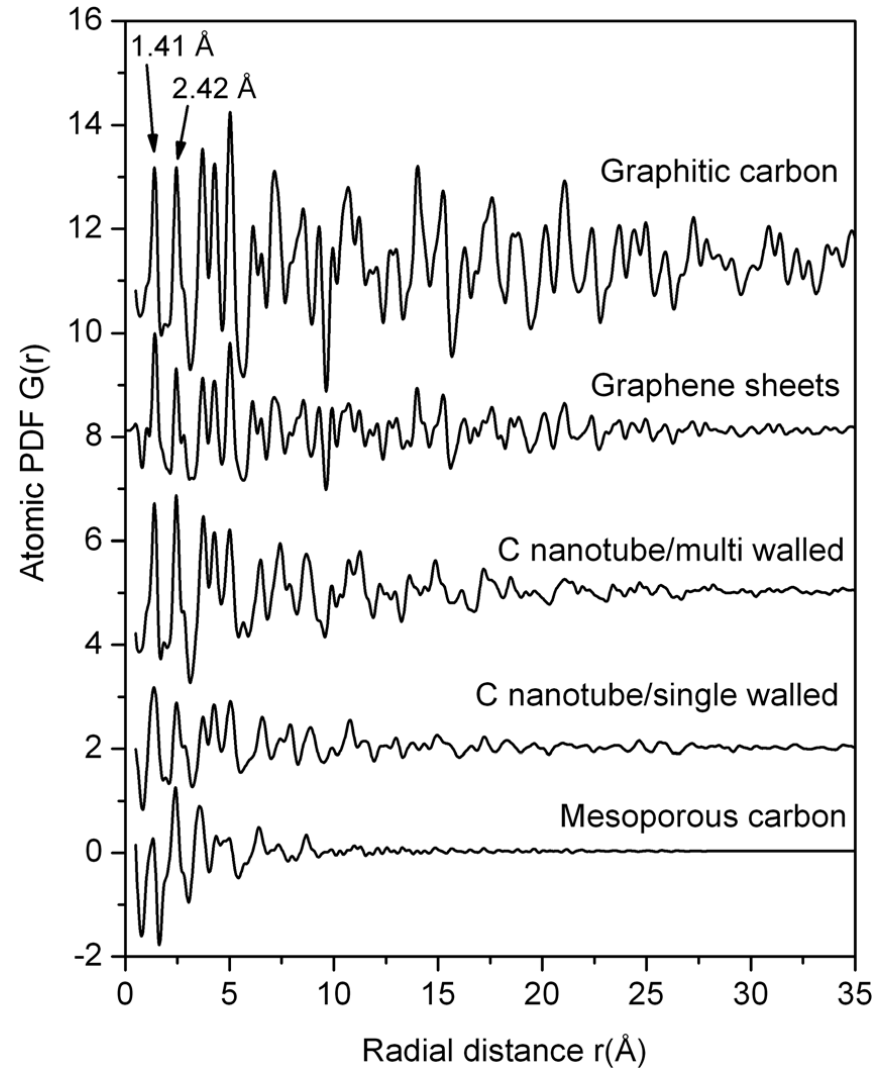


A "typical" liquid $g(r)$



Pair distribution function

$$g(r) = \frac{1}{\rho} \left(\sum_{i \neq 0} \delta(r - r_i) \right)$$
$$= V \frac{N - 1}{N} (\delta(r - r_1))$$



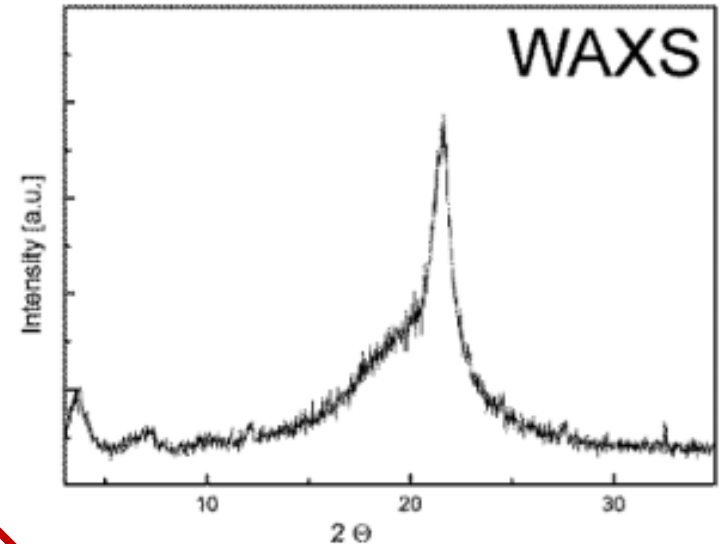
Pair distribution function

Measurement in reciprocal space gives structure factor $F(q)$

$$F(q) = \sum_{i,j} (2 - \delta_{i,j}) c_i c_j b_i b_j S_{i,j}(q)$$

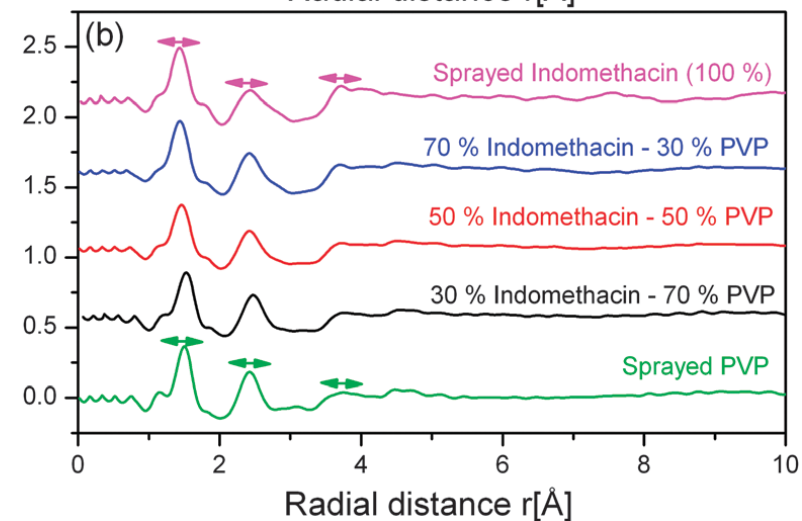
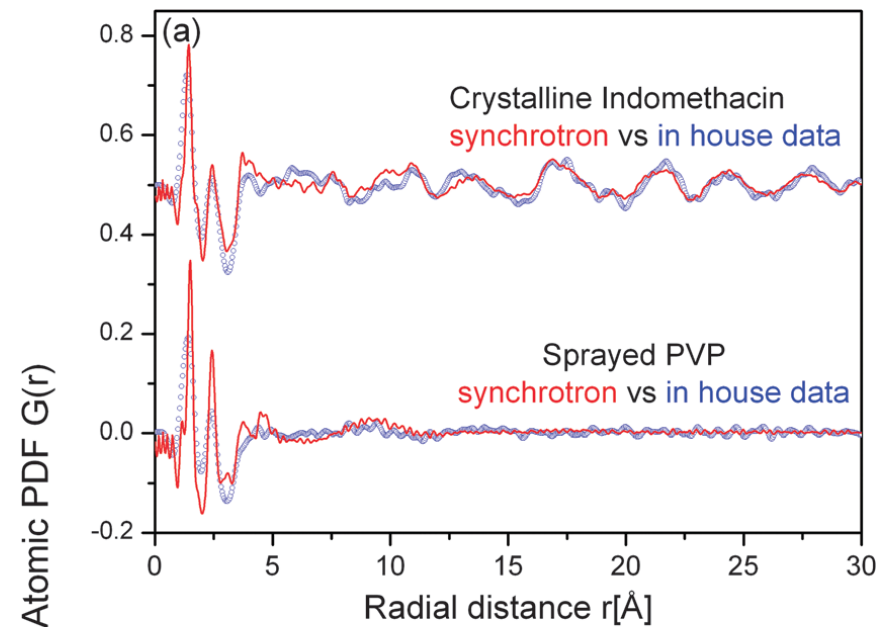
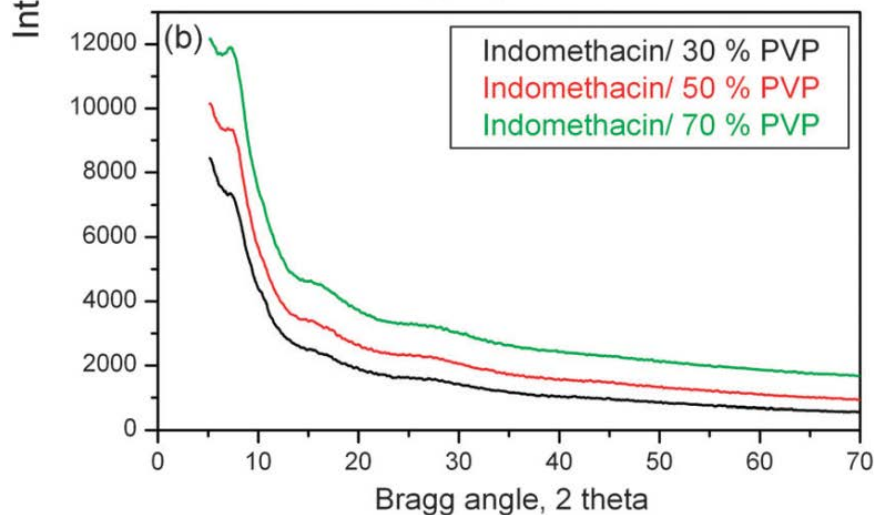
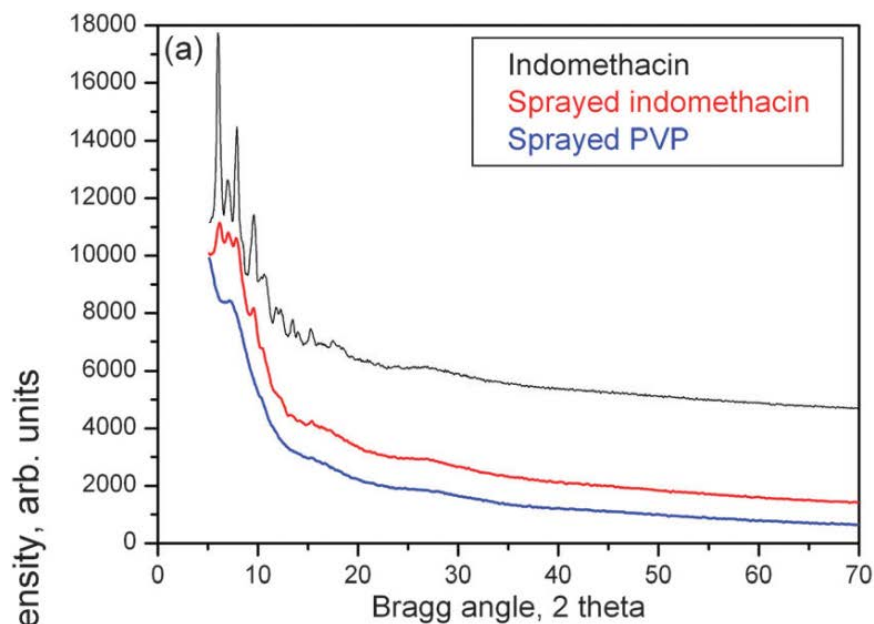
$$S_{i,j}(q) = 1 + \frac{1}{N} \left(\sum_{i \neq j} e^{-iq(r_i - r_j)} \right)$$

$F(q)$ and $S(q)$ are related to respective $g(r)$ by Fourier Transform

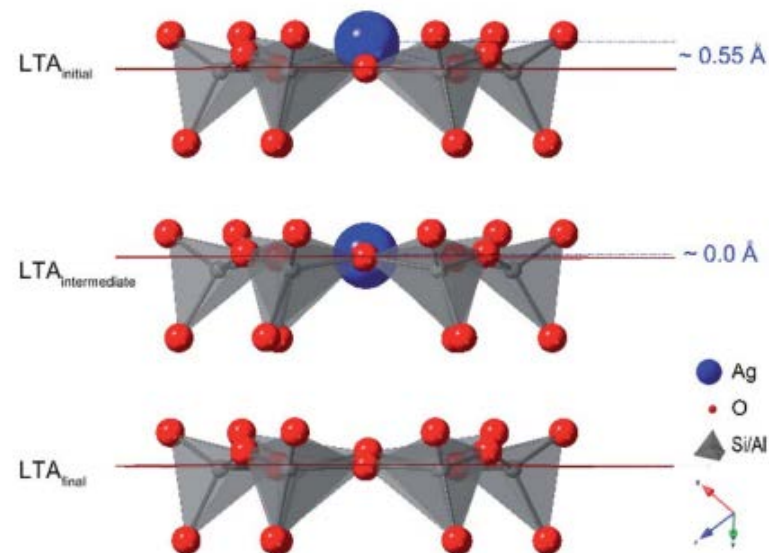
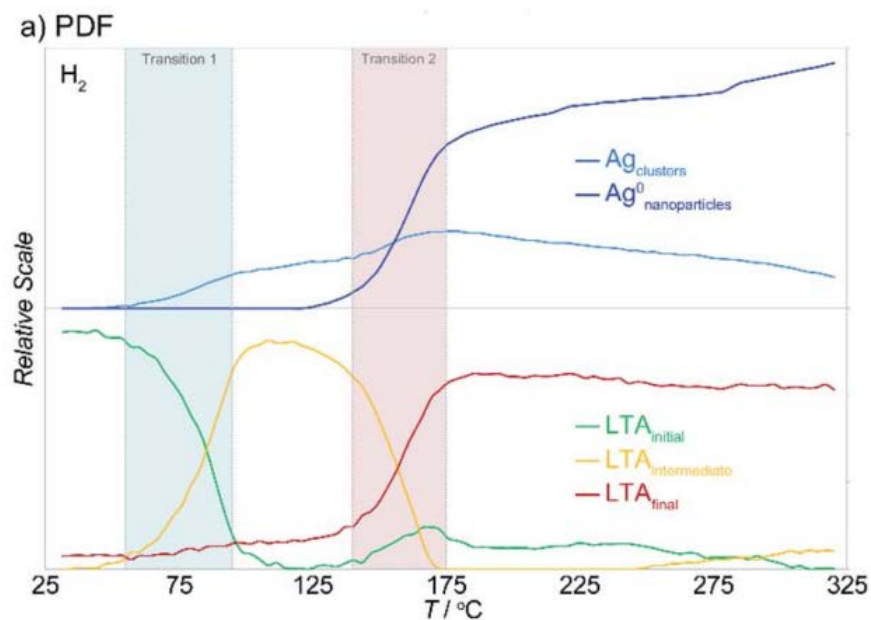
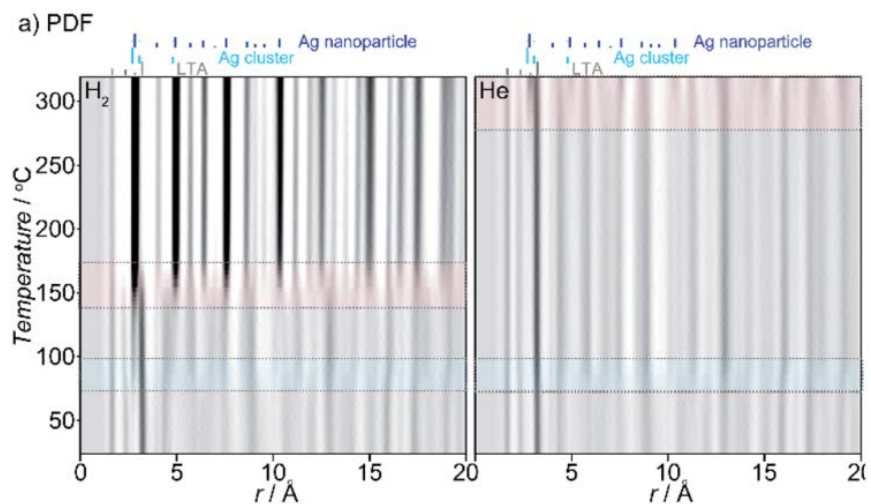


Partial structure factor

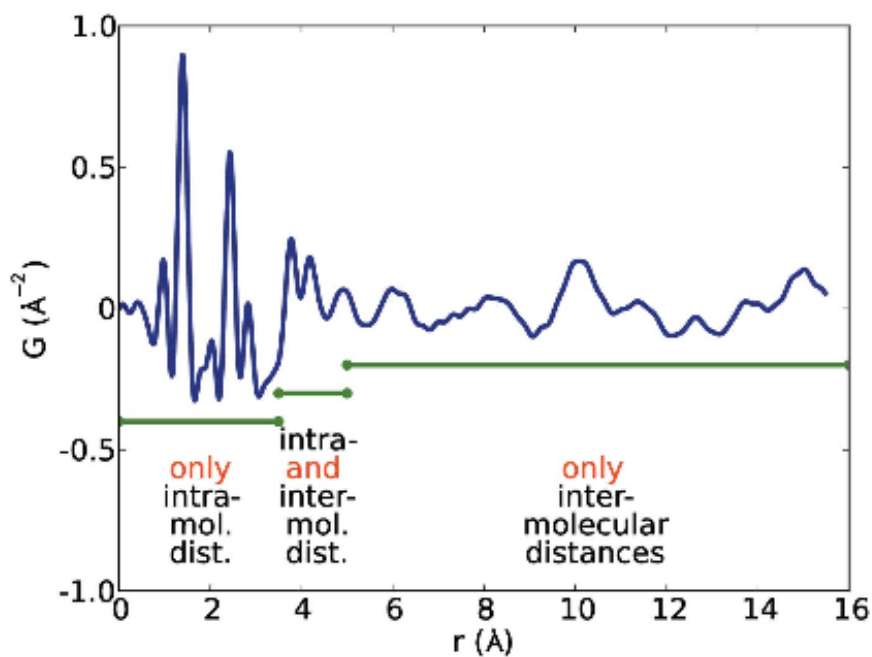
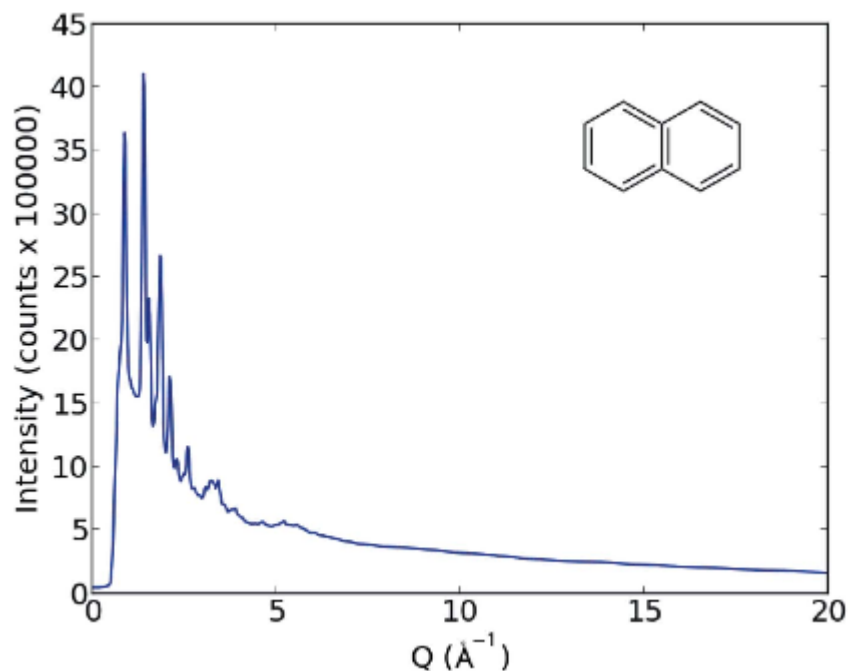
Indomethacin in polymer



Silver nanoparticles in zeolite

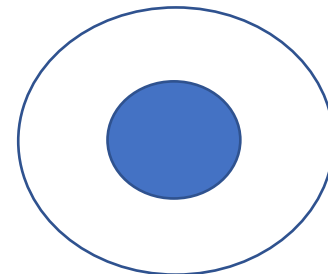
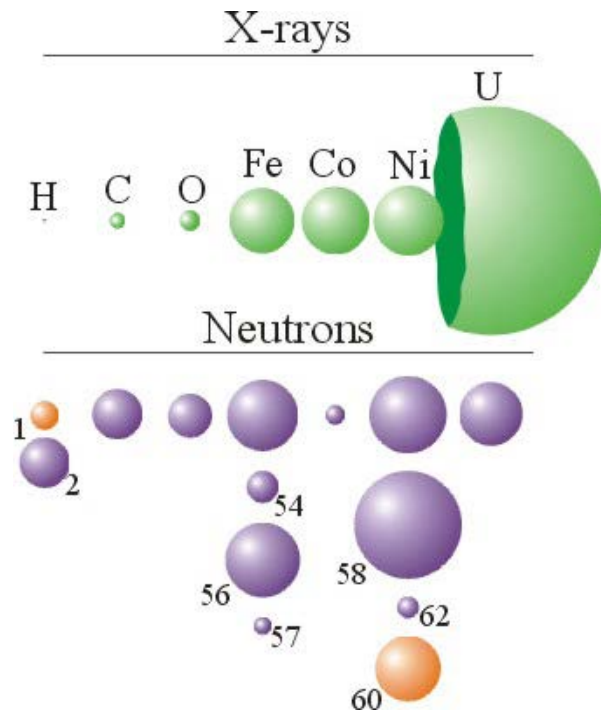


Structure solution from WAXS

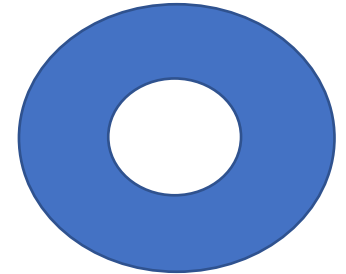


Problem: fitting of too many parameters to one structure factor!

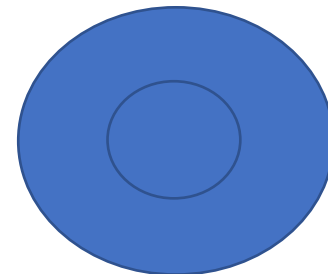
Wide-angle neutron scattering



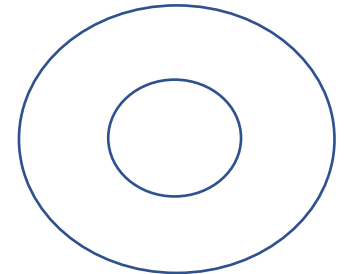
H/D



D/H



H/H



D/D

WANS

$$F(q) = \sum_{i,j} (2 - \delta_{i,j}) c_i c_j b_i b_j S_{i,j}(q)$$

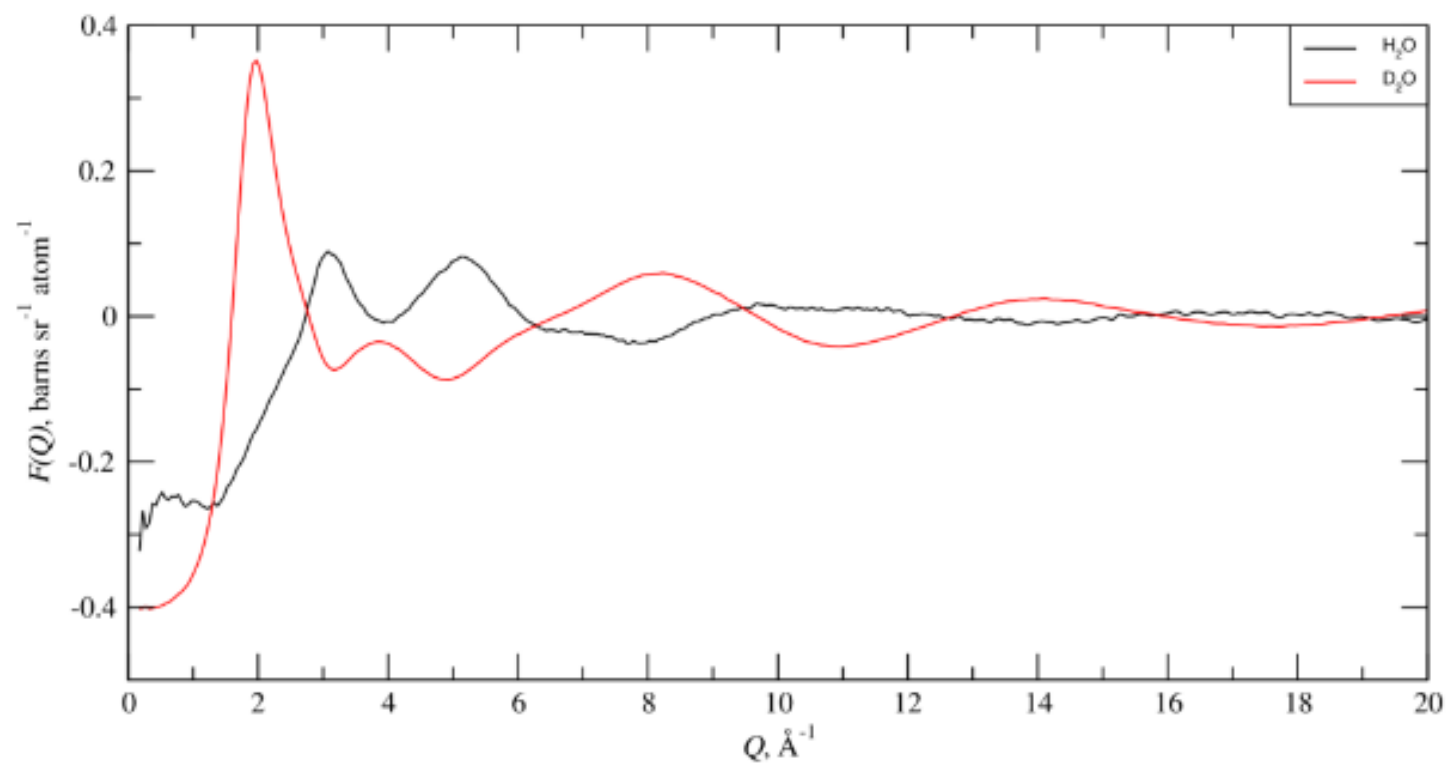
Water

<i>i</i>	<i>j</i>	<i>c_i</i>	<i>c_j</i>	<i>b_i</i> , fm	<i>b_j</i> , fm	<i>c_ic_jb_ib_j</i> = <i>w_{ij}</i> , fm
O	O	1/3	1/3	0.5804	0.5804	0.0374
O	H	1/3	2/3	0.5804	-0.3741	-0.0482
H	H	2/3	2/3	-0.3741	-0.3741	0.0622

Heavy water

<i>i</i>	<i>j</i>	<i>c_i</i>	<i>c_j</i>	<i>b_i</i> , fm	<i>b_j</i> , fm	<i>c_ic_jb_ib_j</i> = <i>w_{ij}</i> , fm
O	O	1/3	1/3	0.5804	0.5804	0.0374
O	D	1/3	2/3	0.5804	0.6674	0.0861
D	D	2/3	2/3	0.6674	0.6674	0.1980

WANS

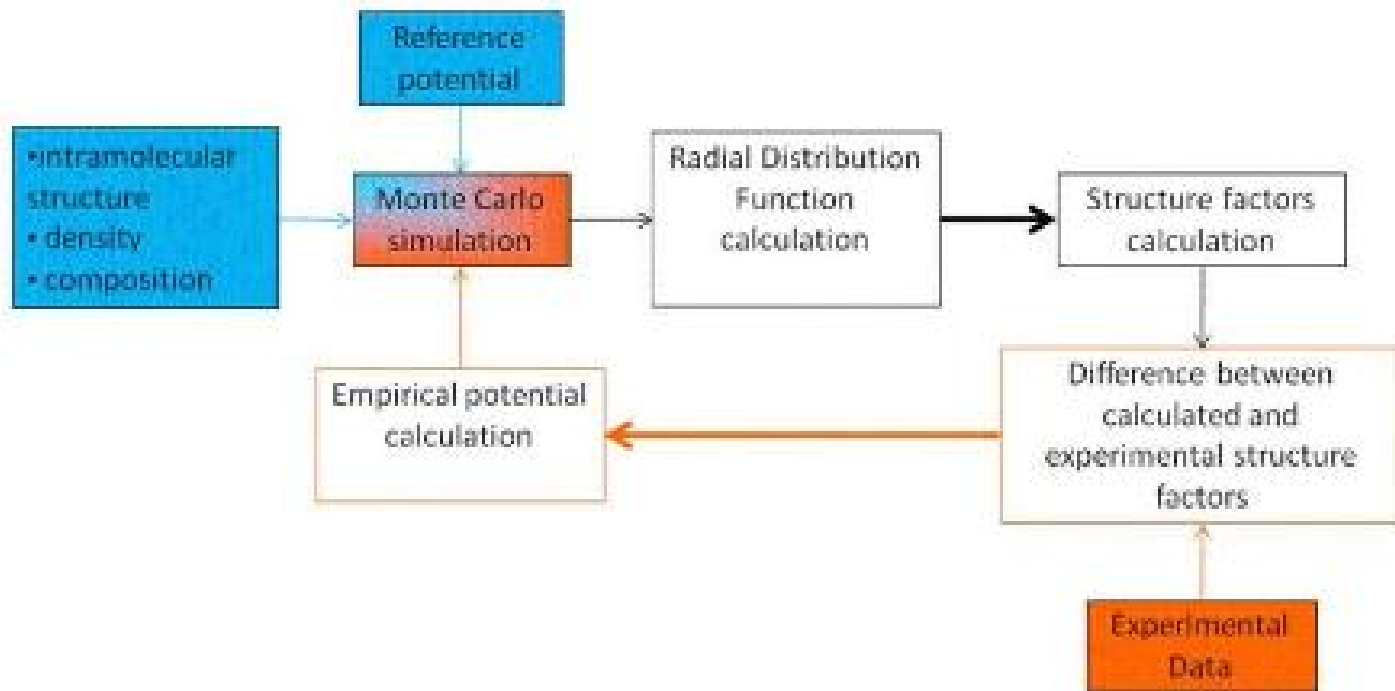


WANS

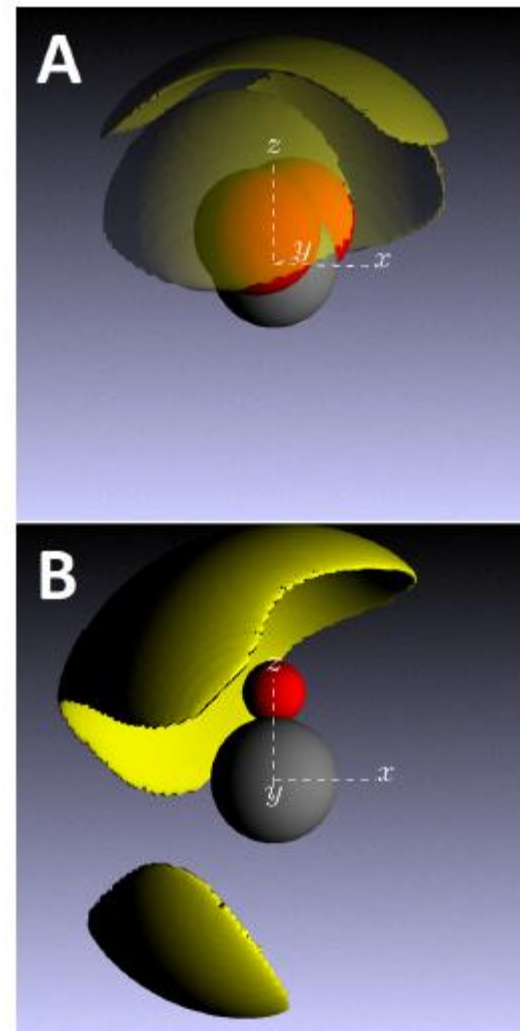
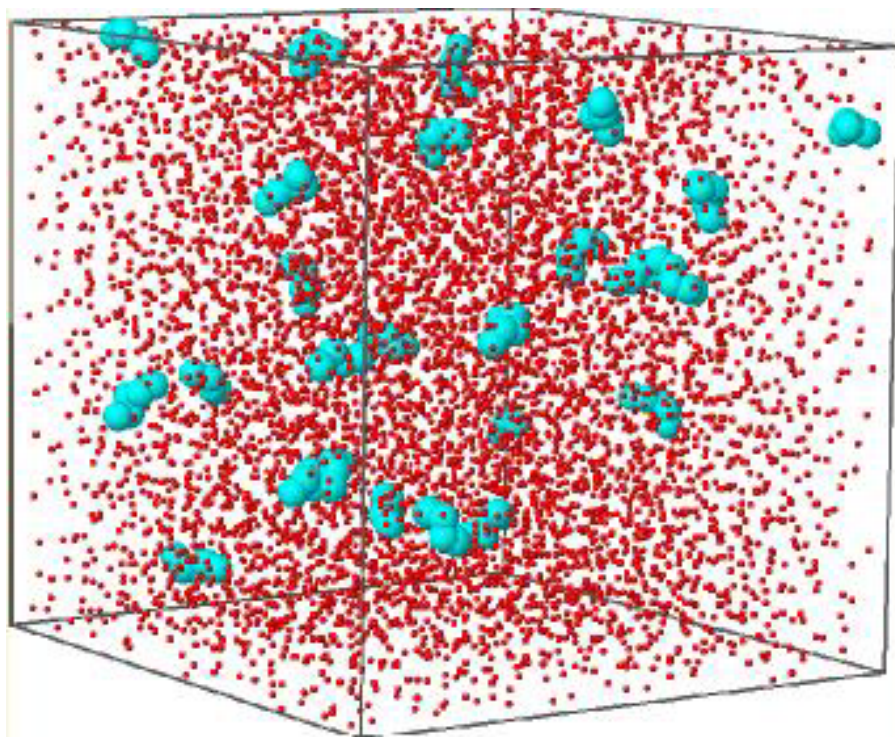
- Each isotopic mixture gives one structure factor
- Different correlations can be extracted from each structure factor

Generation of structural models

EPSR (empirical potential structure refinement)

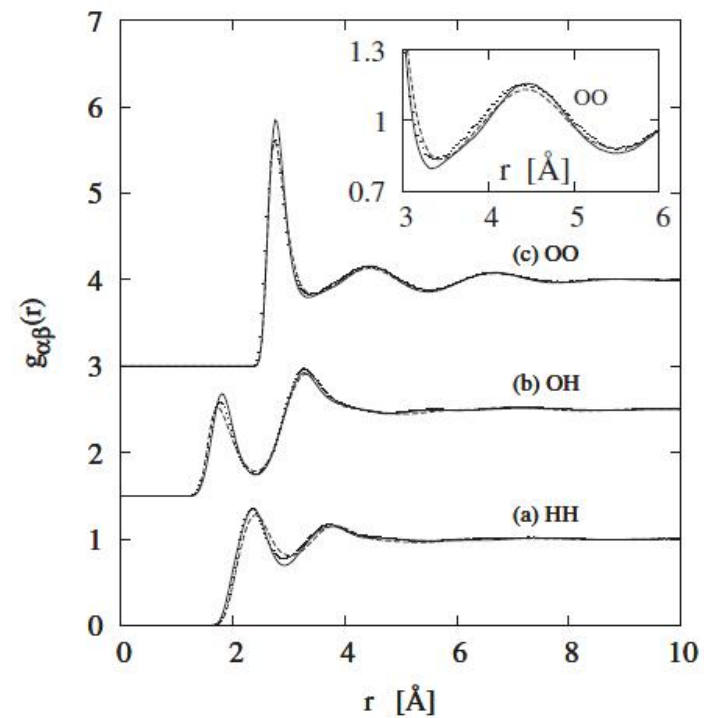
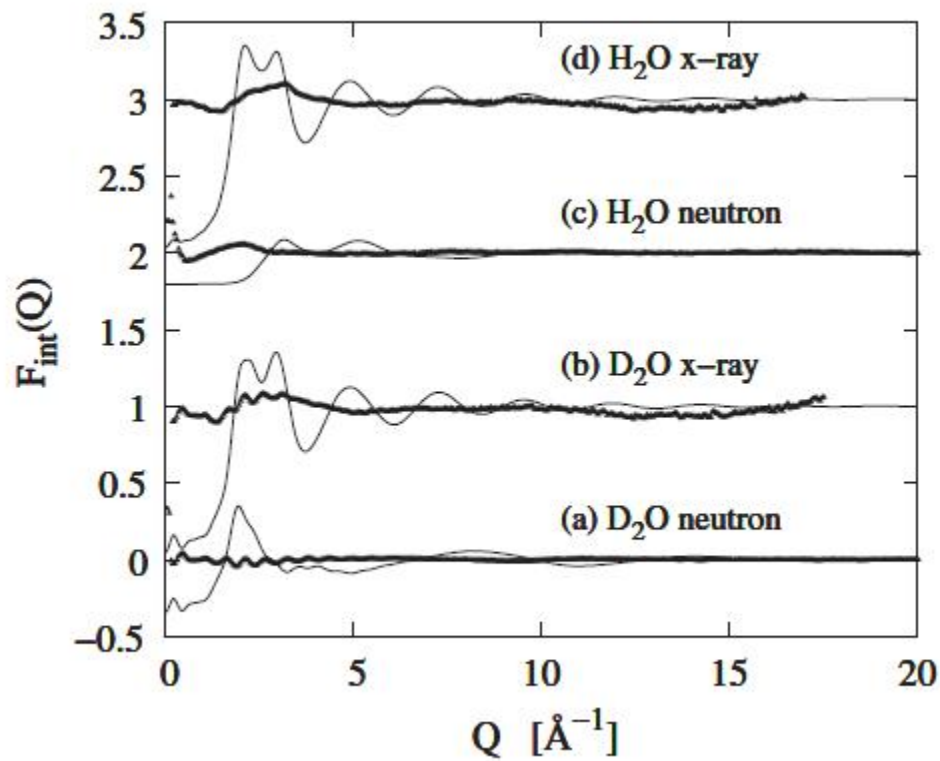
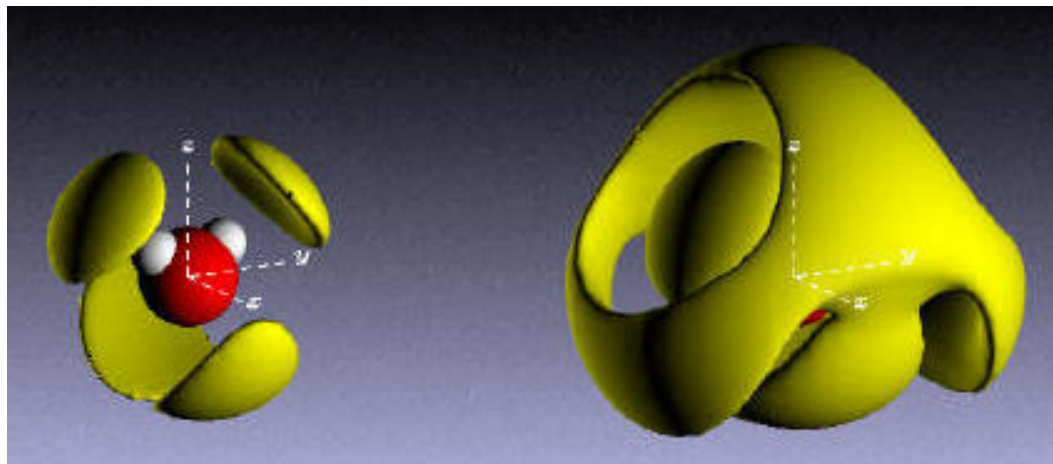


Generation of structural models

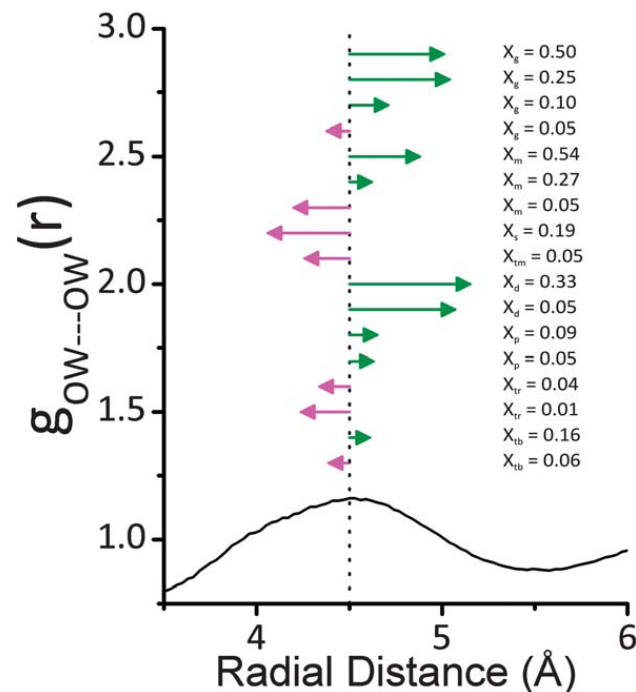
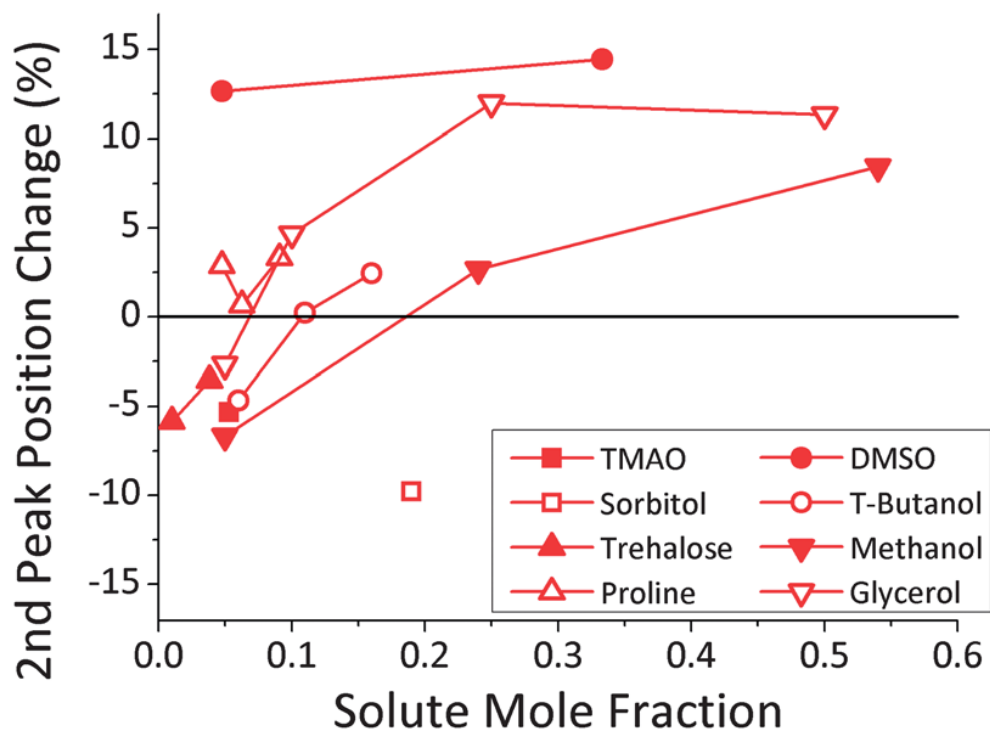
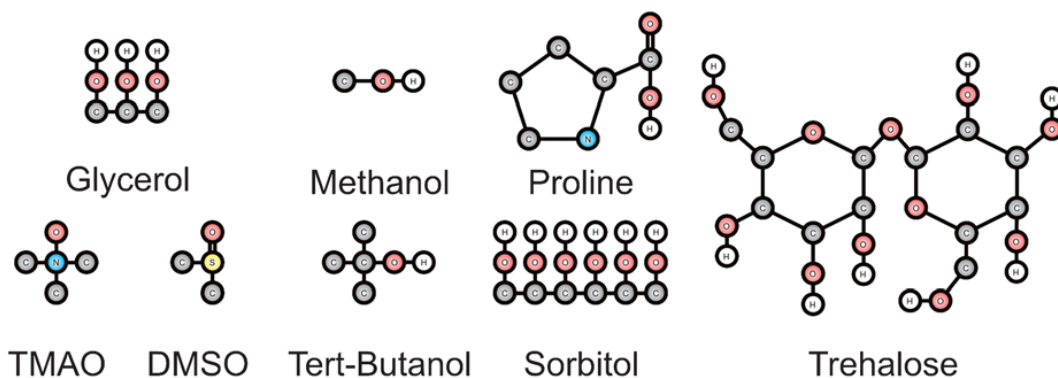


Applications

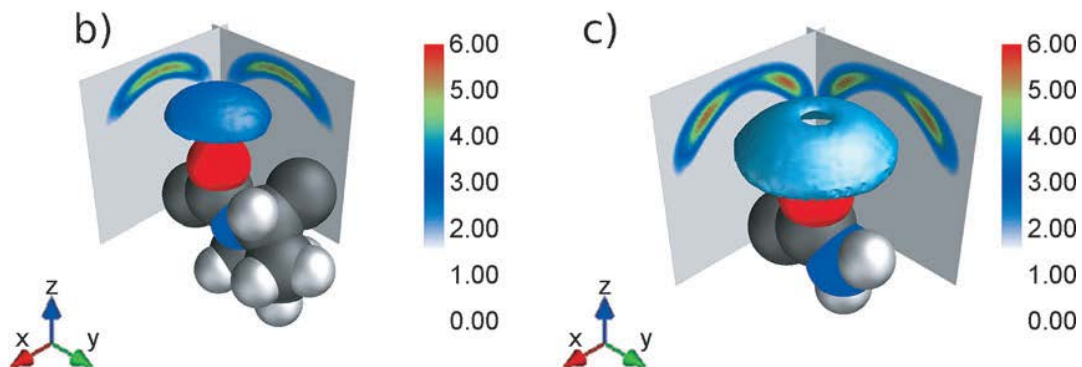
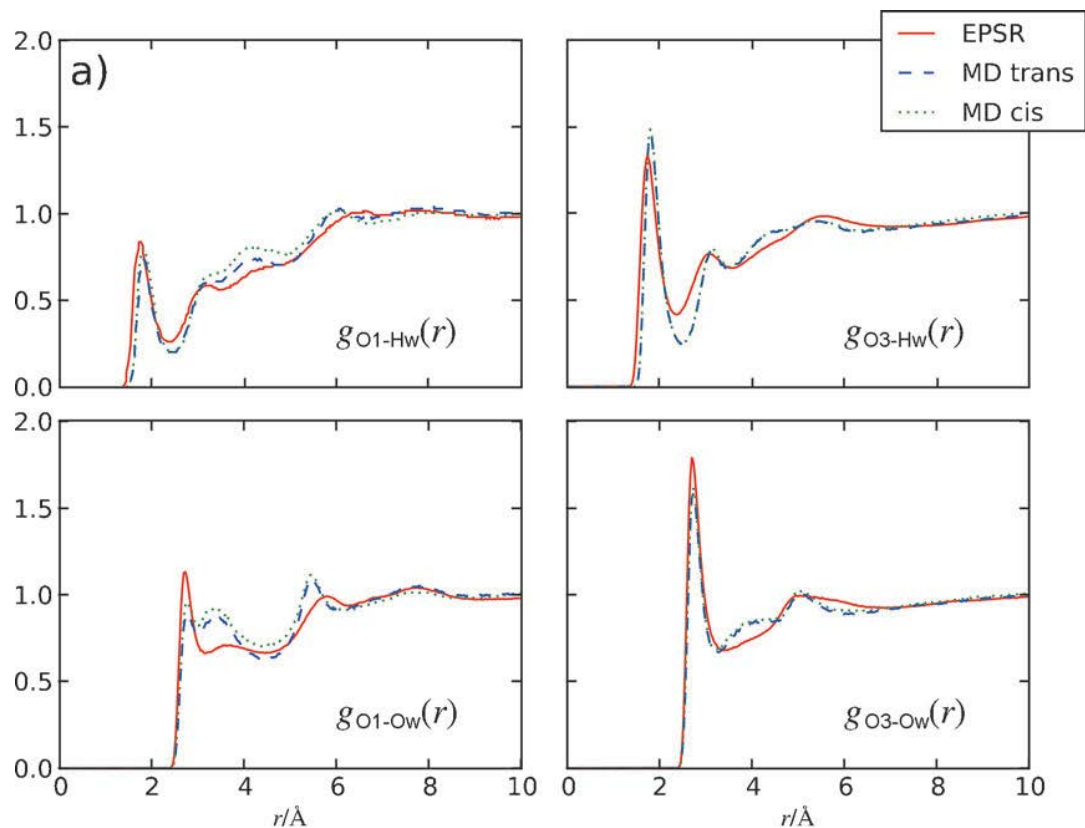
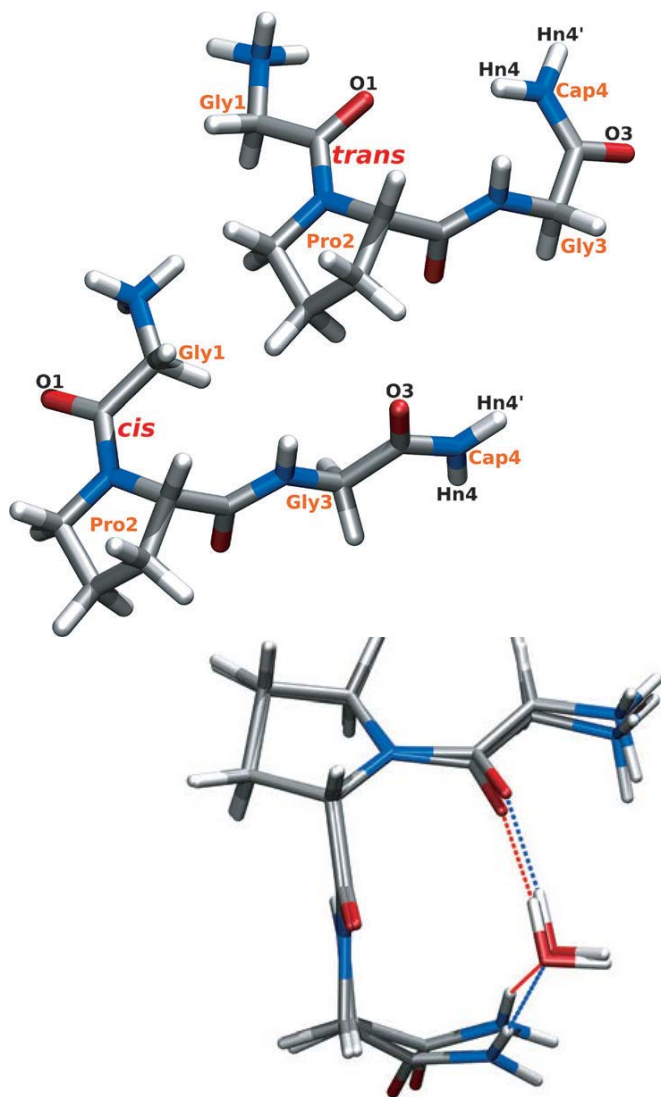
Water



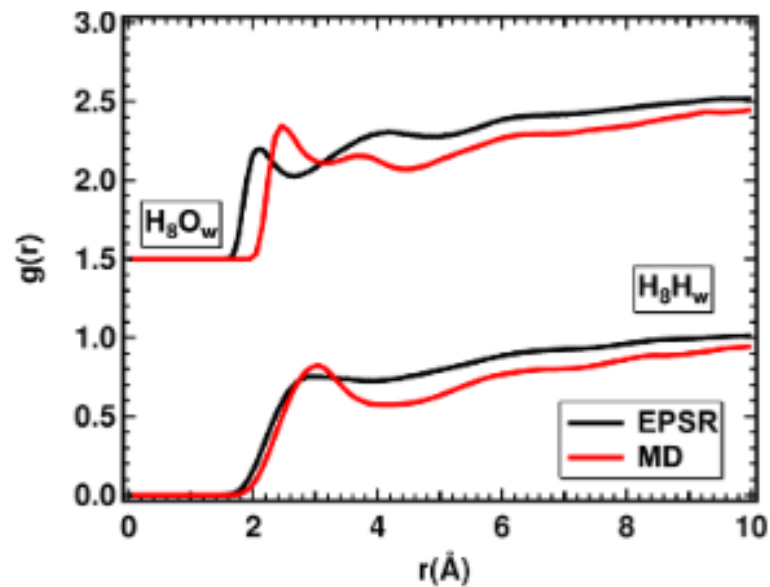
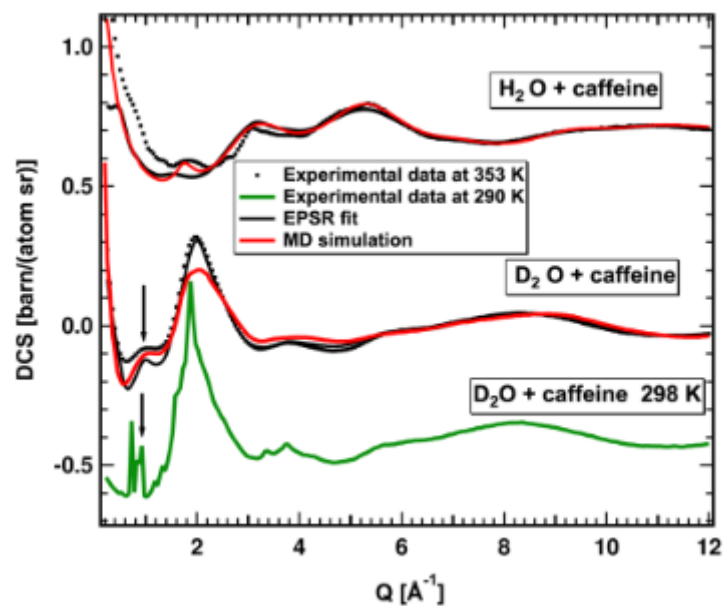
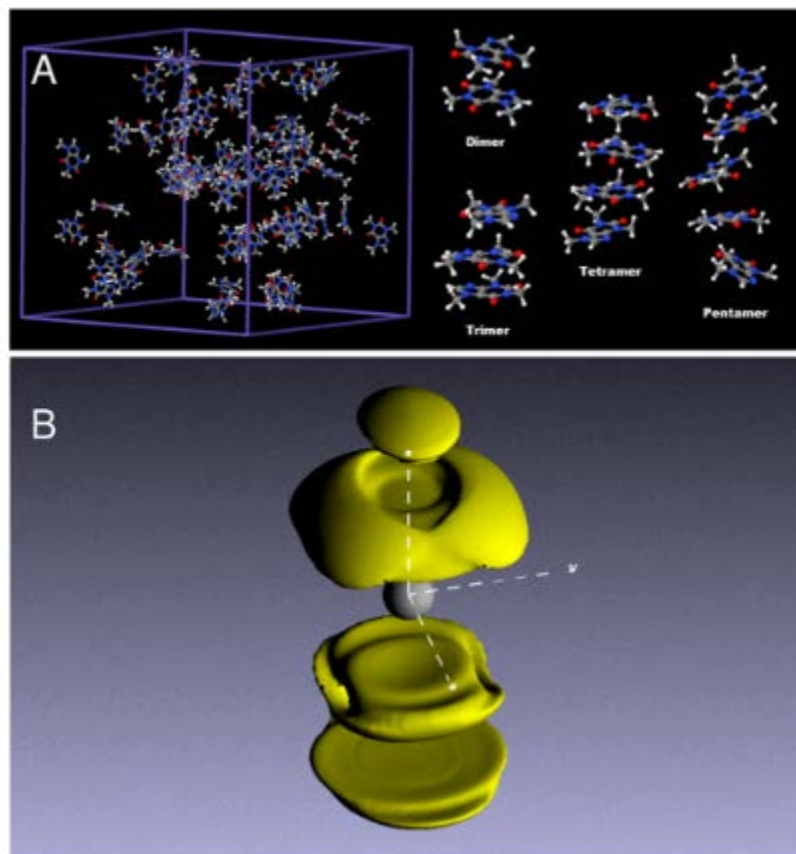
Antifreeze effect



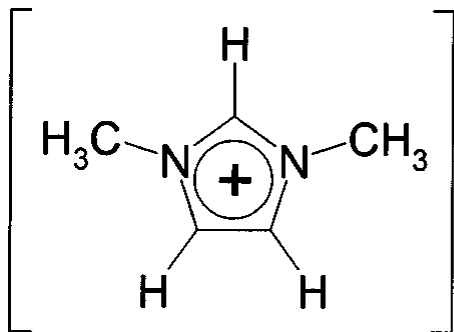
Small peptides



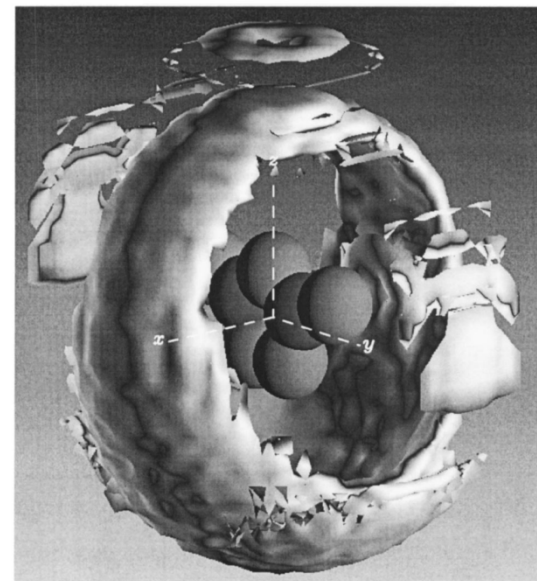
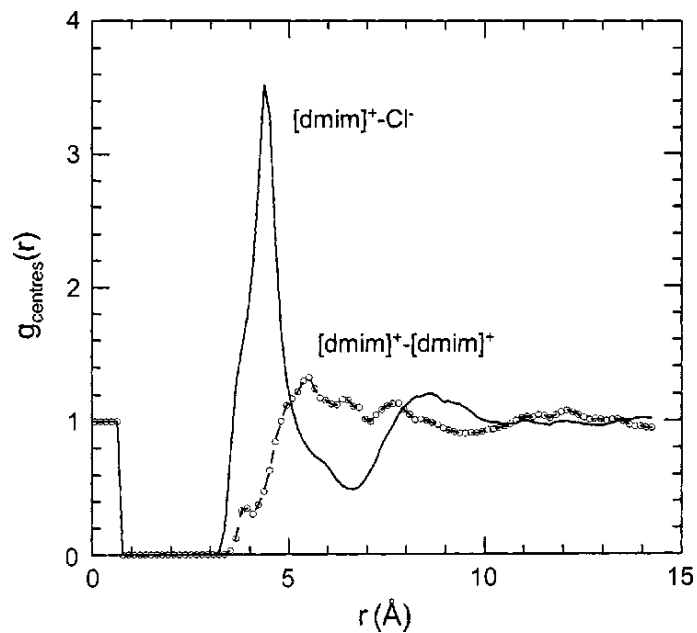
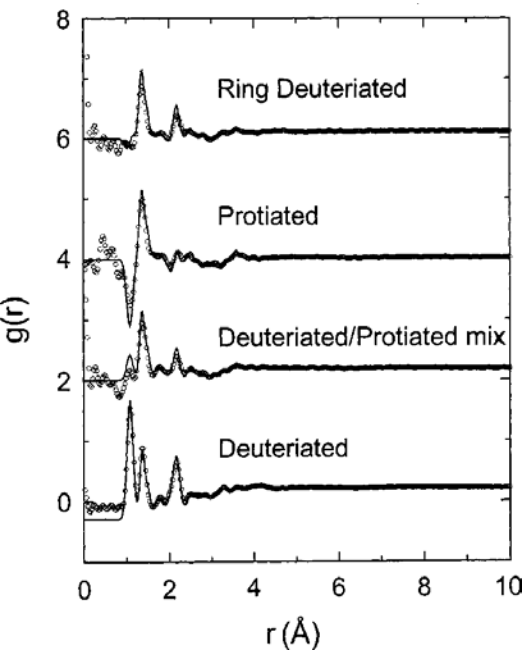
Drug compounds



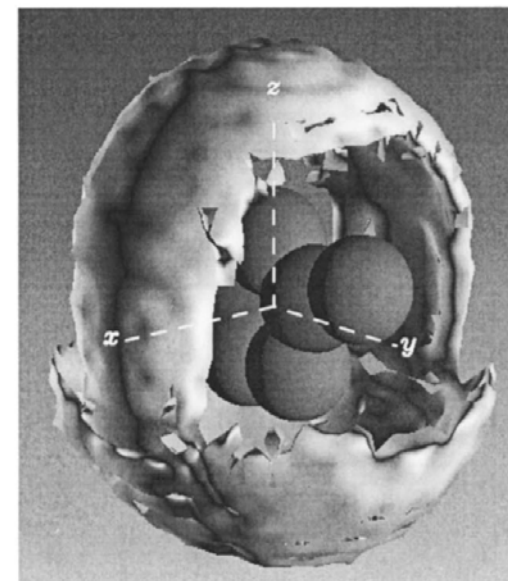
Ionic liquid/ salt melt



Cl⁻

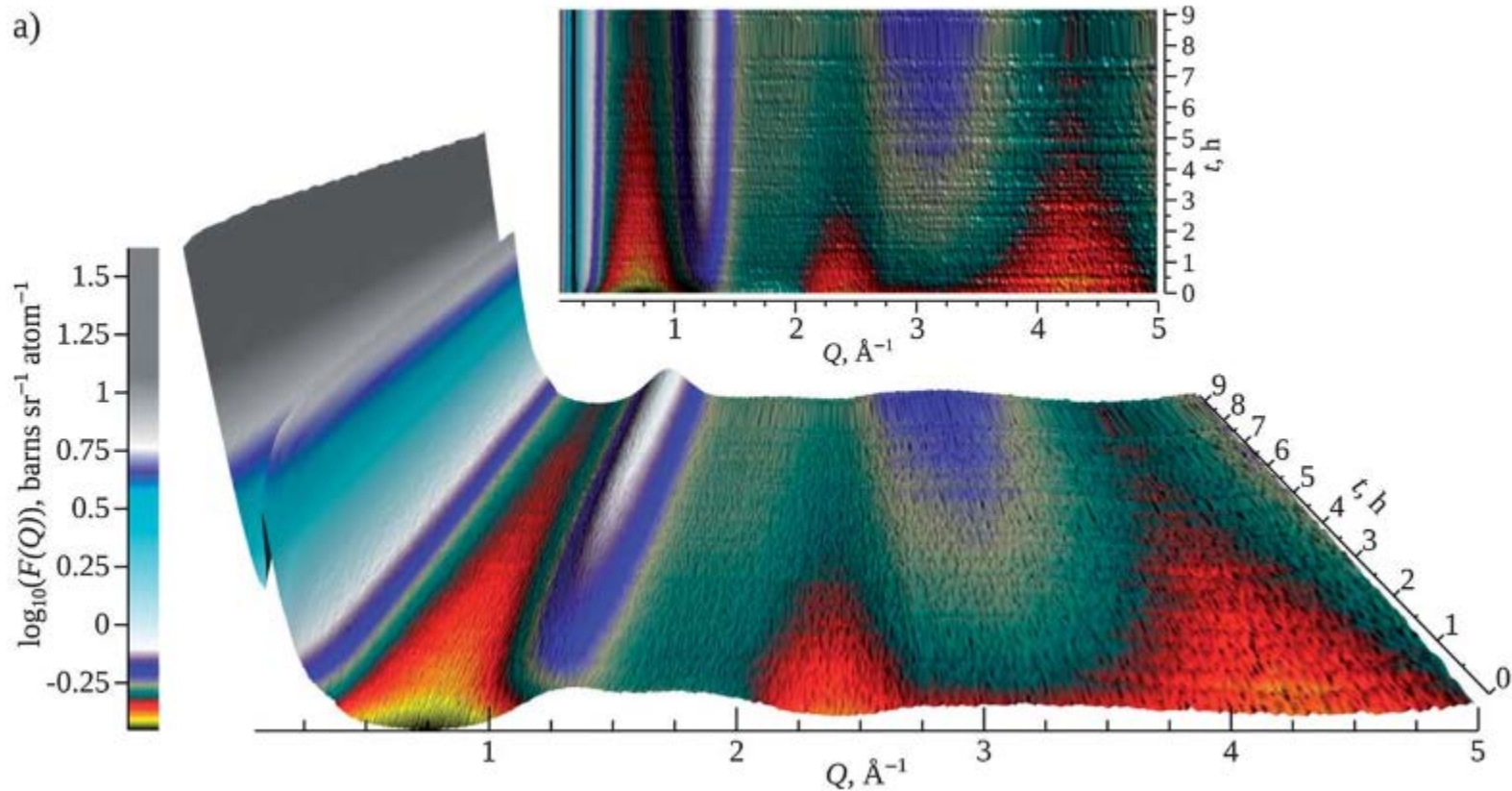
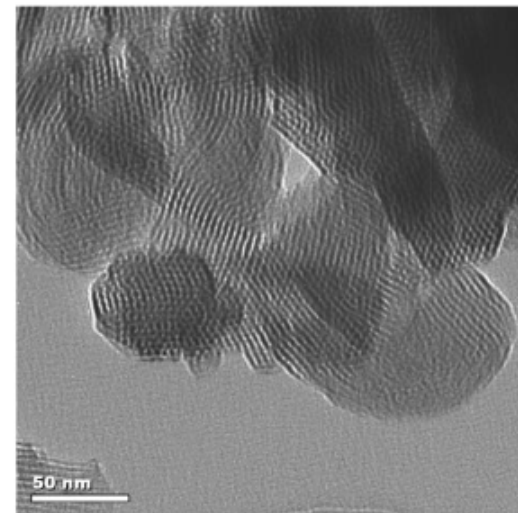


Imidazole-imidazole distance



Imidazole-chloride distance

Heterogeneous catalysis



Conclusion

- Wide angle scattering gives atomic resolution data
- Potential samples are
 - disordered crystalline materials
 - Nanomaterials
 - Solutions
 - Glasses
- Using WANS and WAXS in combination with Monte Carlo simulation can give a structural snap-shot of the disordered phase