Wide Angle Scattering and Pair Distribution Functions

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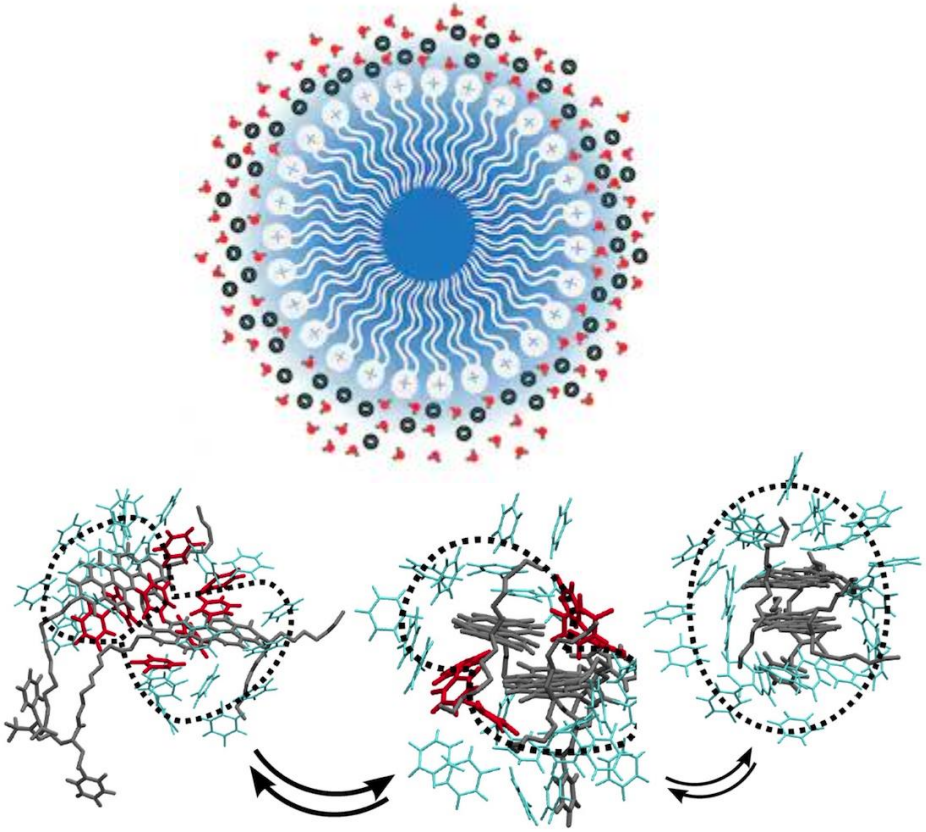
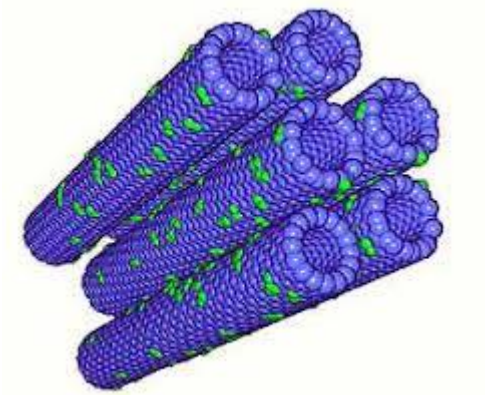
Overview

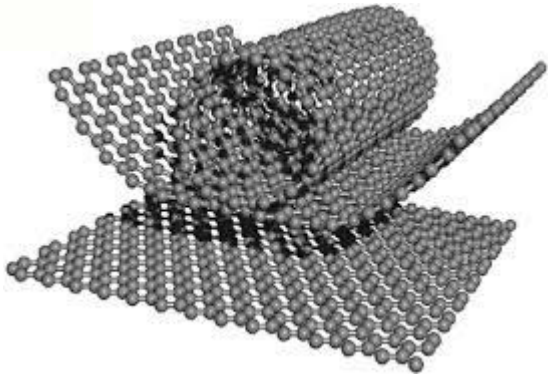
- Diffraction
  - What are the effects of increasing disorder?
- Small vs wide angle scattering
- Pair distribution function
- Examples

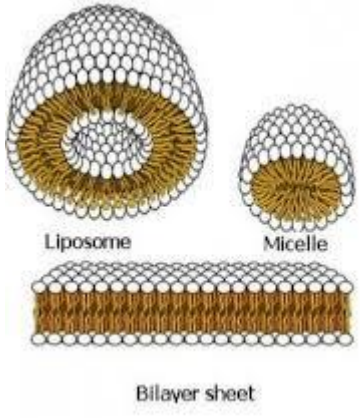
Wide vs small angle scattering

Wide Angle Scattering < 10^{-9} m





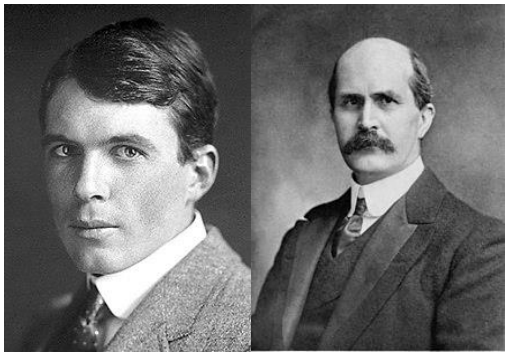




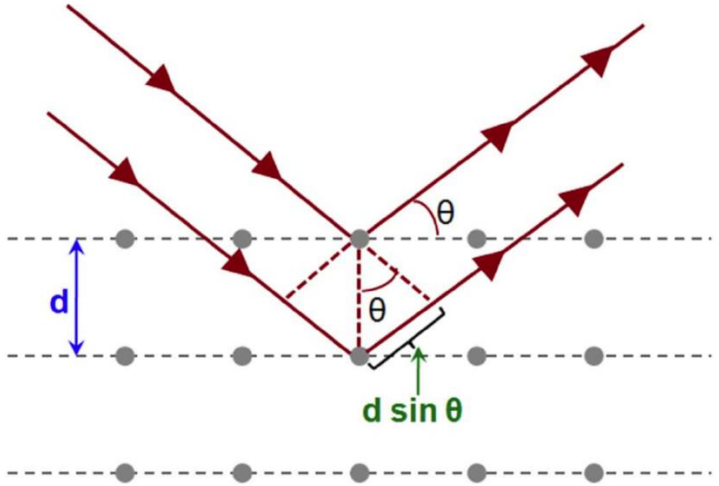
Small Angle Scattering > 10^{-9} m

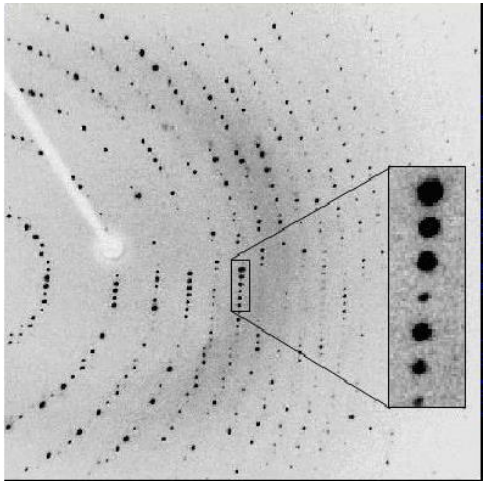
Diffraction and disorder

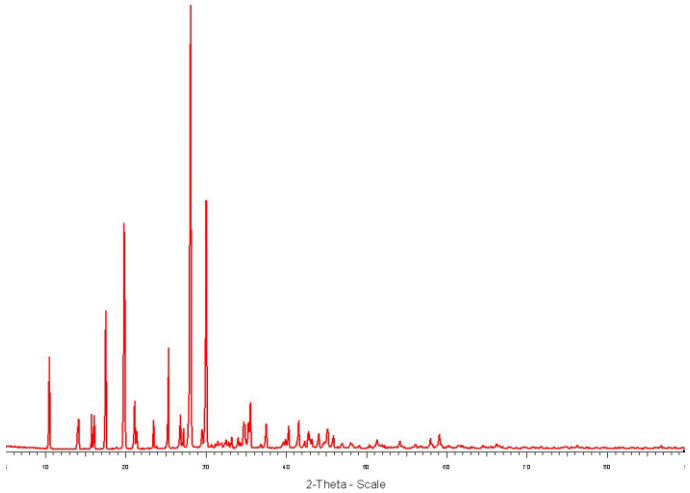
Diffraction



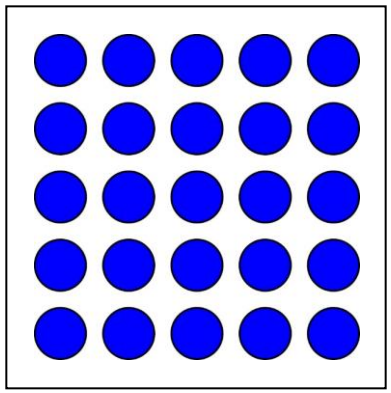
$$n\lambda = 2d\ sin(\theta)$$

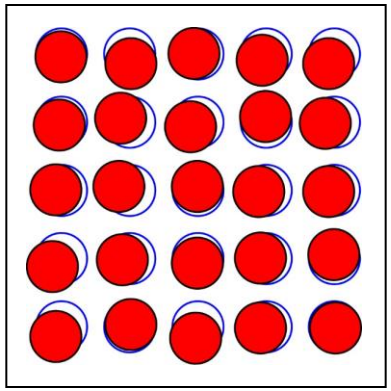


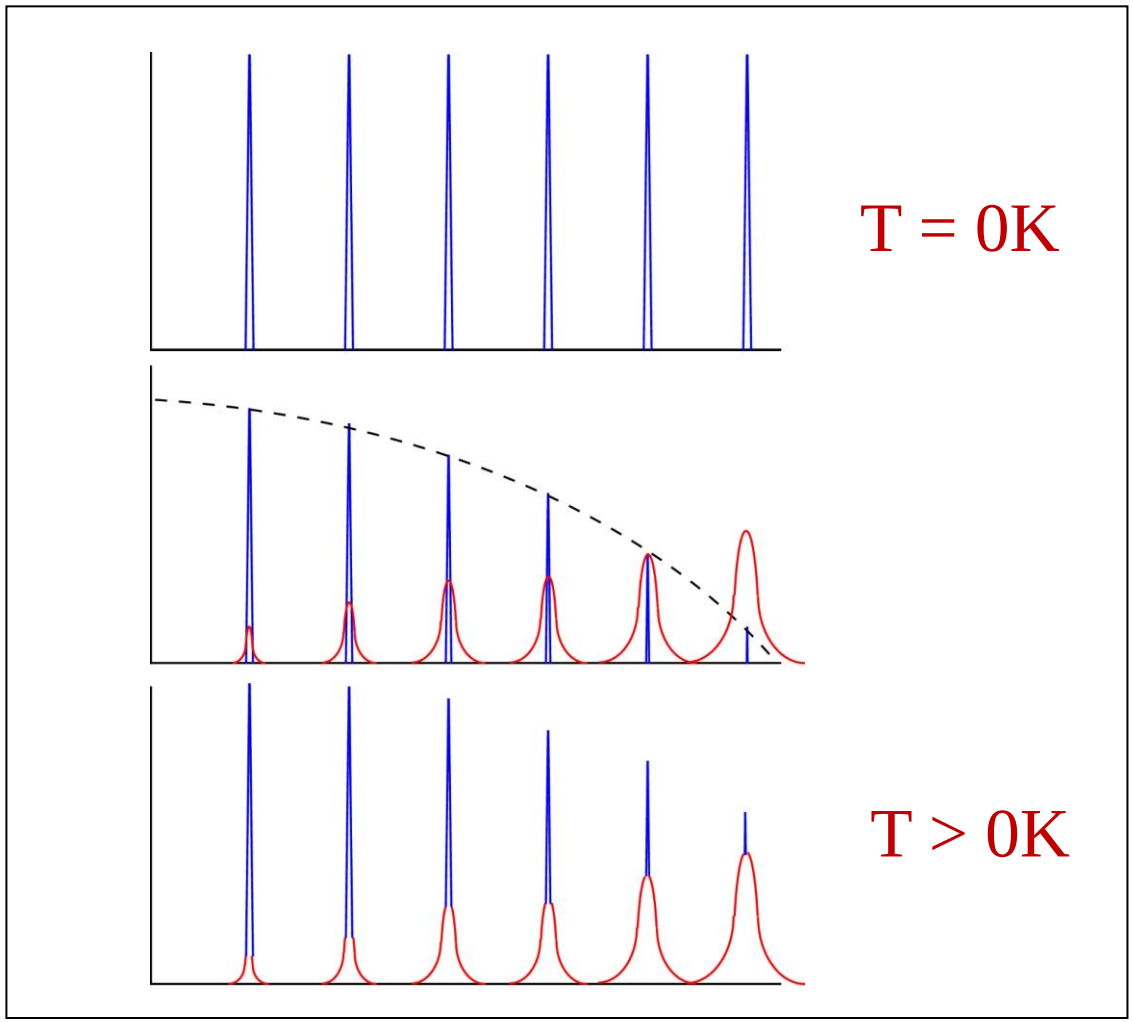




The effect of temperature

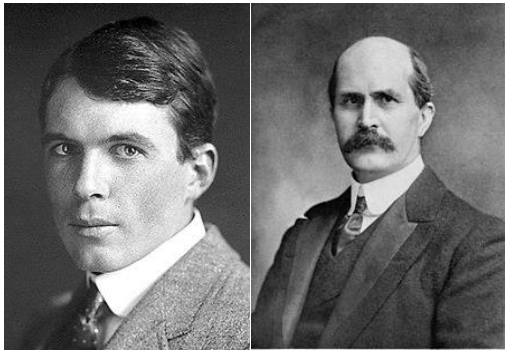




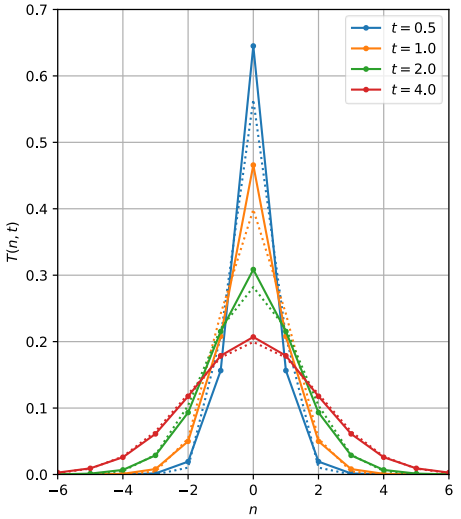


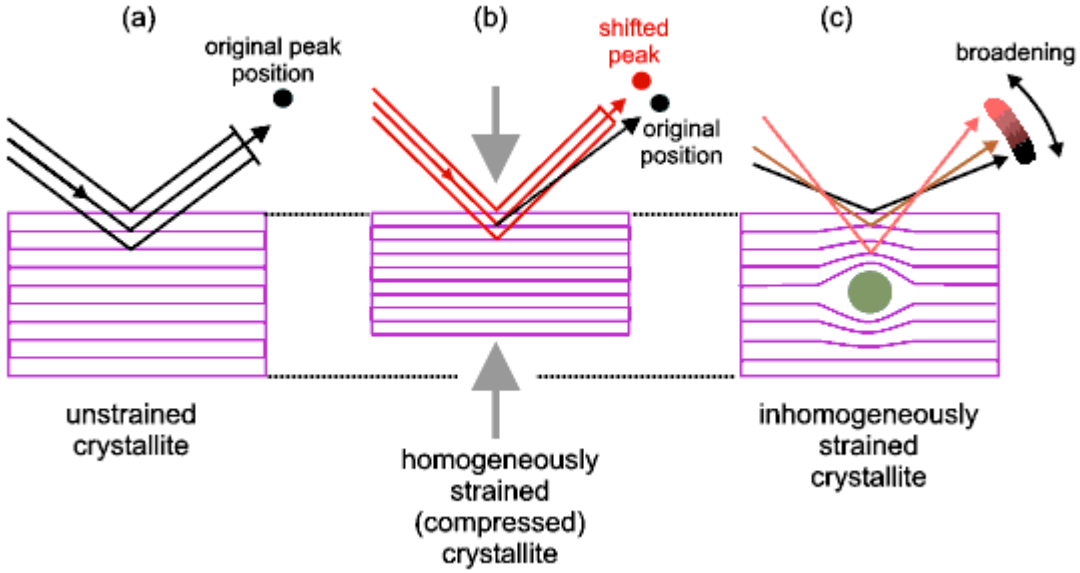
Debye-Waller factor

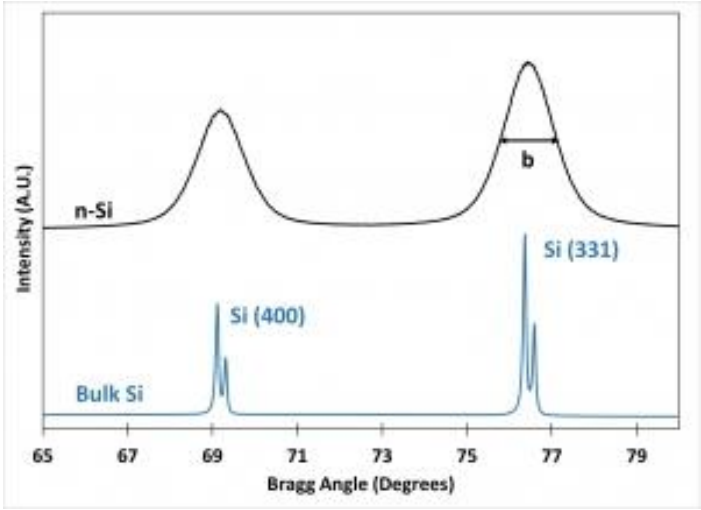
Diffraction



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

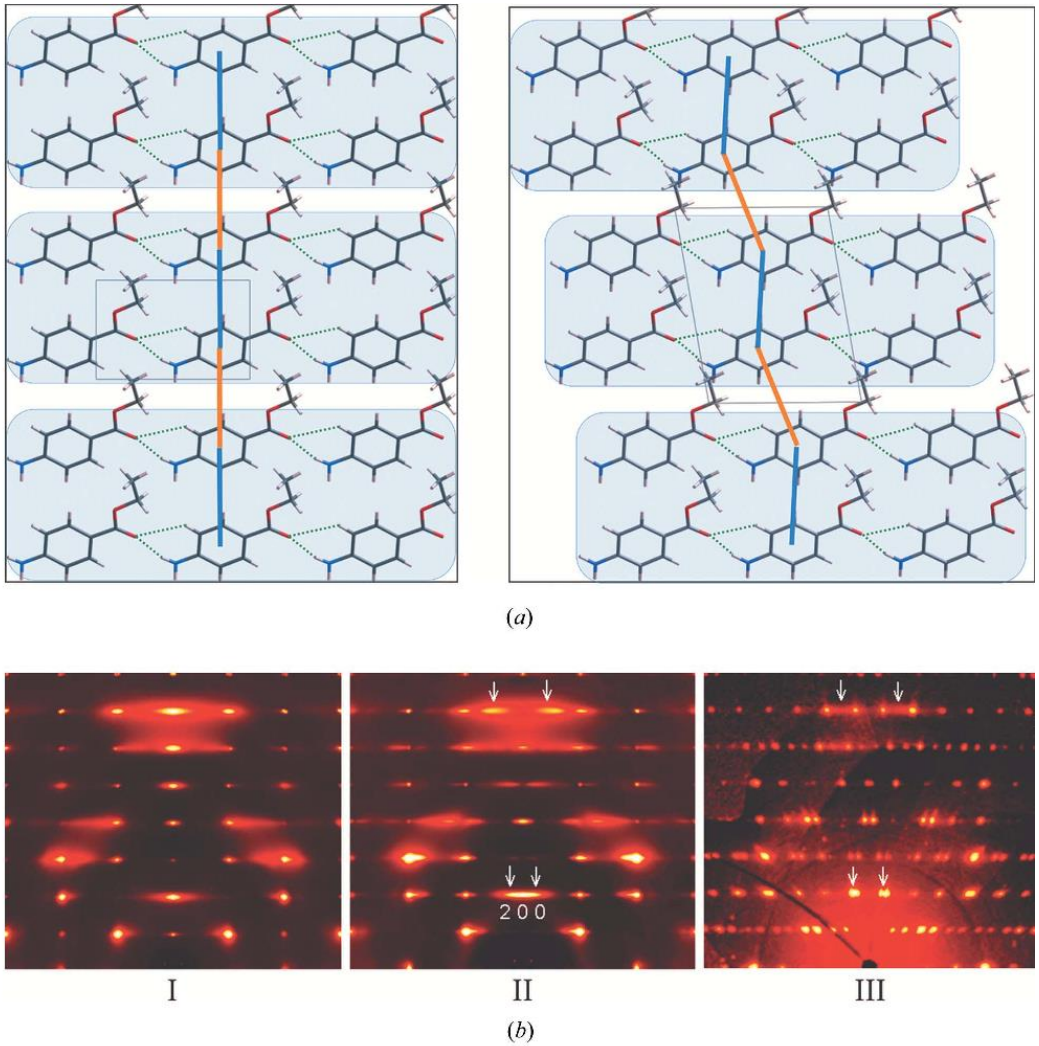






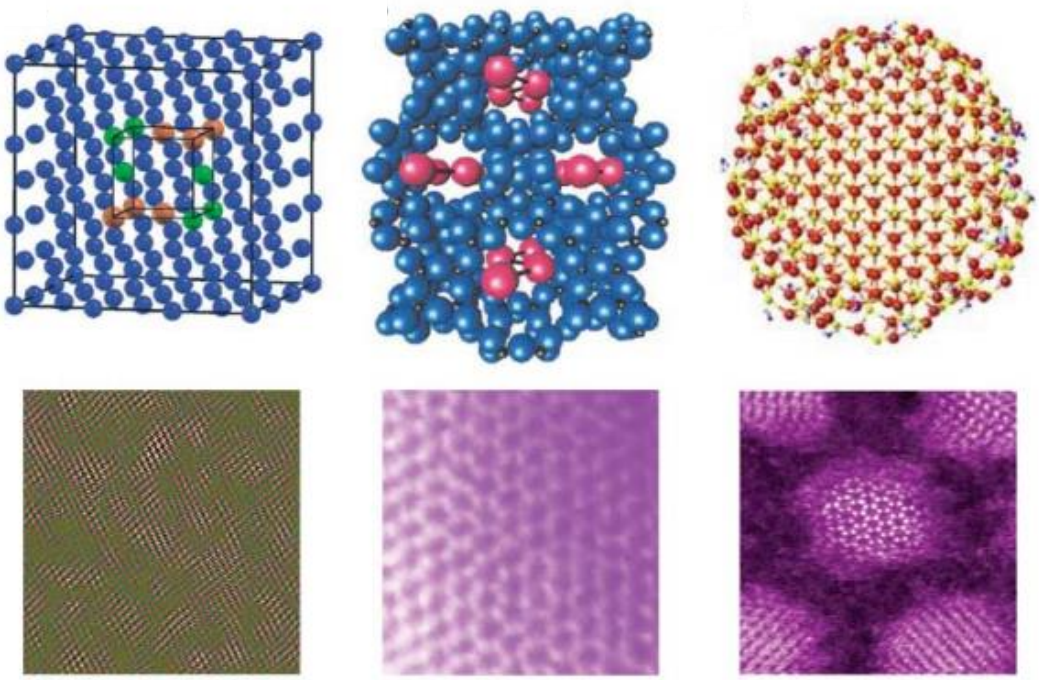
Birkbeck College

The effect of dislocation



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

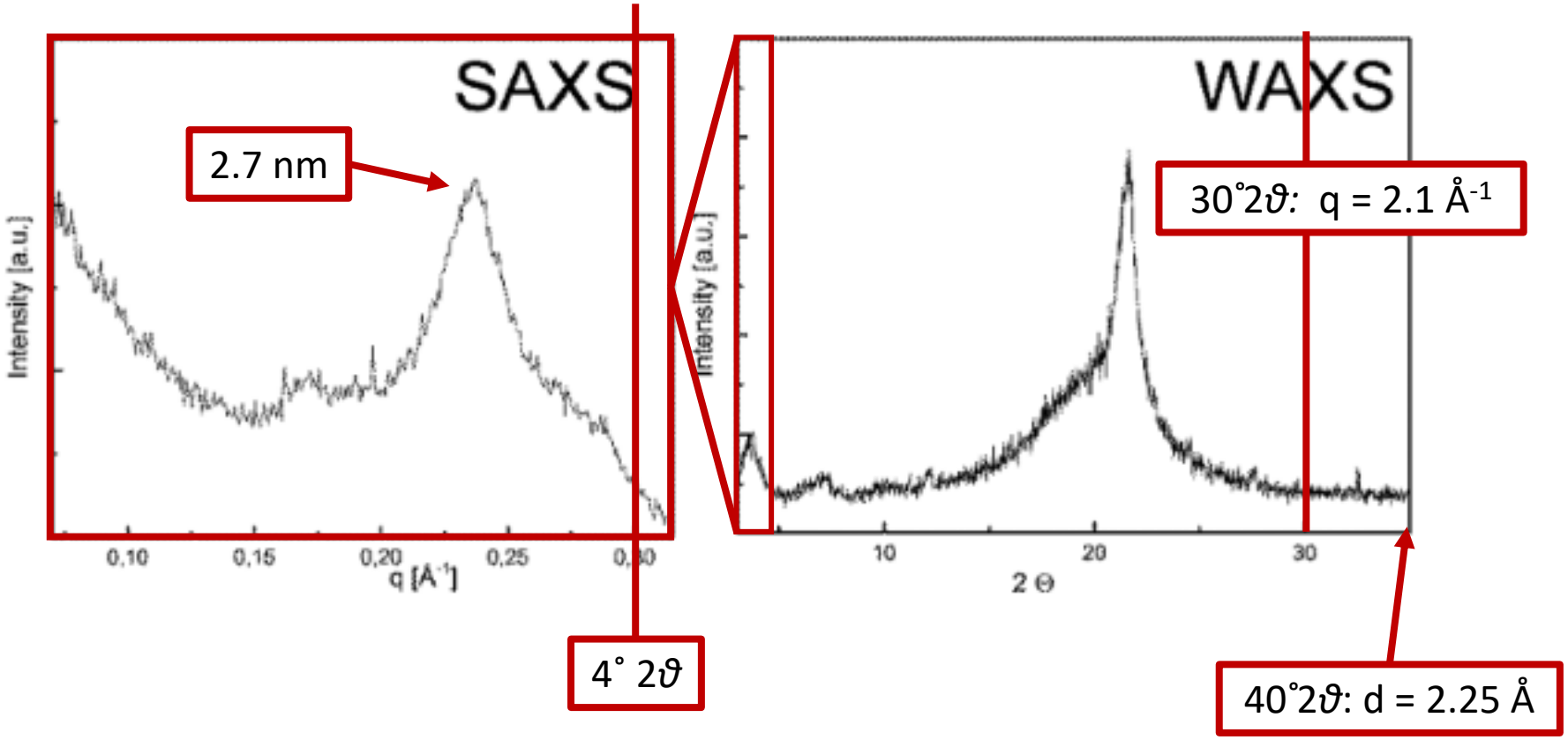


Science, 2007, 316, 561

Wide vs small angle scattering

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

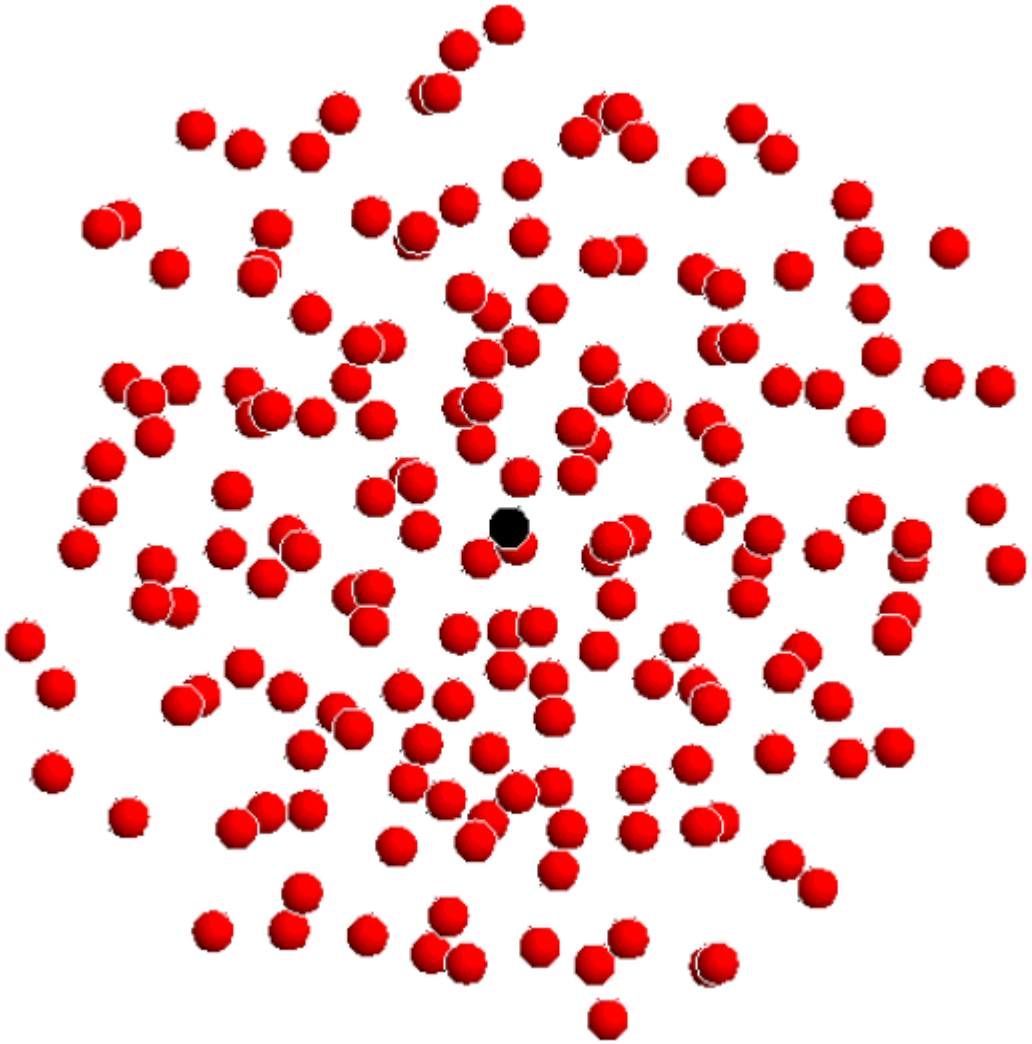
Amorphous poly(phosphoamidate), data acquired with Cu Kα radiation (λ = 1.54 Å)



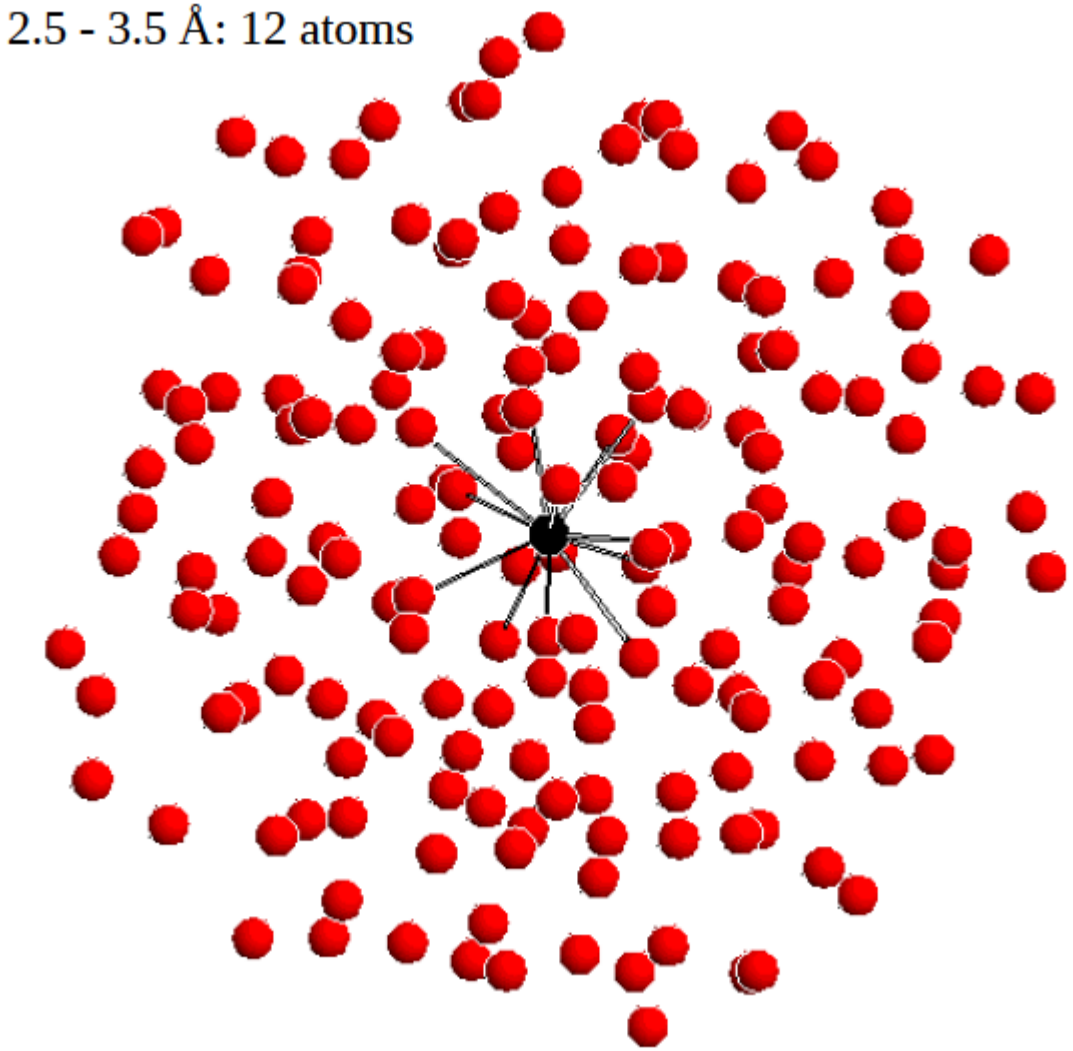
Polym. Chem.,2016, 7, 5004–5010

Pair distribution function

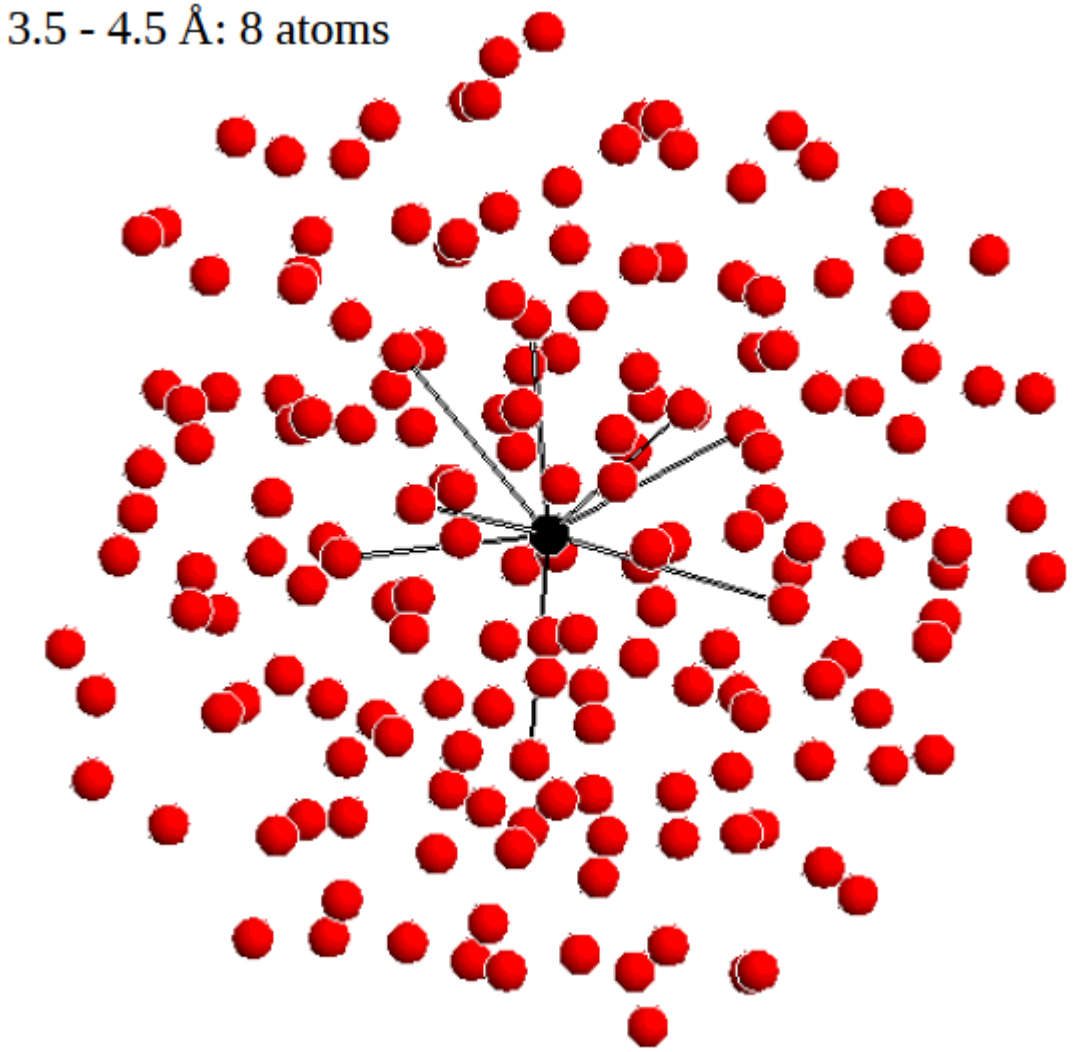
Pair distribution function



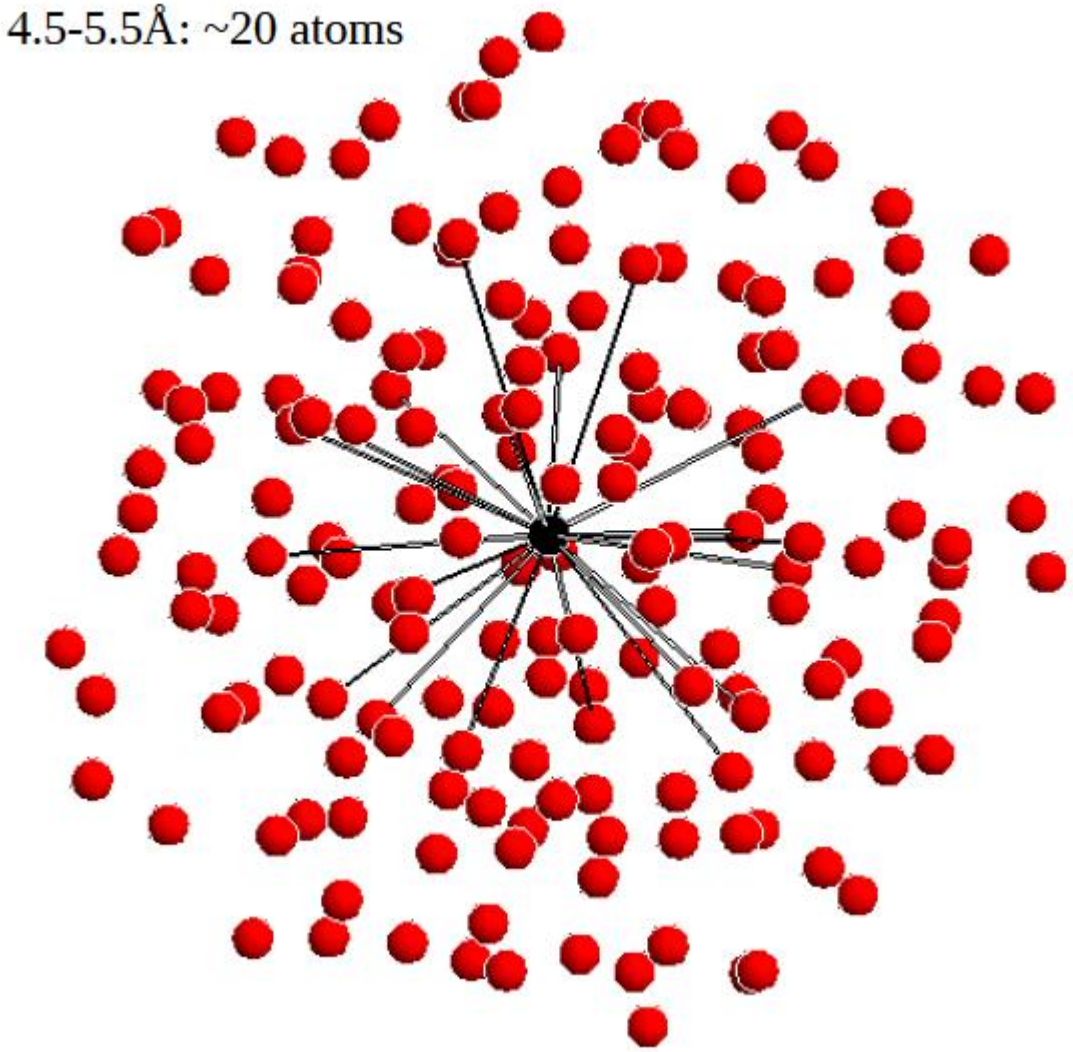
Pair distribution function



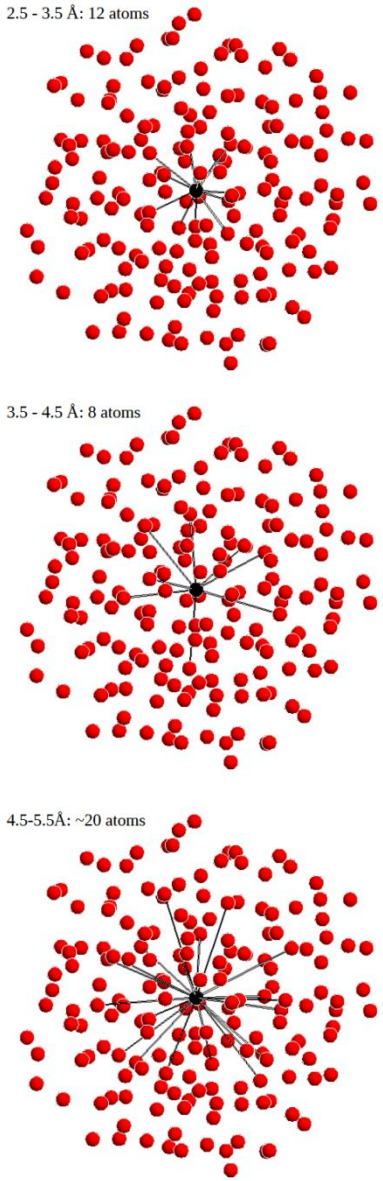
Pair distribution function

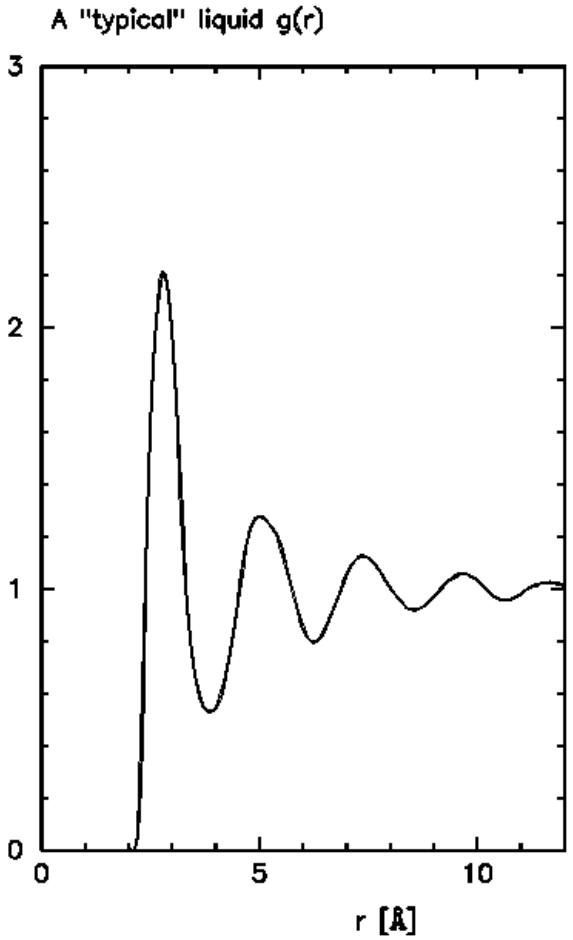


Pair distribution function



Pair distribution function

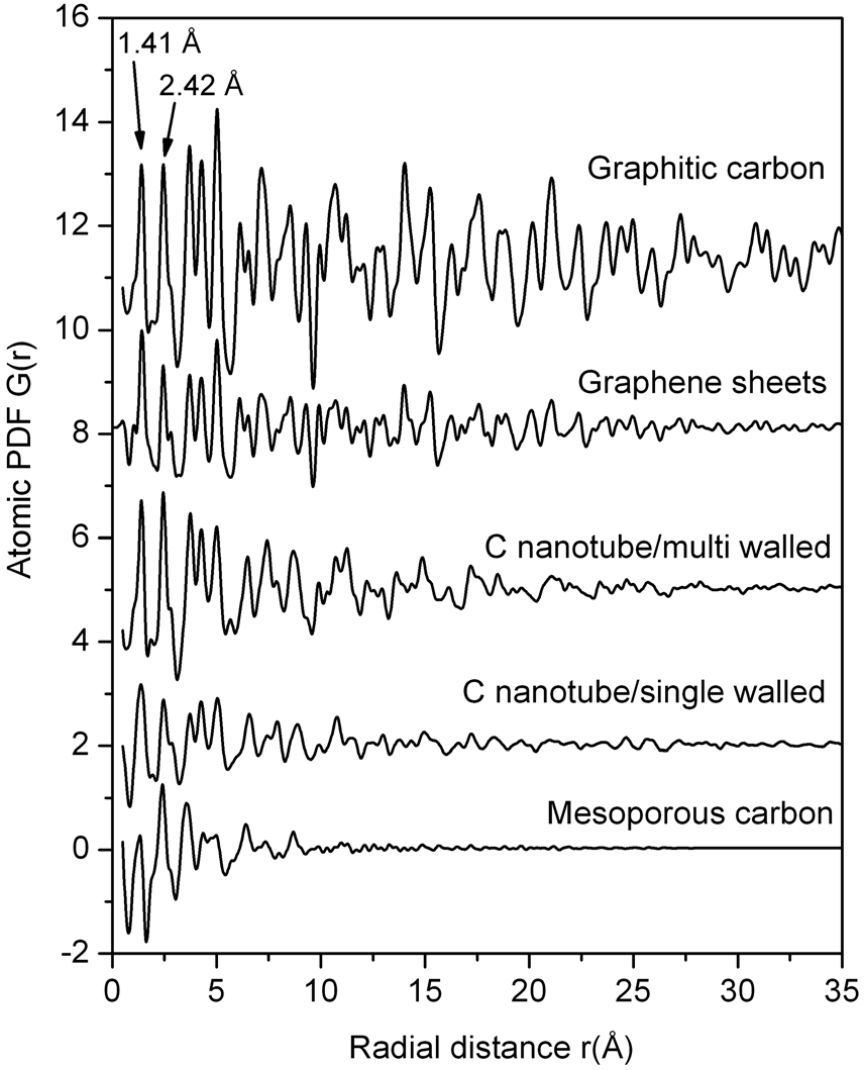




Pair distribution function

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

$$= V\frac{N-1}{N}(\delta(r - r_1)$$

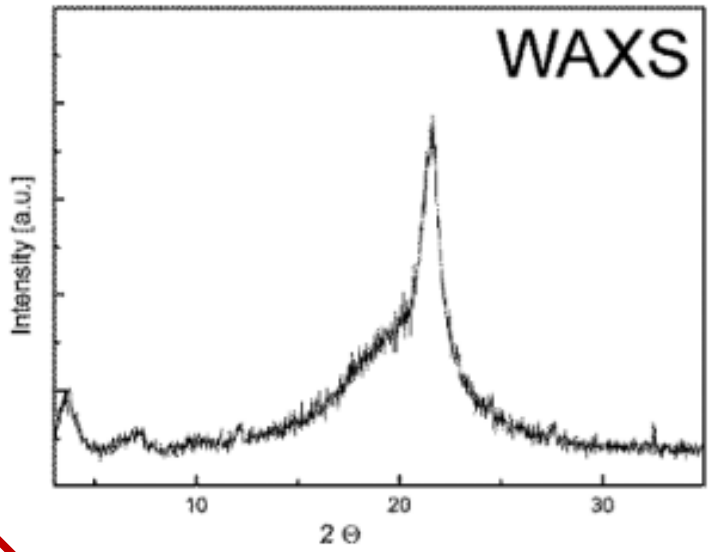


Pair distribution function

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

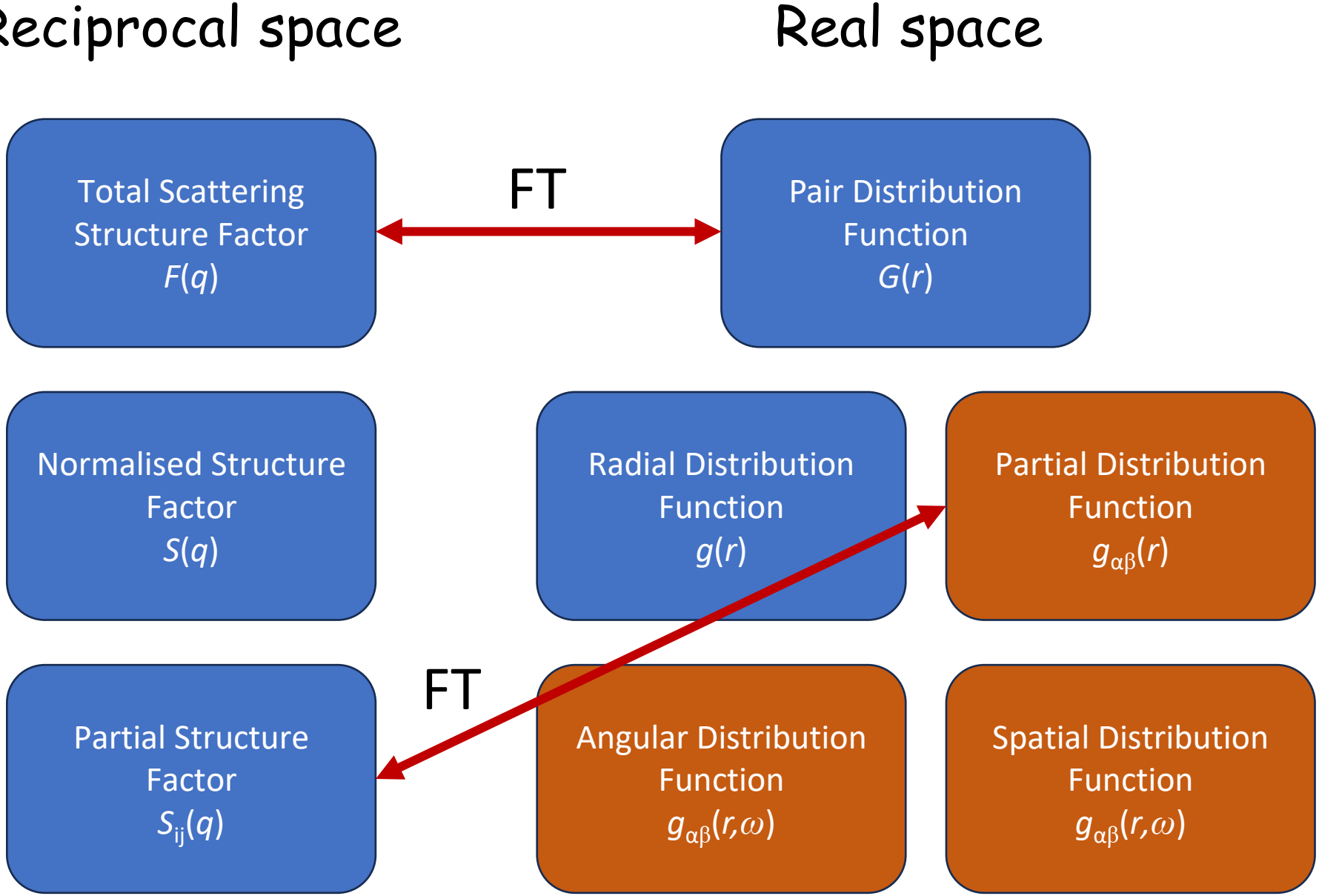
$$F(q) = \sum_{i,j} (2 - \delta_{i,j}) c_i c_j b_i b_j S_{i,j}(q)$$

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



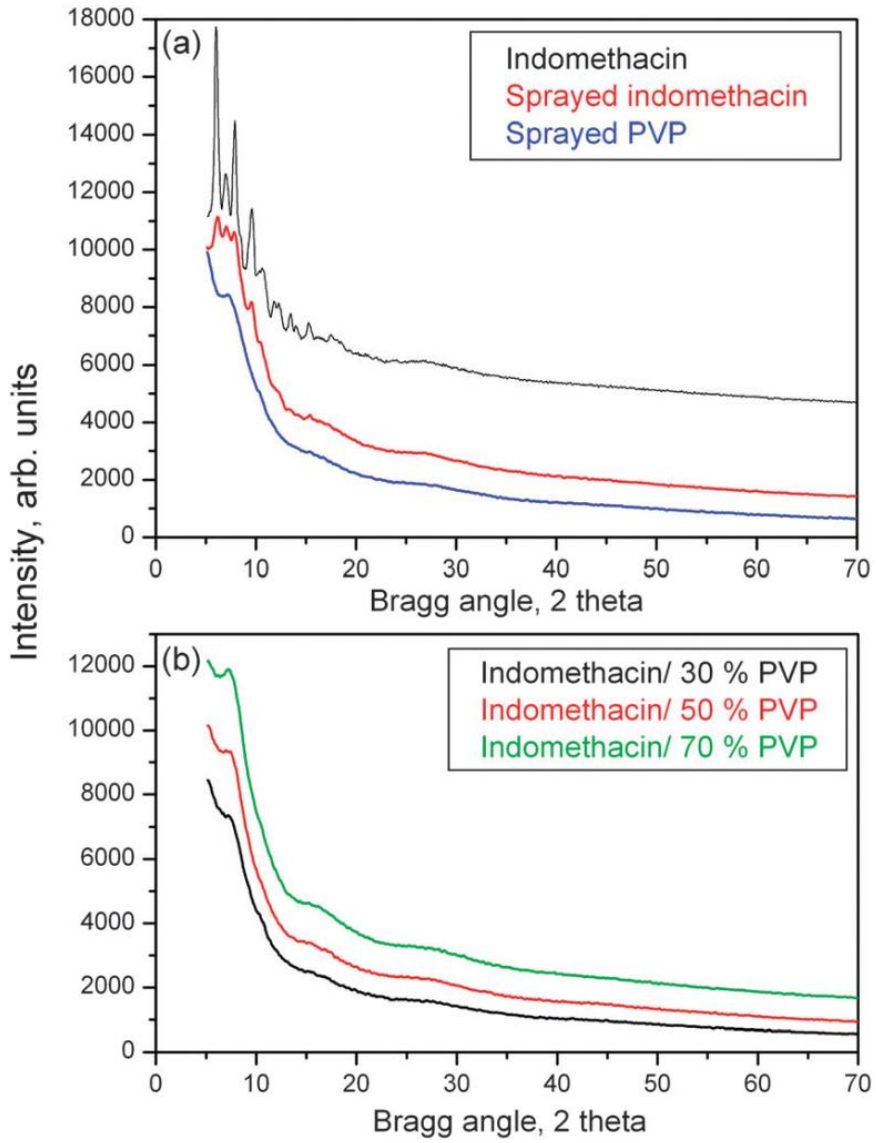
Partial structure factor

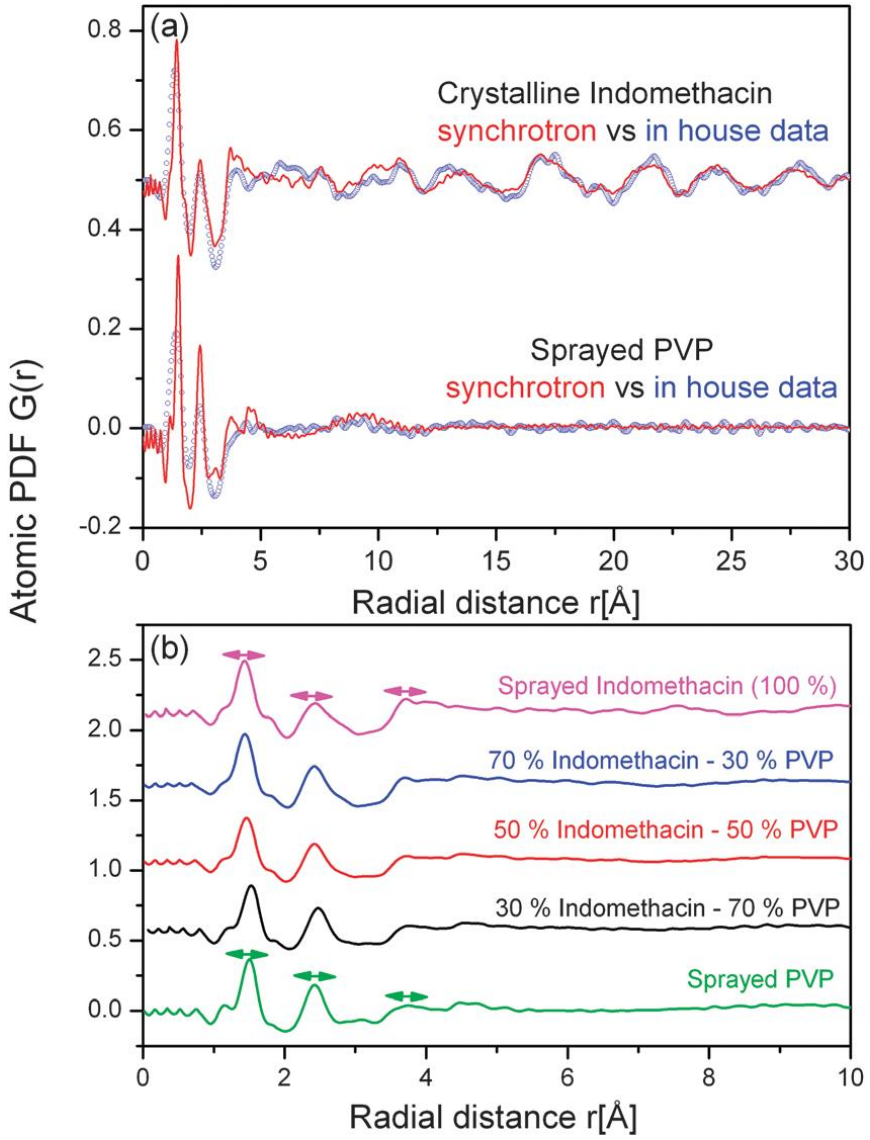
$F(q)$ and $S(q)$ are related to respective $G(r)$ and $g_{\alpha\beta}(r)$ by Fourier Transform



J. Appl. Cryst. (2001). 34, 172-177

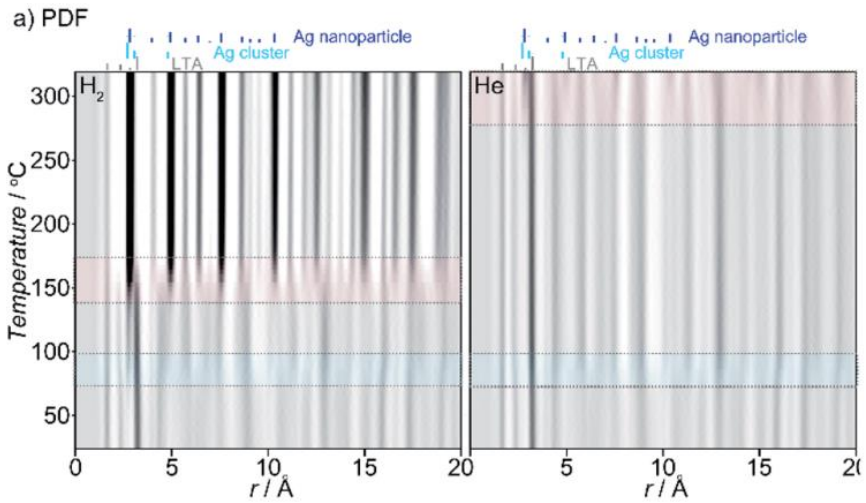
Indomethacin in polymer

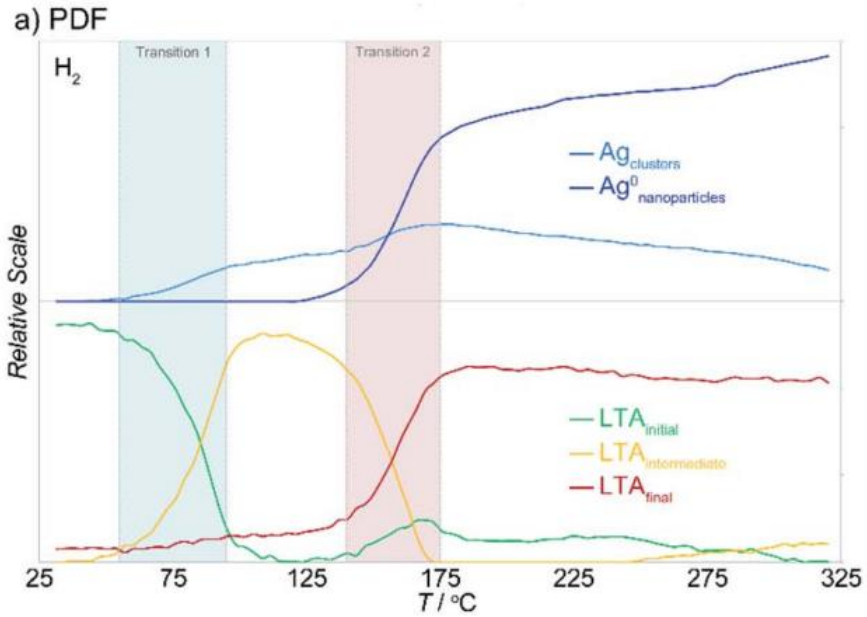


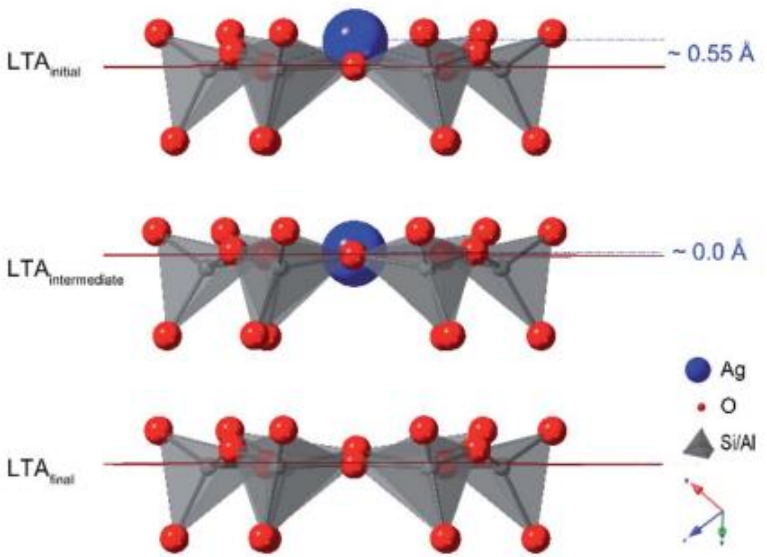


V. Petkov, Y. Ren, S. Kabekkodu, D. Murphy, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8544

Silver nanoparticles in zeolite

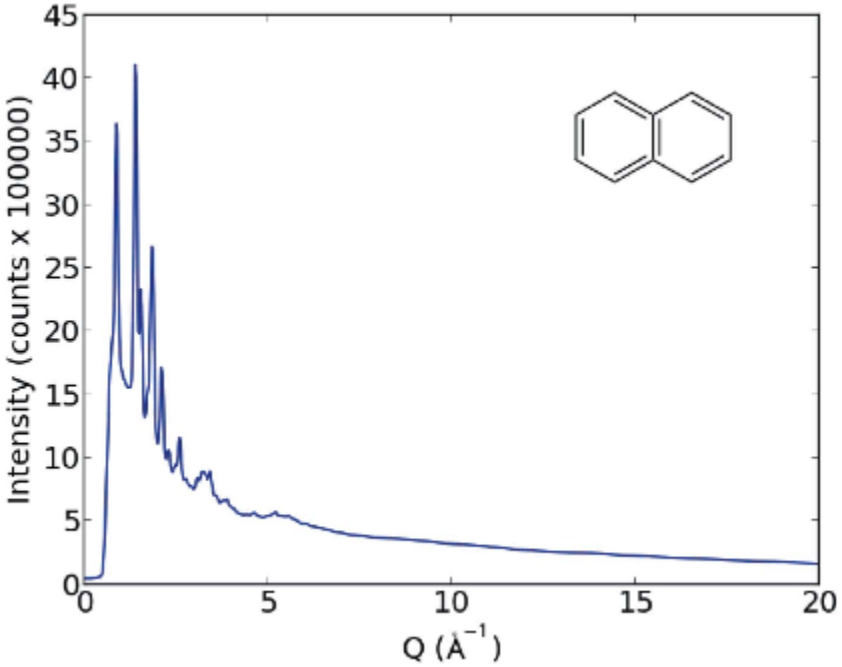


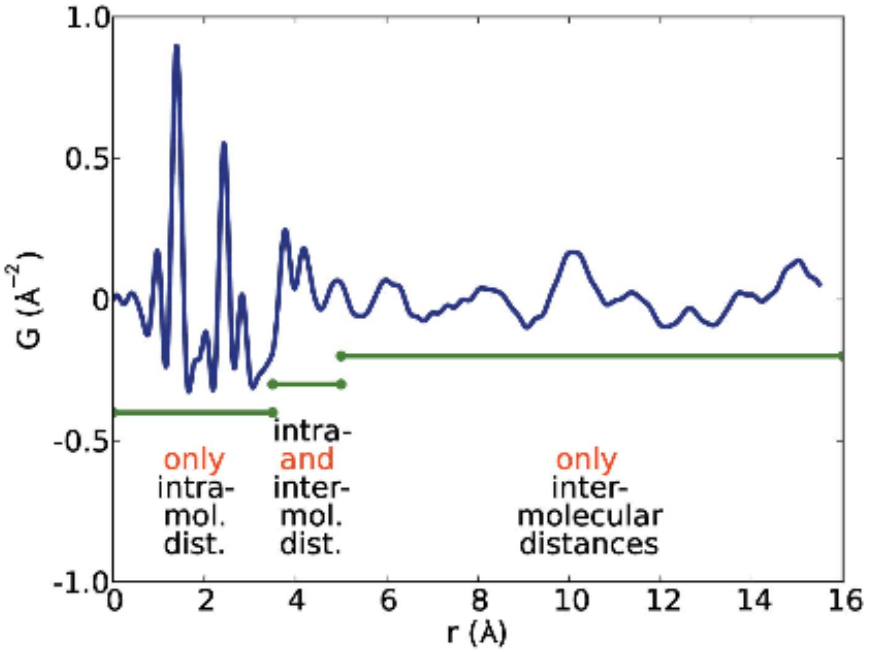




D. O'Nolan, H. Zhao, Z. Chen et al., *Chem. Sci.*, 2021, **12**, 13836

Structure solution from WAXS

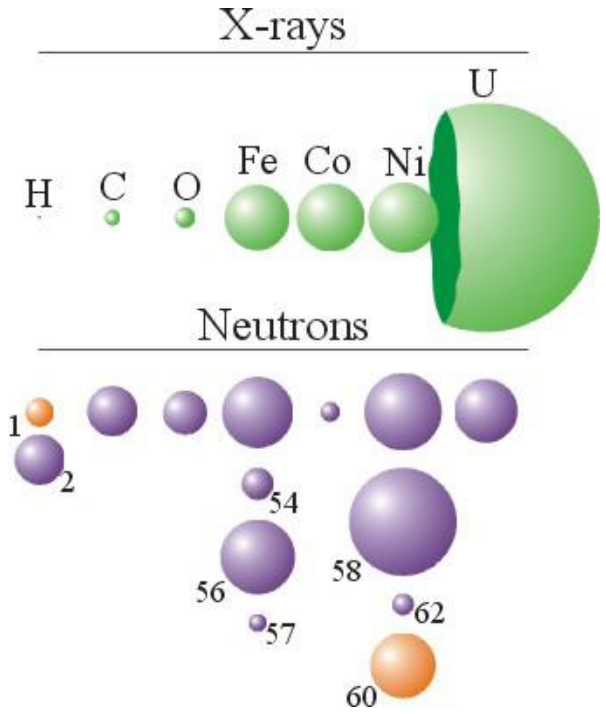


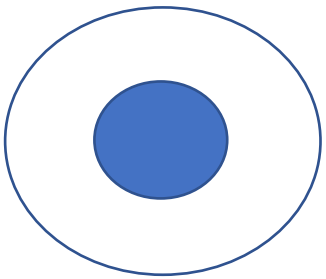


Problem: fitting of too many parameters to one structure factor!

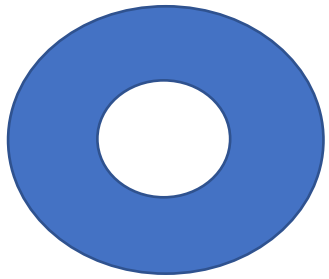
D. Prill, P. Juhas, M.U. Schmidt, S.J.K. Billinge, *J. Appl. Cryst.*, 2015, **48**, 171

Wide-angle neutron scattering

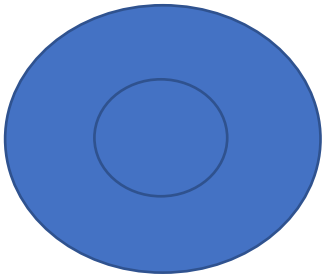




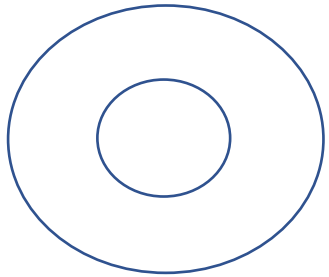
H/D



D/H



H/H



D/D

5 mol% H/D exchange on part of the sample we want to see

WANS

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

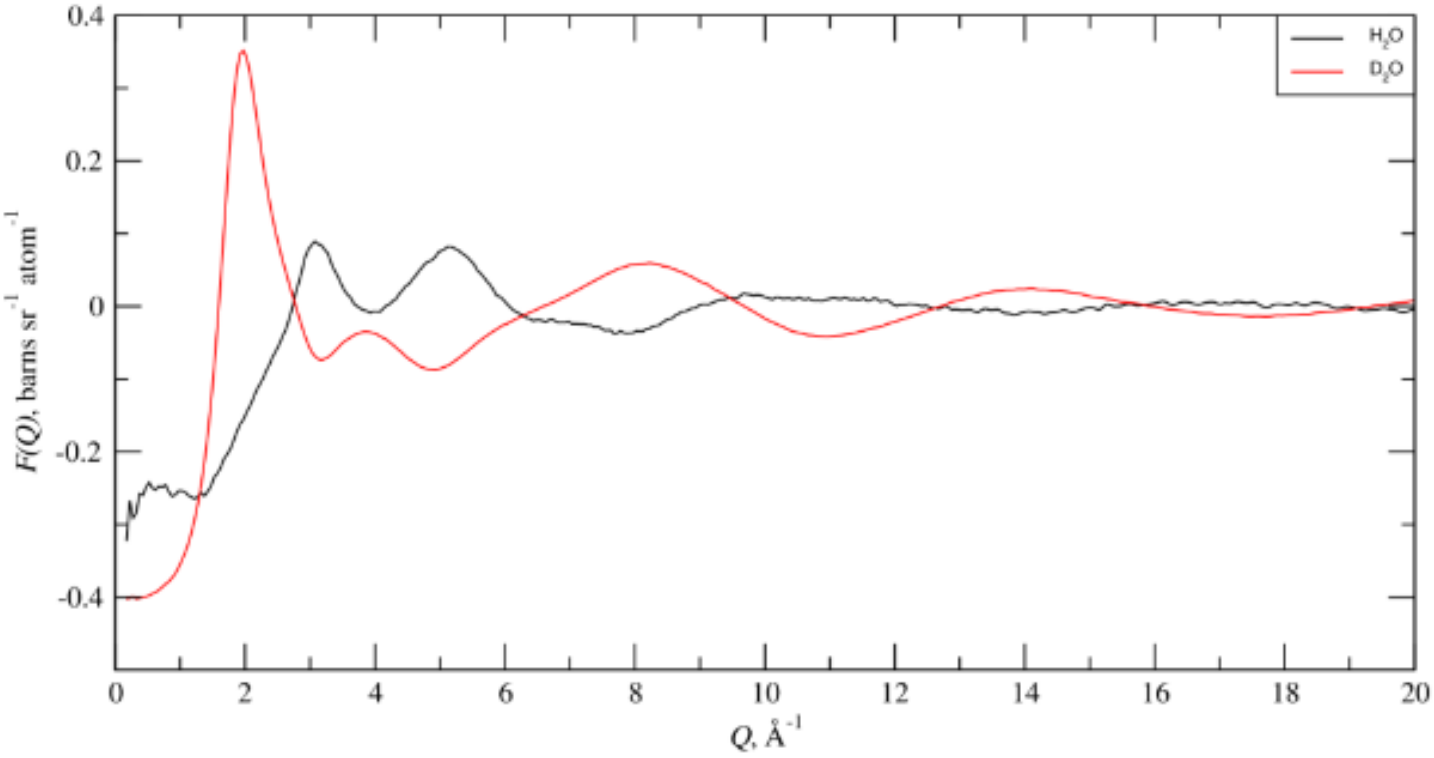
Water

i	j	c_i	c_j	b_i, fm	b_j, fm	$c_i c_j b_i b_j = w_{ij}$, 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

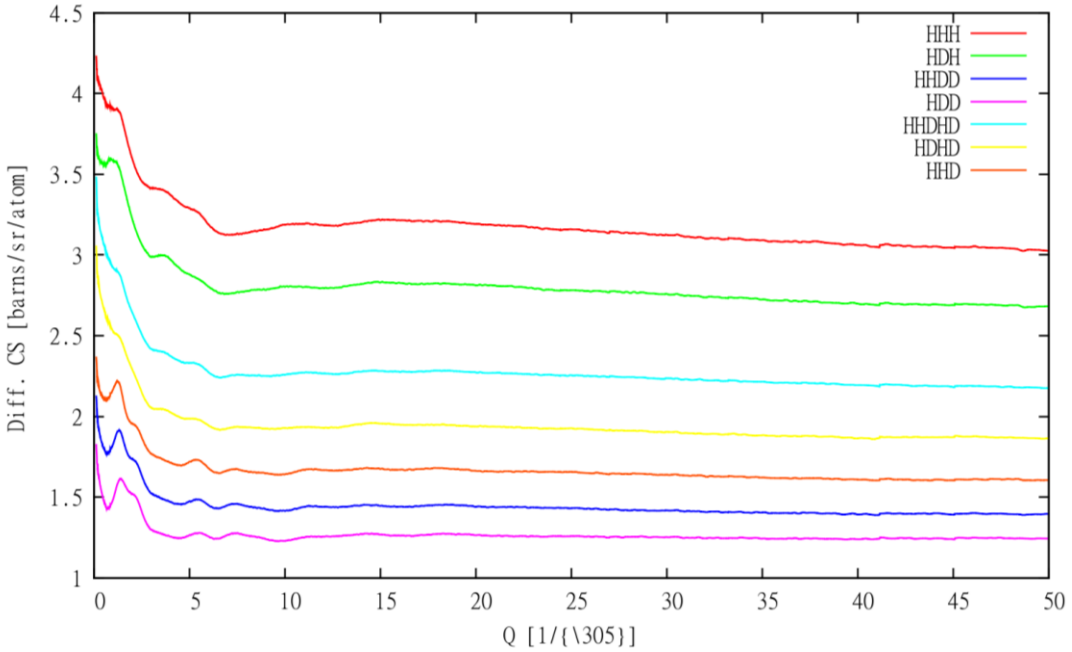
i	j	c_i	c_j	b_i, fm	b_j, fm	$c_i c_j b_i b_j = w_{ij}$, fm
O	O	1/3	1/3	0.5804	0.5804	0.0374
O	D	1/3	2/3	0.5804	0.6674	0.0861
D	D	2/3	2/3	0.6674	0.6674	0.1980

WANS


0.4
0.2
0
-0.2
-0.4
F(Q), barns sr-1 atom-1
0
2
4
6
8
10
12
14
16
18
20
Q, Å-1
H2O
D2O

WANS

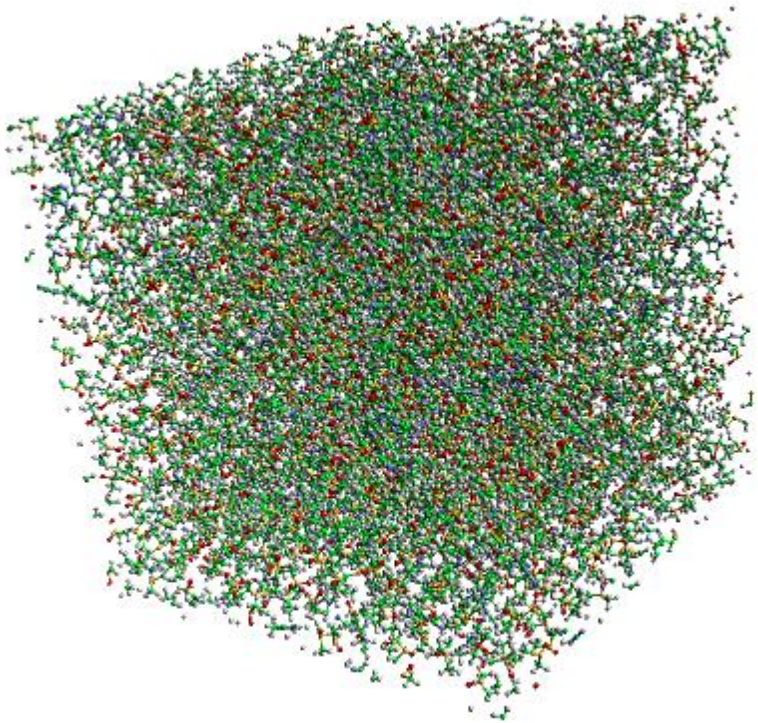
incoherency



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

https://www.isis.stfc.ac.uk/OtherFiles/Disordered%20Materials/DM%20Isotopic%20Substitution%20Experiments%20v1.0.pdf

DISSOLVE



- Molecular structure
- Density
- Composition

Force field

Monte Carlo Simulation

Potential relaxation

Radial Distribution function calculation

Structure factors calculation

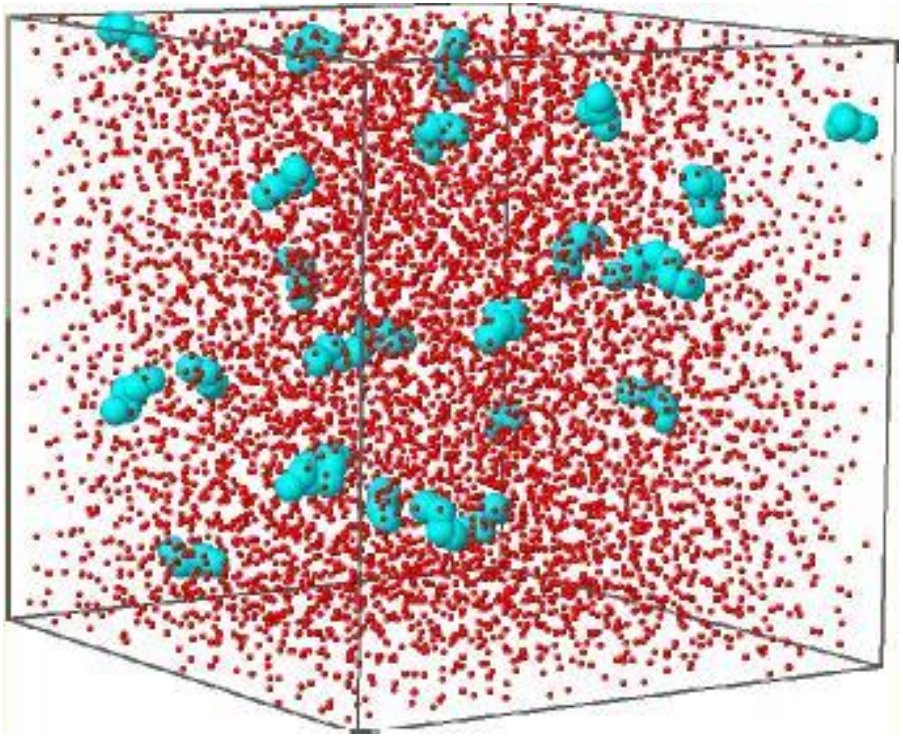
Difference between calculated and experimental structure factors

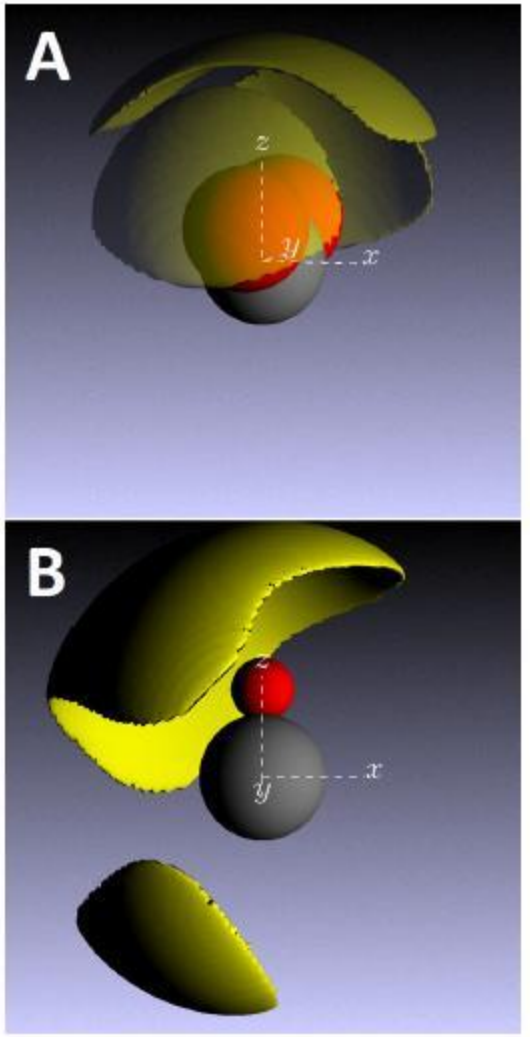
Experimental data

Mol. Phys. (2019), **117(22)**, 3464-3477

https://github.com/disorderedmaterials/dissolve

Generation of structural models

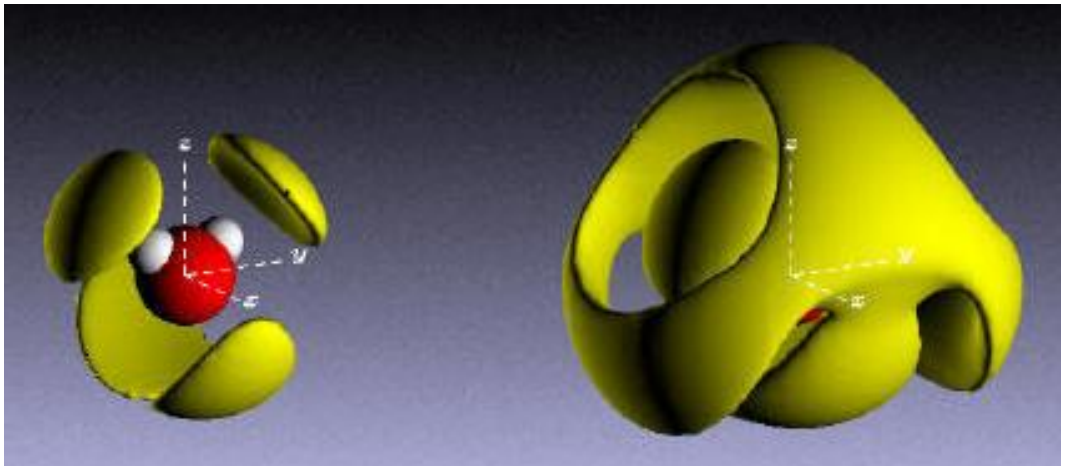


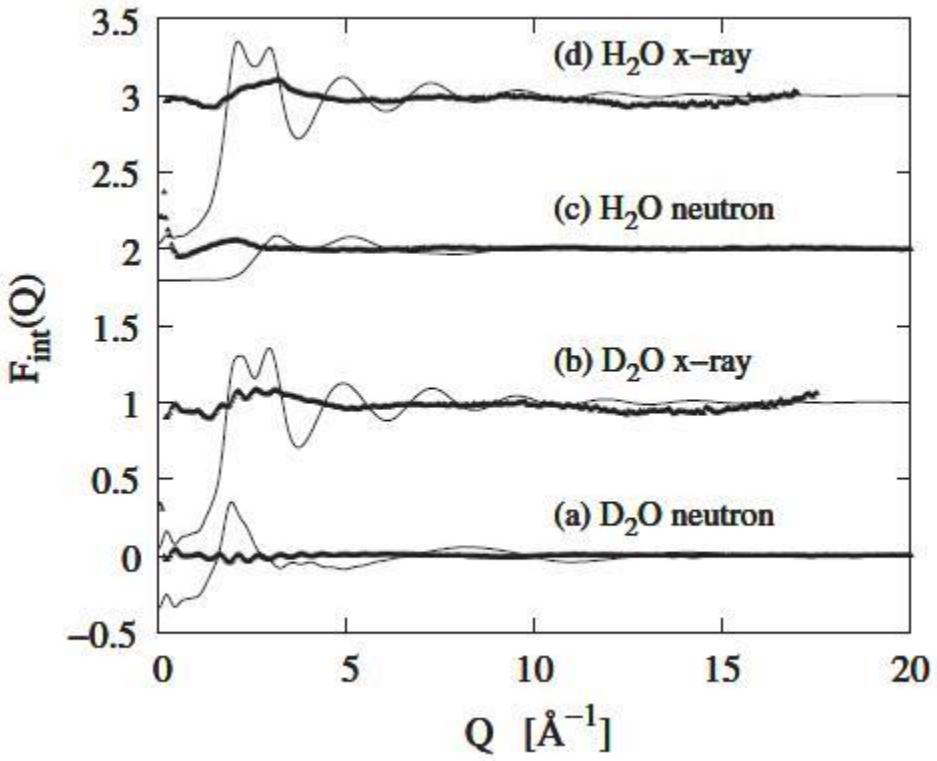


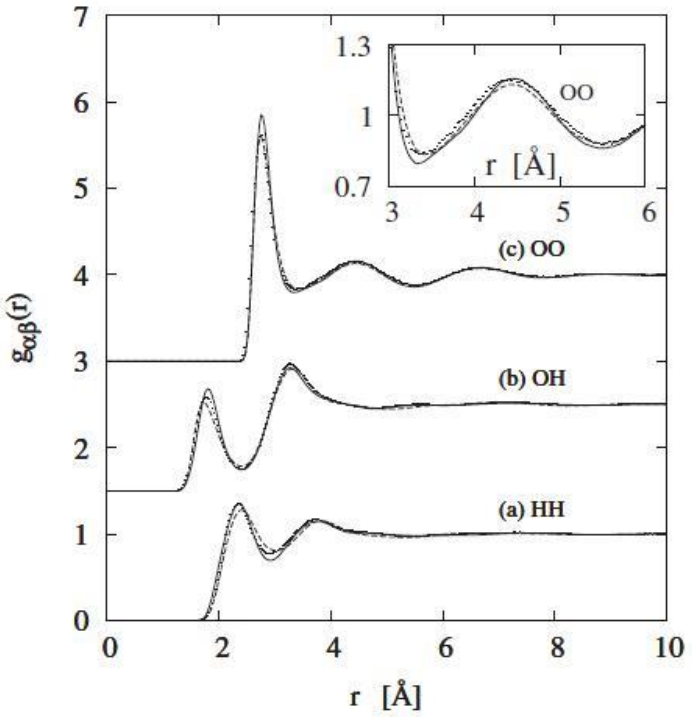
N.H. Rhys, A.K. Soper, L. Dougan, *J. Phys. Chem. B*, 2012, **116**, 13308

Applications

Water

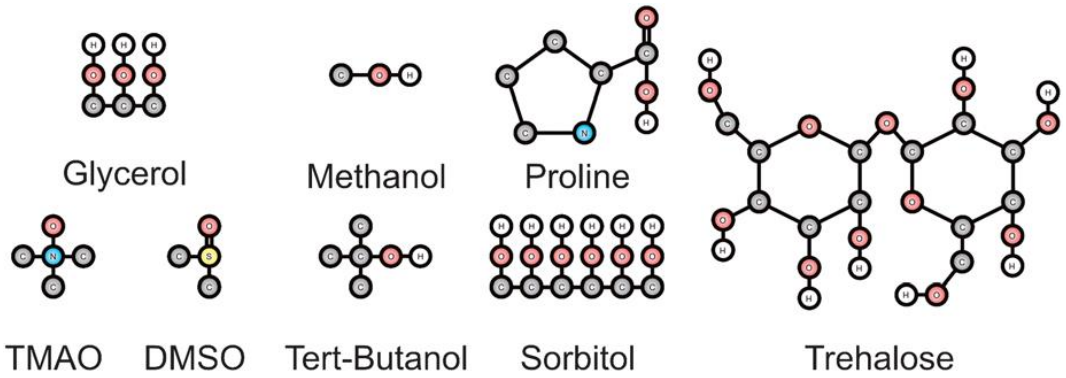


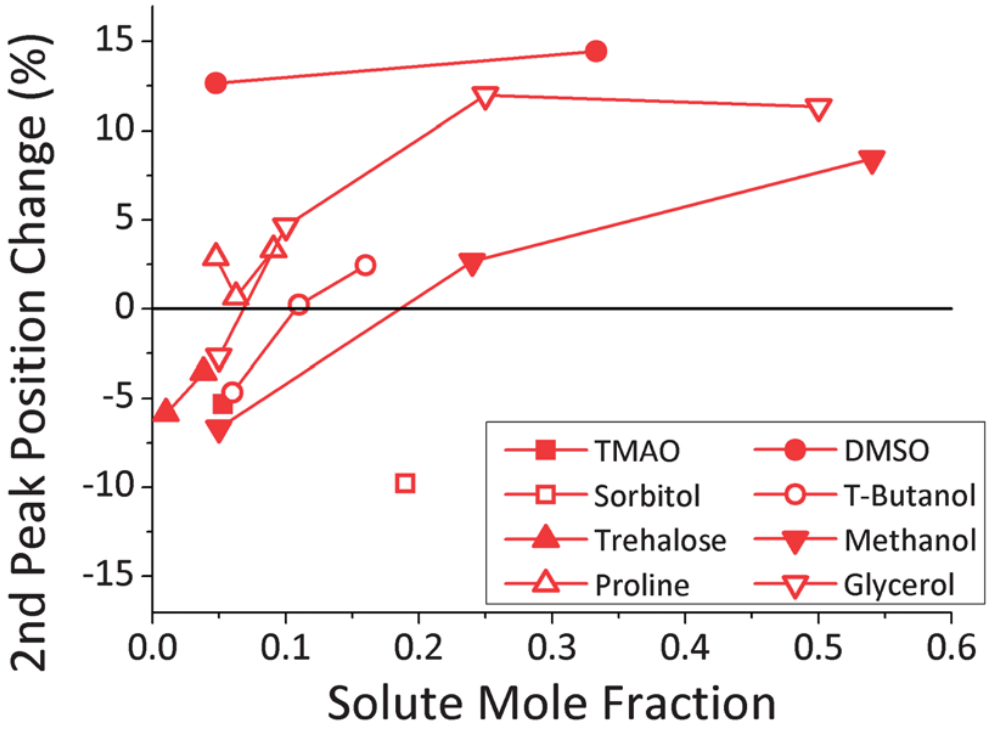


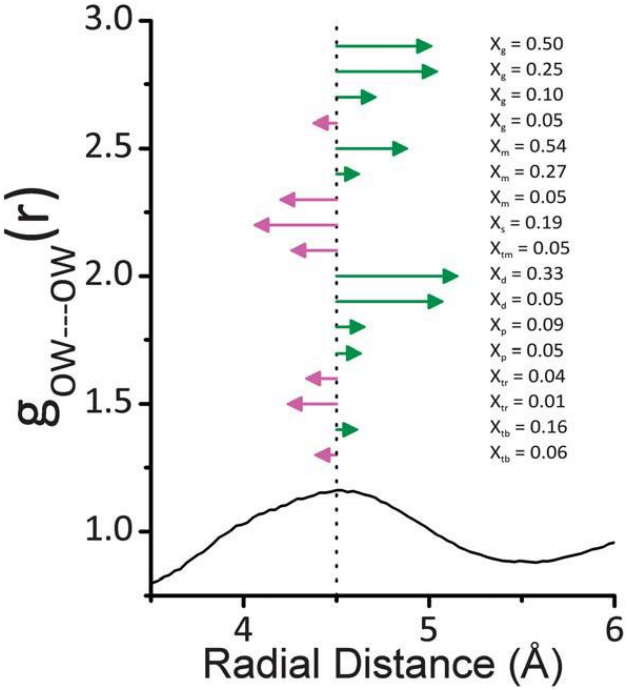


A. Soper, C.J. Benmore, *Phys. Rev. Lett.*, **101**, 065502

Antifreeze effect

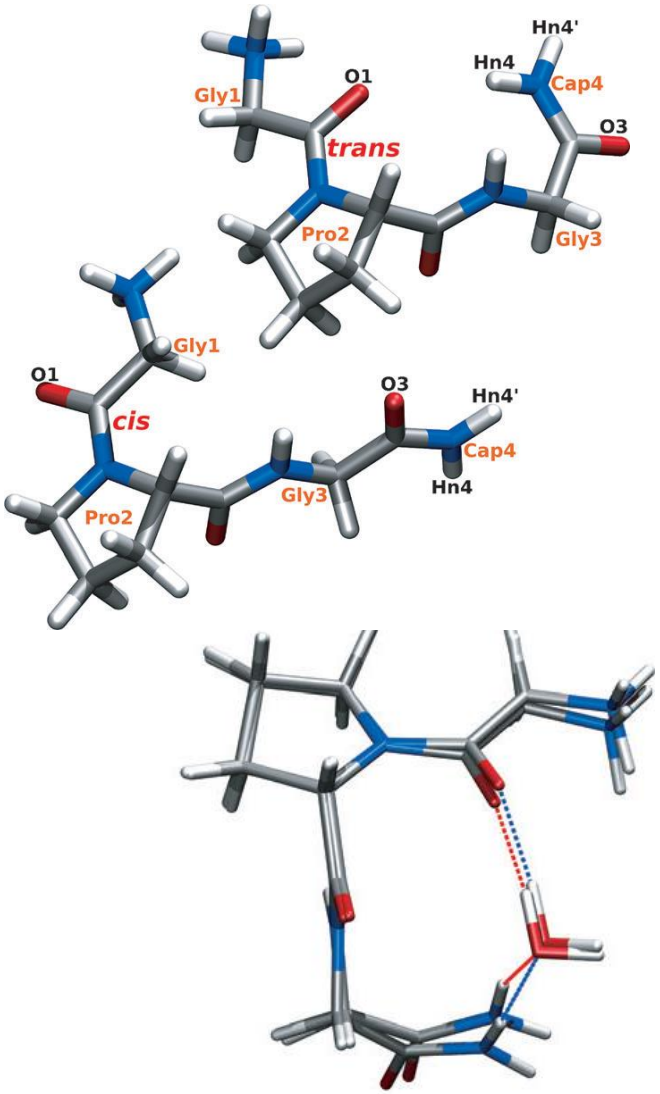


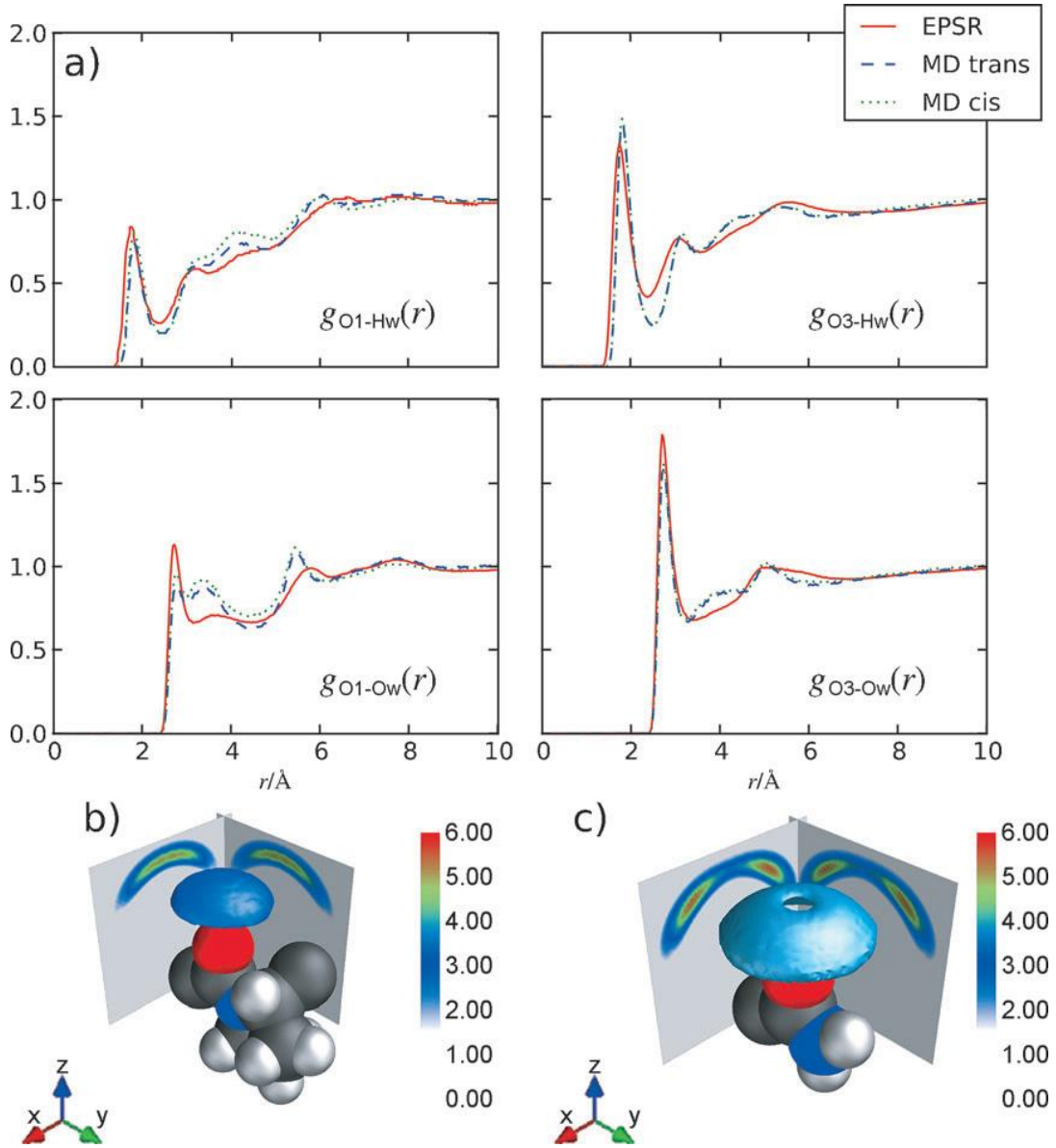




J.J. Towey, A.K. Soper, L. Dougan, *Faraday Disc.* 2013, DOI 10.1039/c3fd00084b

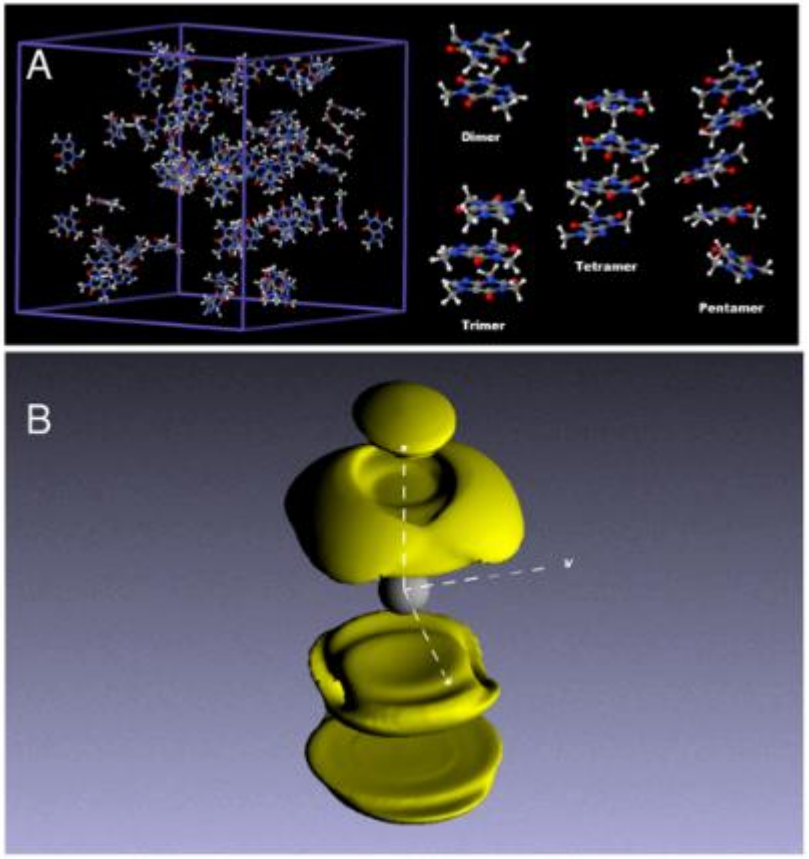
Small peptides

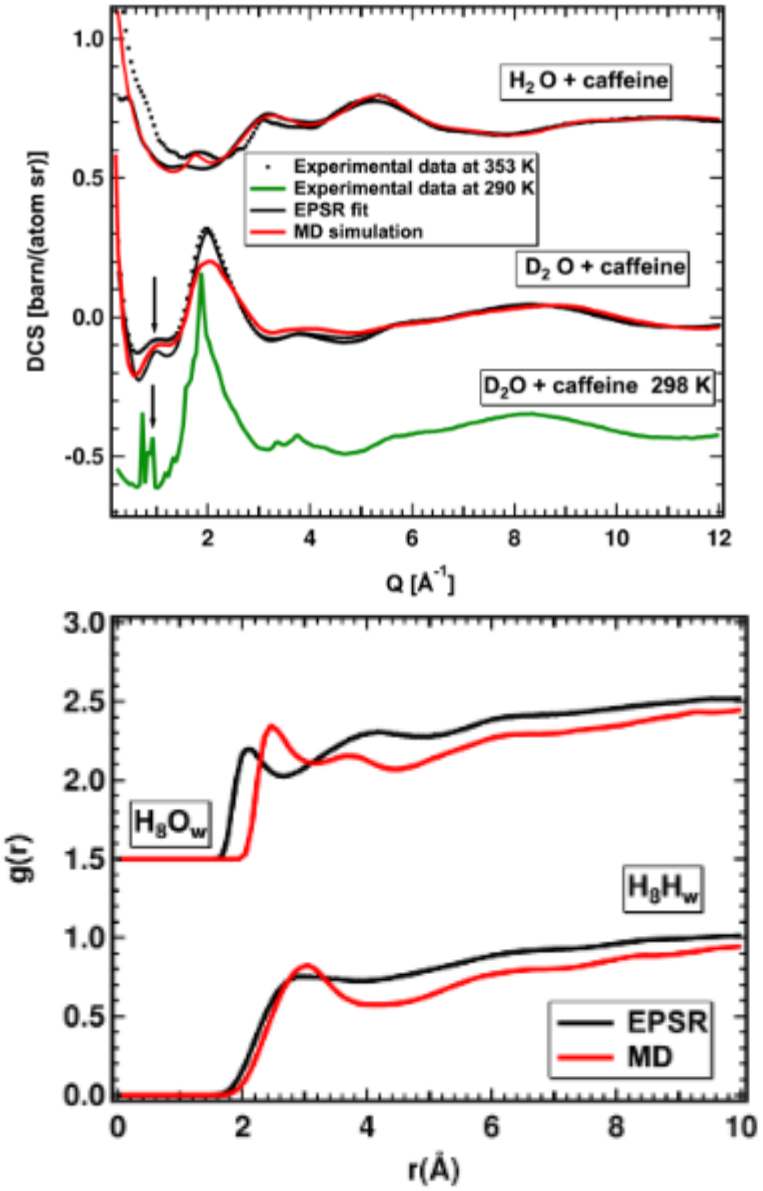




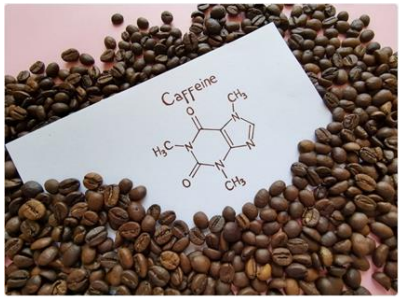
S. Busch, C.D. Bruce, C. Redfield, C.D. Lorenz, S.E. McLain, *Angew. Chem. Int. Ed.*, 2013, **52(49)**, 13091

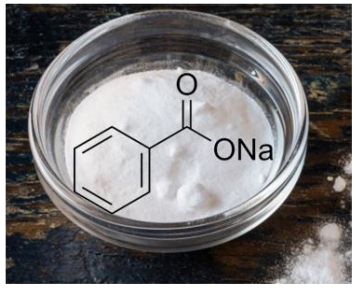
Drug compounds

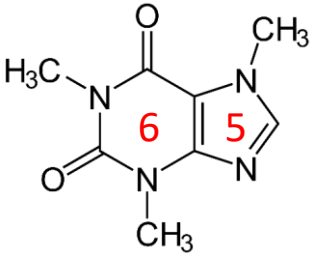




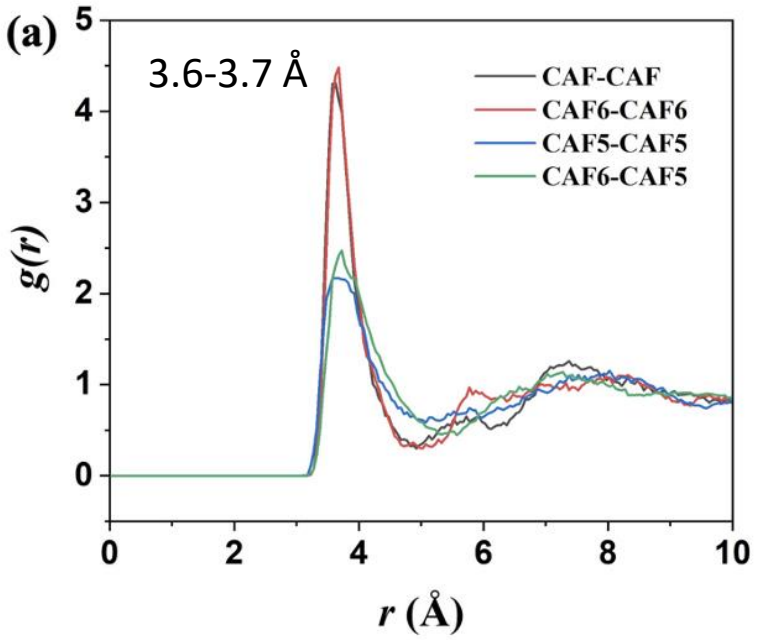
L. Tavagnacco, J.W. Brady, F. Bruni, S. Callear, M.A. Ricci, M.L. Saboungi, A. Cesaro, *J. Phys Chem. B*, 2015, **119**, 13294

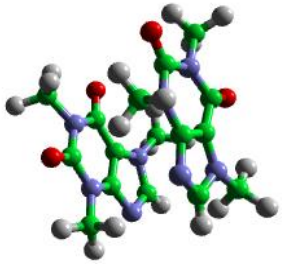


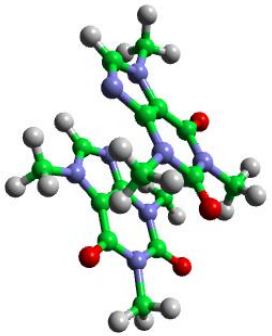




Pure CAF: 4.1 Å





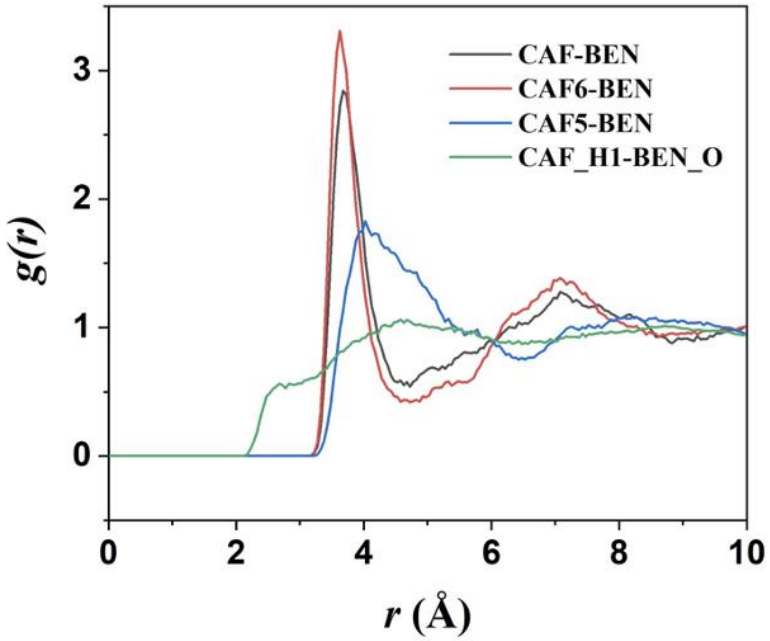


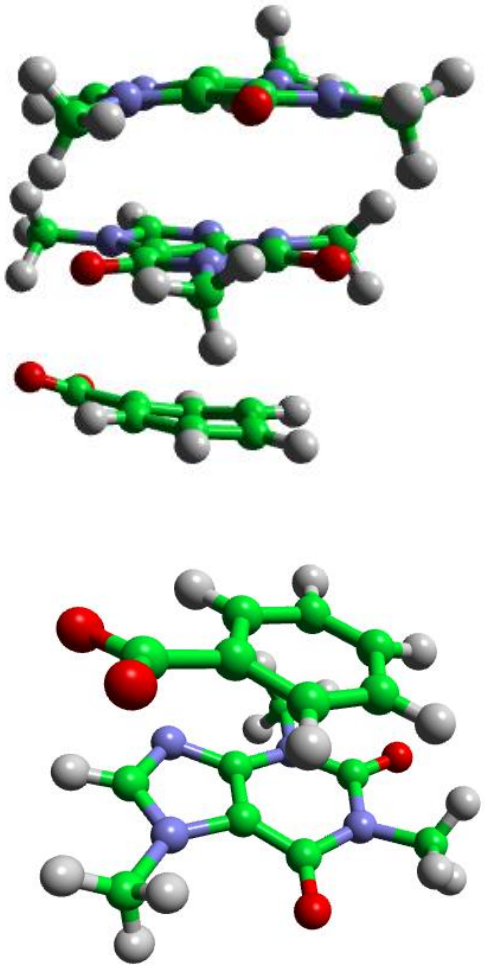
Correlation	Co-ordination number (atoms)
CAF-CAF	0.39 ± 0.05
CAF6-CAF6	0.39 ± 0.06
CAF5-CAF5	0.27 ± 0.03
CAF6-CAF5	0.47 ± 0.05

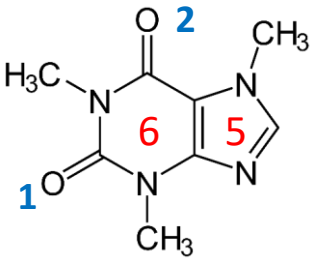
Int. J. Pharmaceut., 2023, 647, 123520 j.ijpharm.2023.123520

J. Phys. Chem. B 2015, 119(42), 13294-13301

CAF-Benzoate

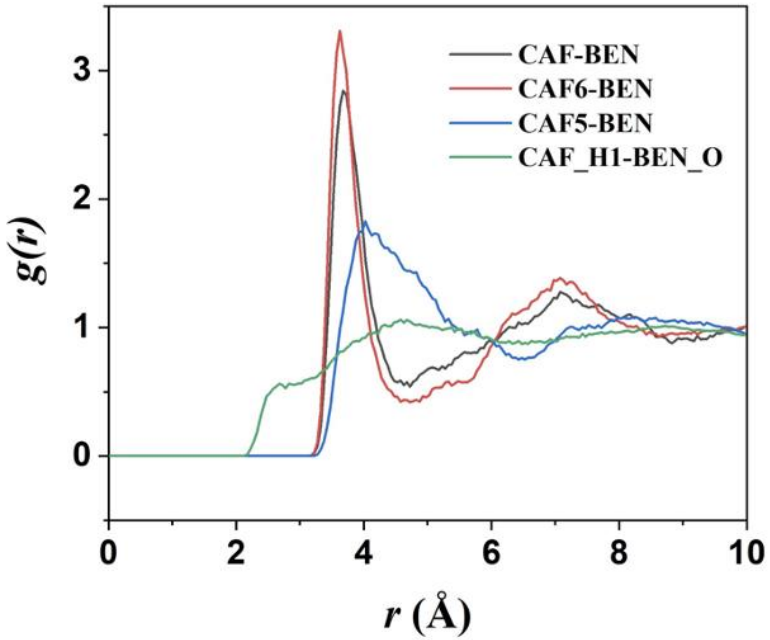




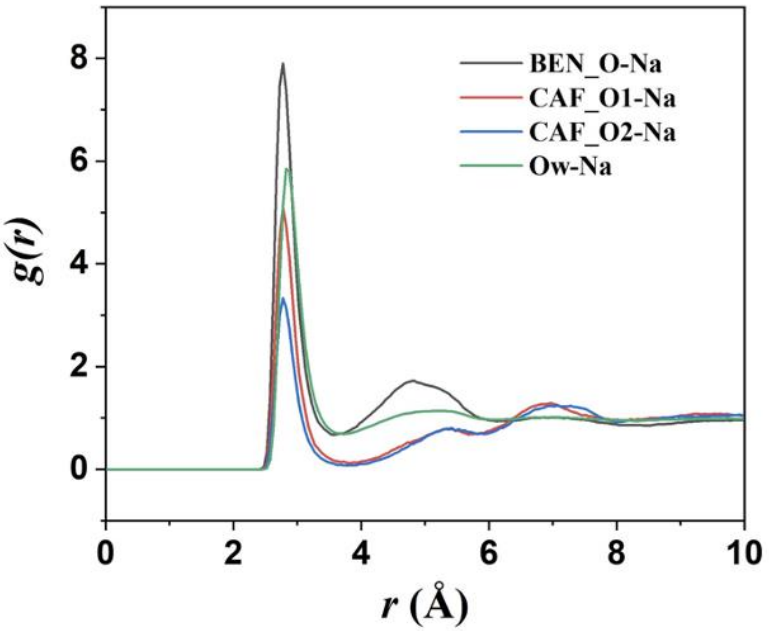


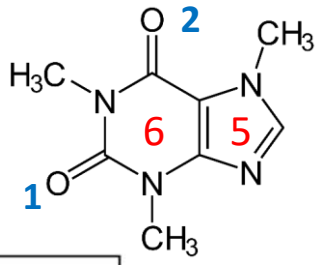
Int. J. Pharmaceut., 2023, 647, 123520 [j.ijpharm.2023.123520]

CAF-Benzoate



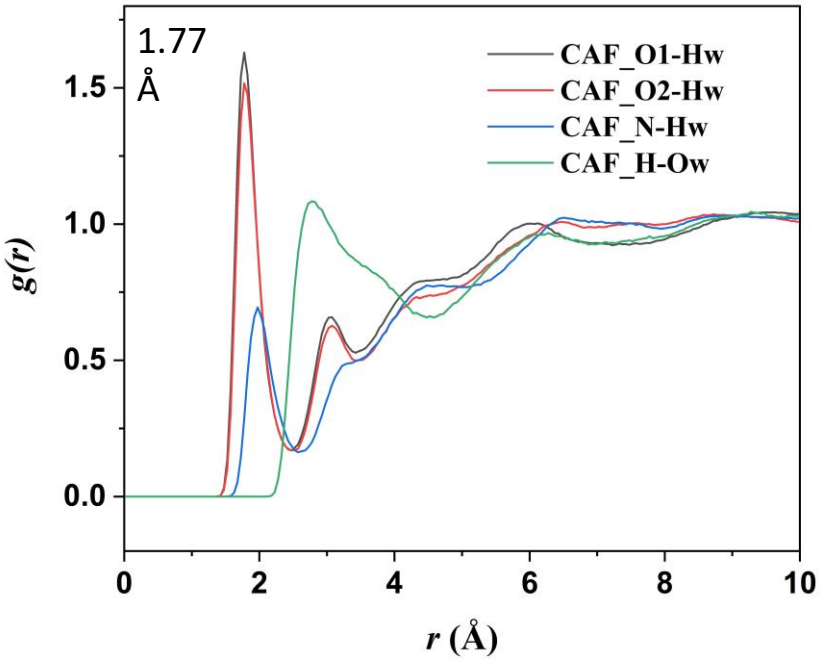
CAF/Benzoate-Na⁺

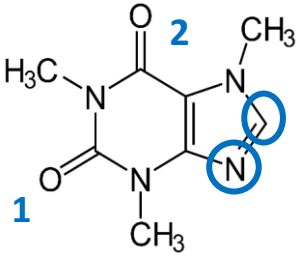


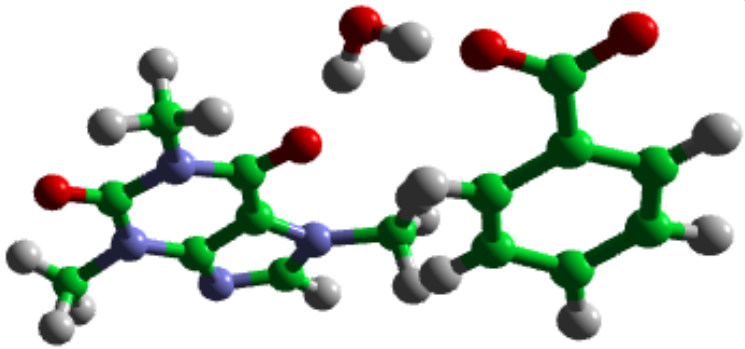


Int. J. Pharmaceut., 2023, 647, 123520 [j.ijpharm.2023.123520]

Pure CAF in water: 2.05 Å

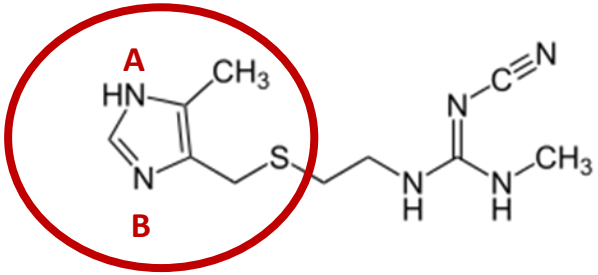




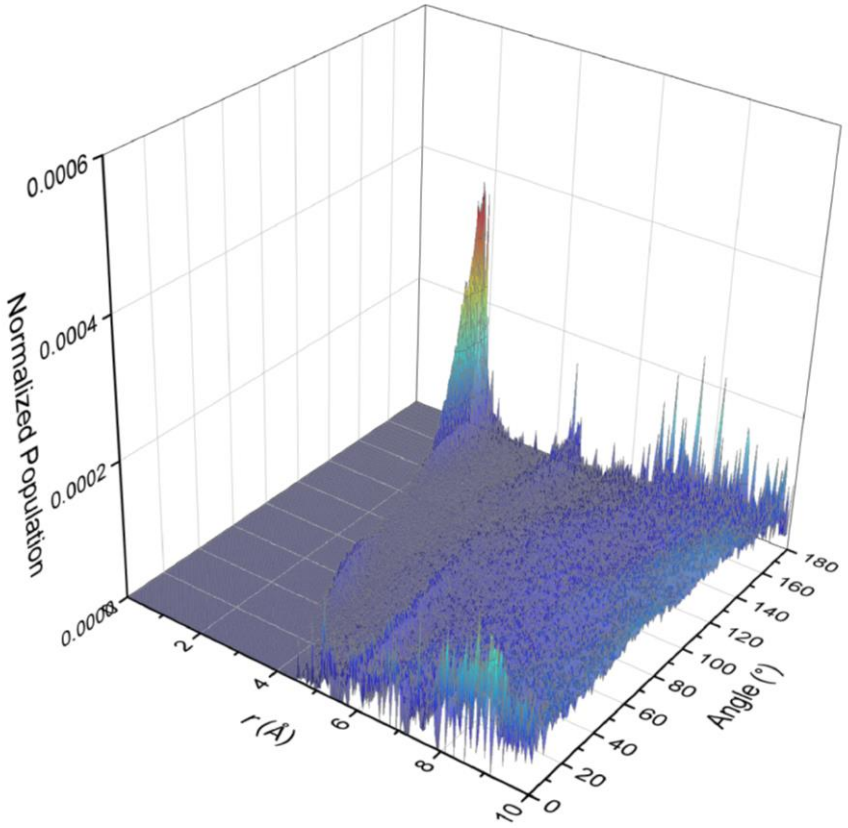


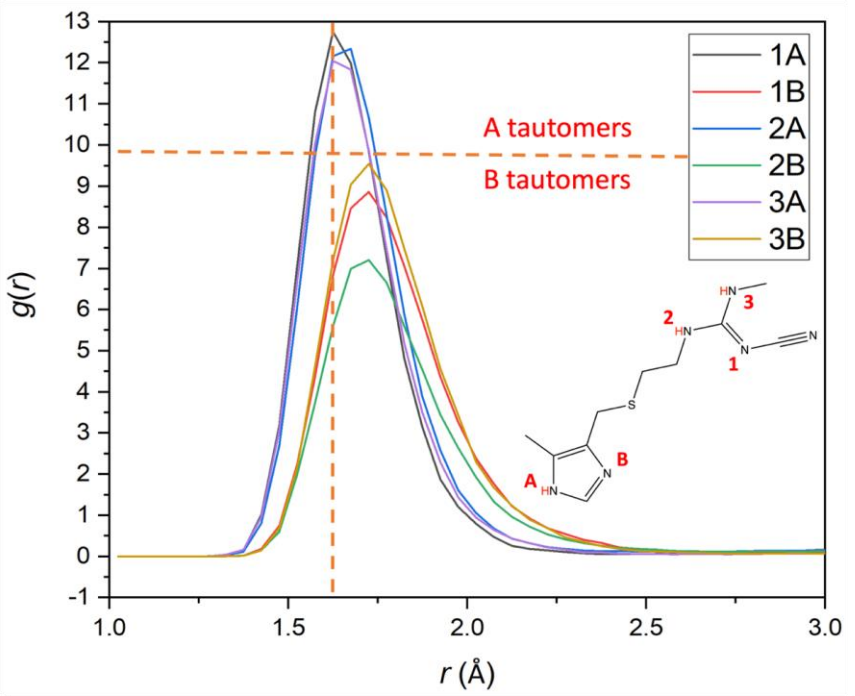
Int. J. Pharmaceut., 2023, 647, 123520 j.ijpharm.2023.123520

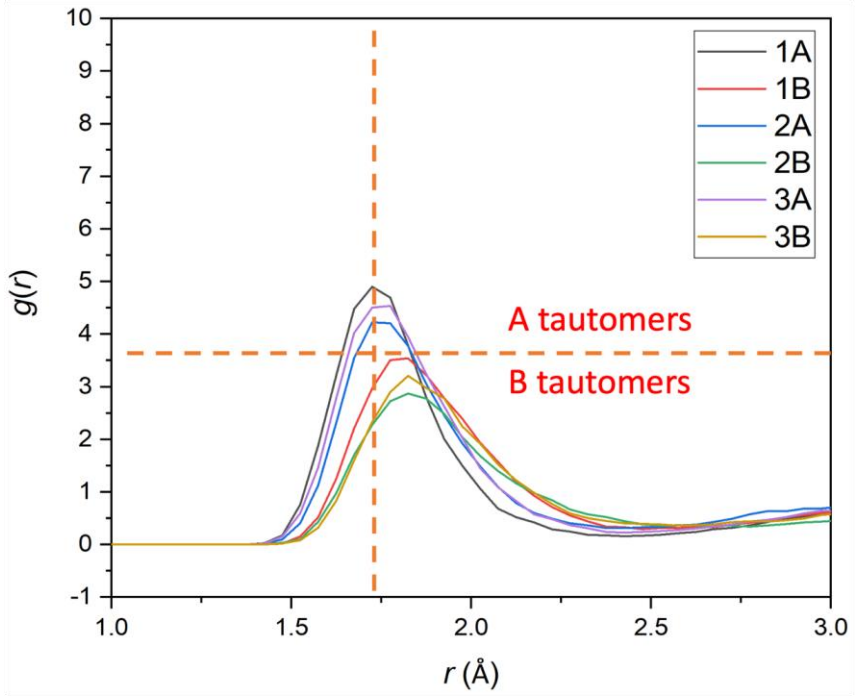
J. Phys. Chem. B 2015, **119(42)**, 13294-13301



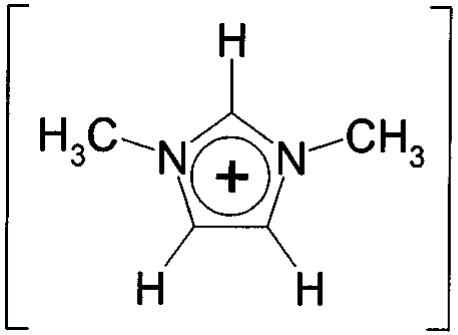
Binding to DMSO



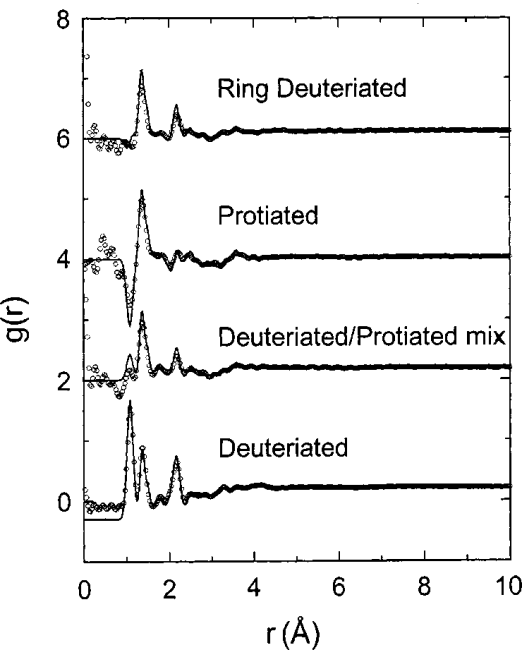


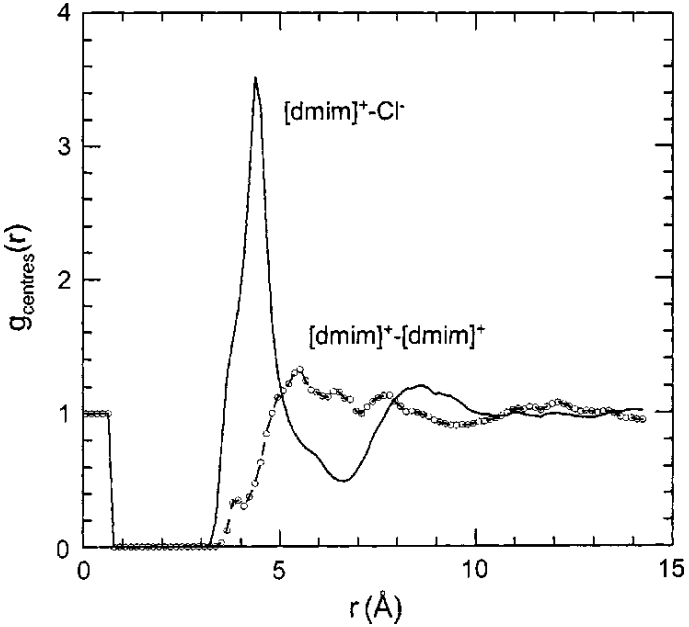


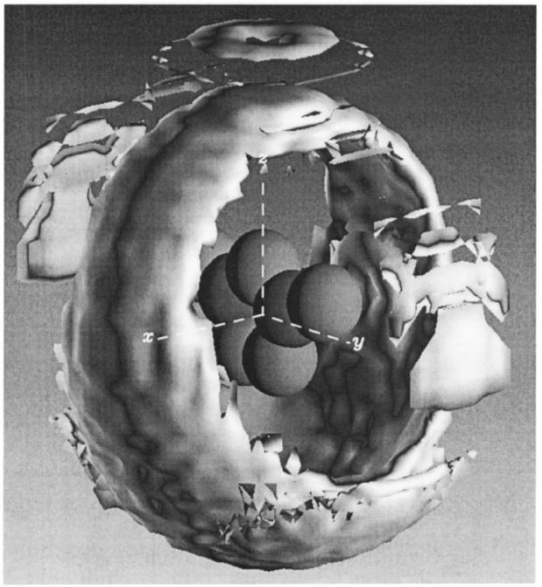
Ionic liquid/ salt melt



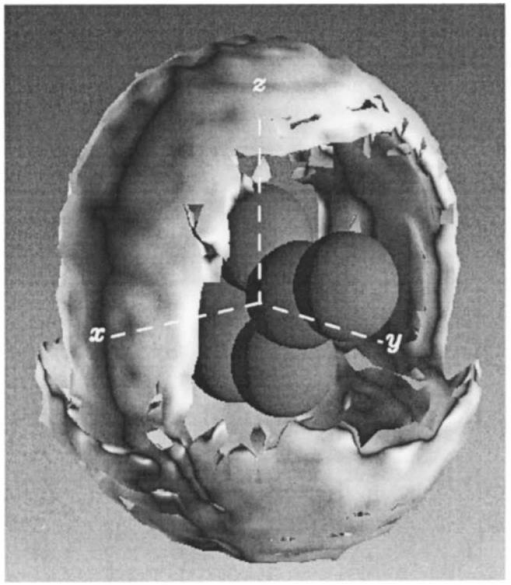
Cl-







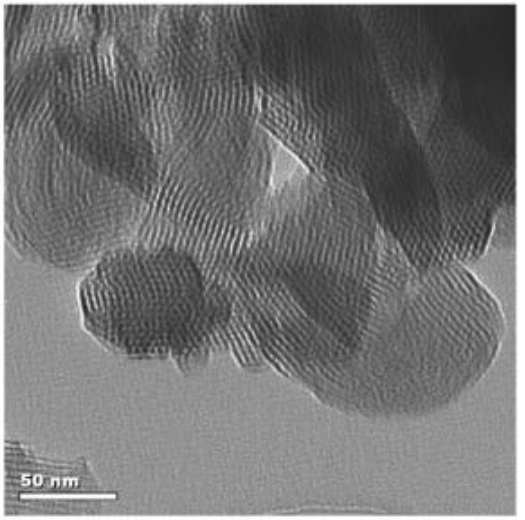
Imidazole-imidazole distance

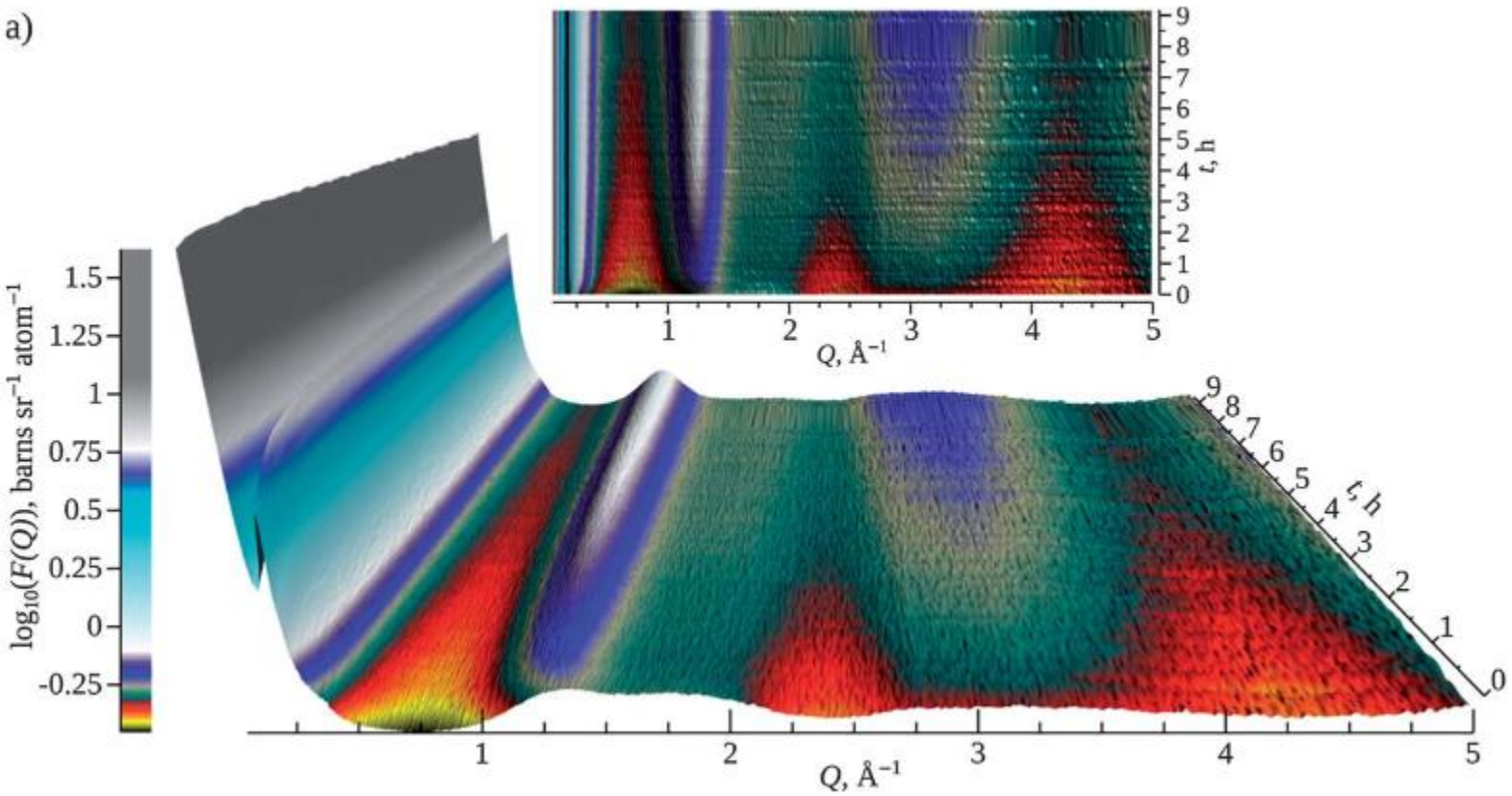


Imidazole-chloride distance

C. Hardacre, J.D. Holbrey, S.E.J. McMath, D.T. Bowron, A.K. Soper, J. *Chem. Phys.*, 2003, **118**, 273

Heterogeneous catalysis





T.G.A. Youngs, H. Manyar, D.T. Bowron, L.F. Gladden, C. Hardacre, *Chem. Sci.*, 2013, **4**, 3484

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