# Wide Angle Scattering and Pair Distribution Functions

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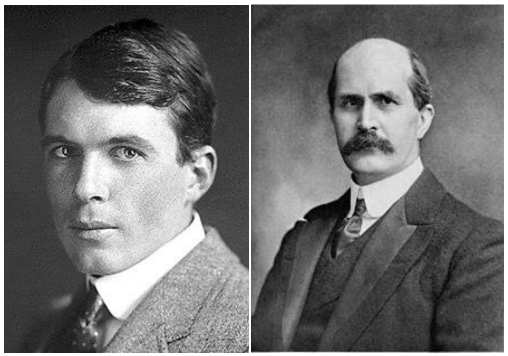
Queen's University Belfast

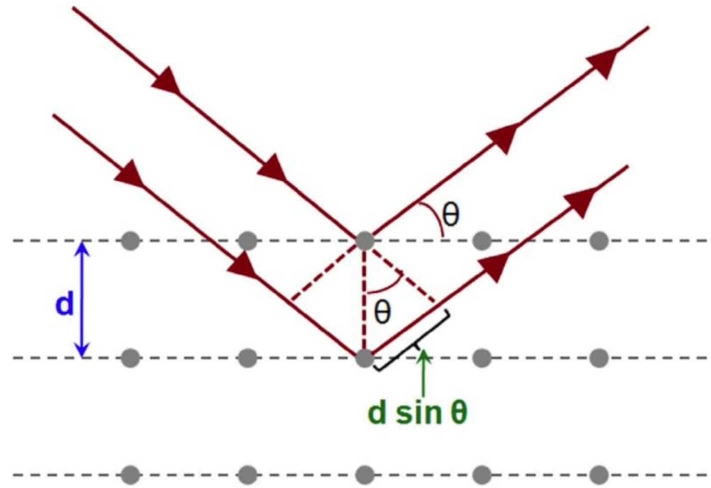
# Overview

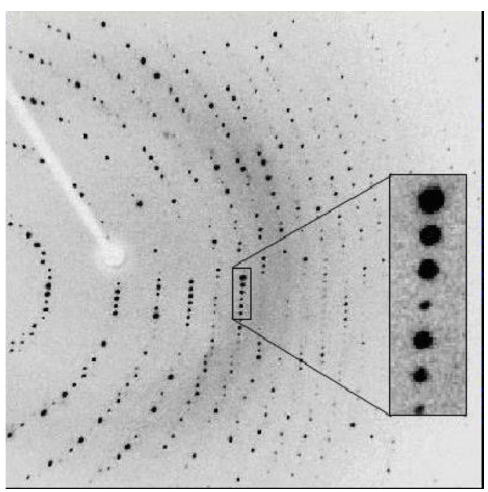
- Diffraction
  - What are the effects of increasing disorder?
- Small vs wide angle scattering
- Pair distribution function
- Examples

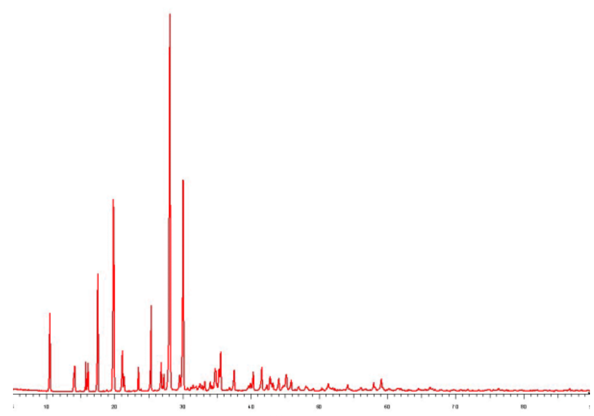
# Diffraction



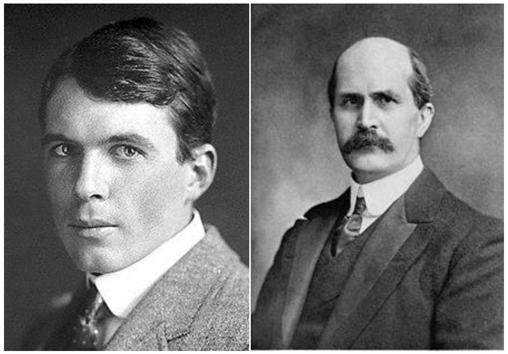
$$n\lambda = 2d\ sin(\theta)$$



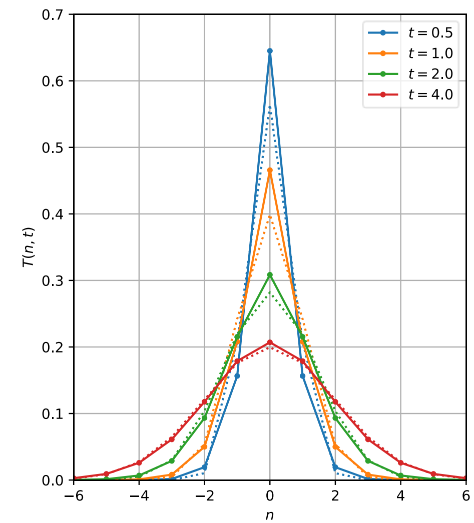



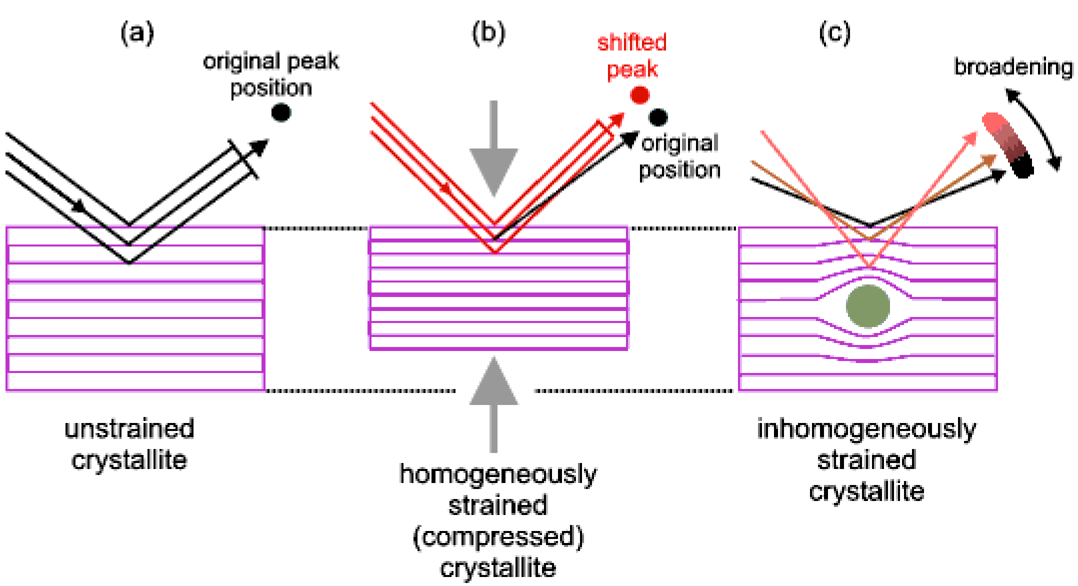


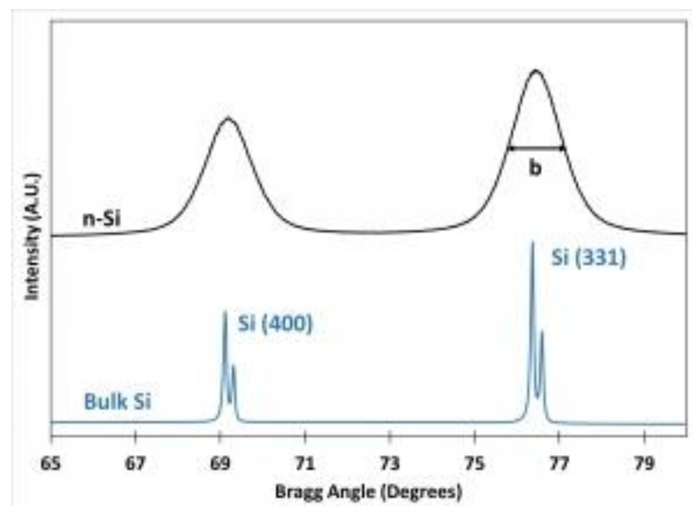
# Diffraction



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

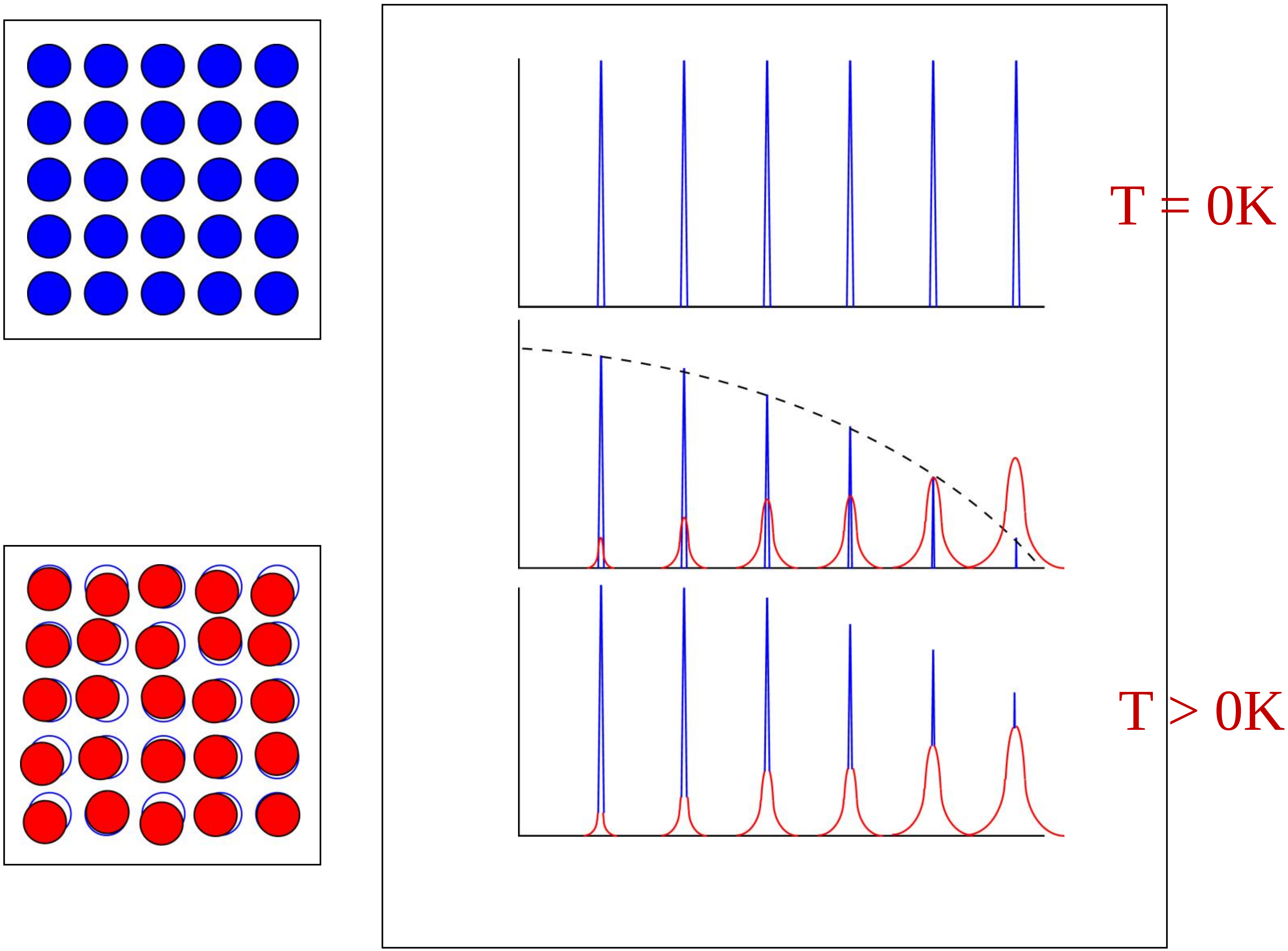


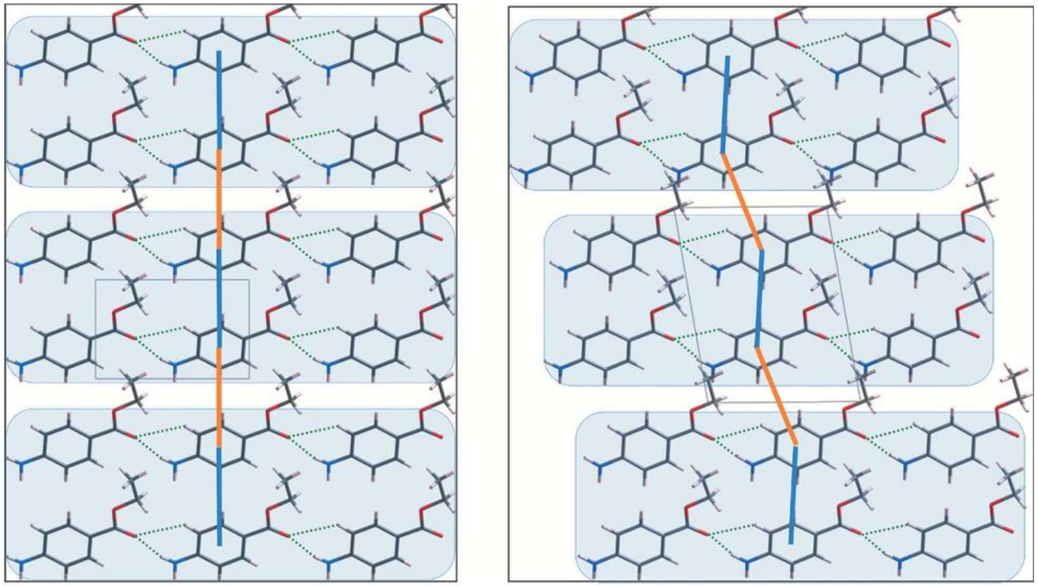




Birkbeck College

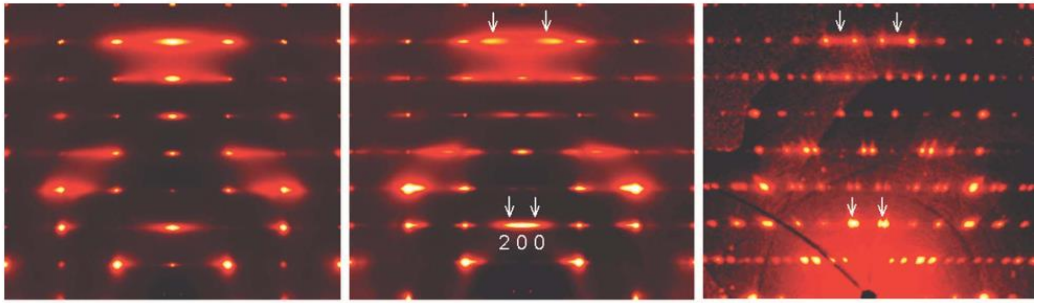
# The effect of temperature



# The effect of dislocation



(a)

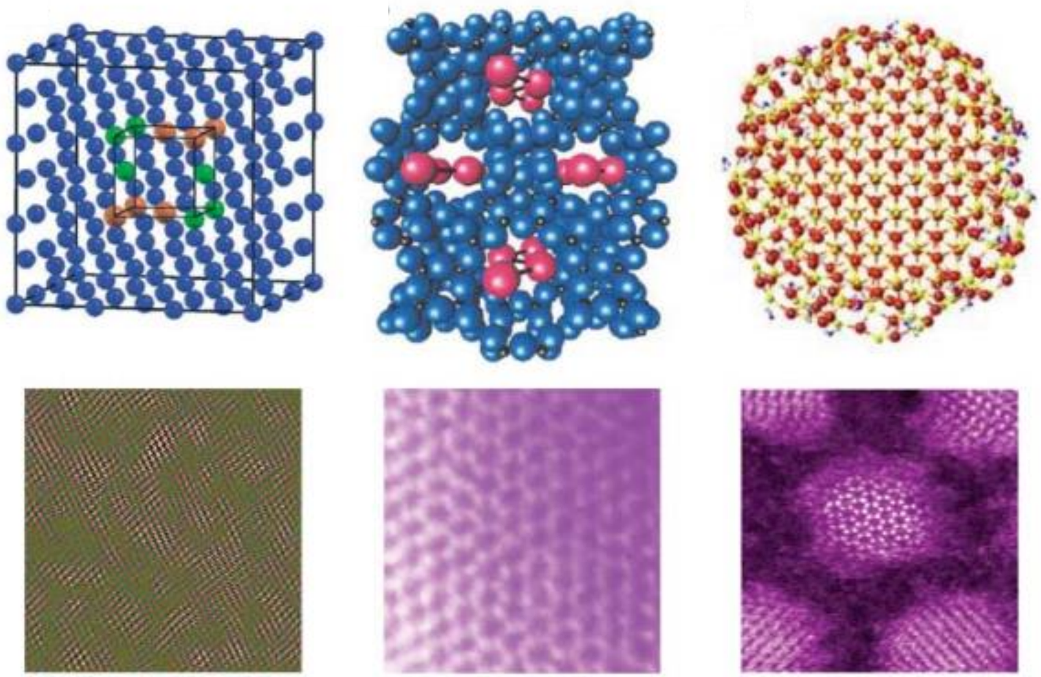



I II III

(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**

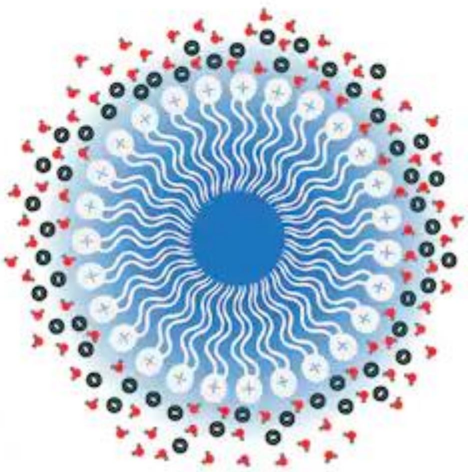
# Nanoscale structure

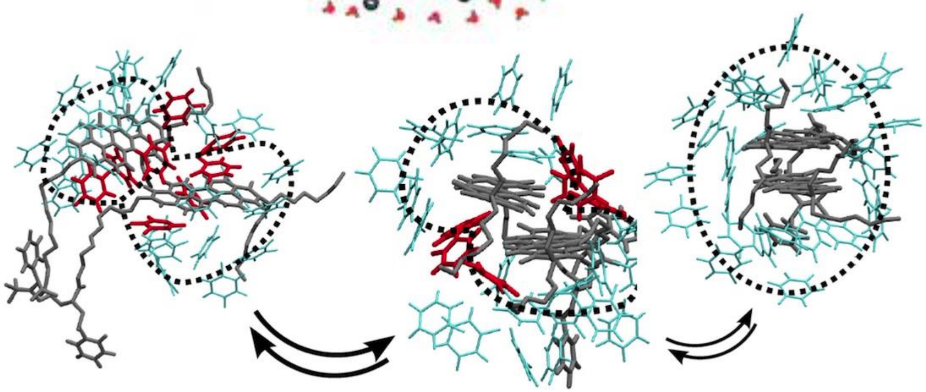


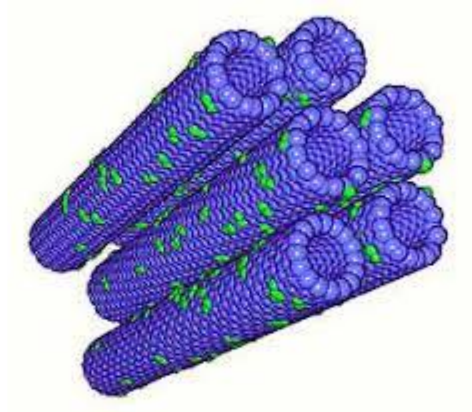
Science, 2007, 316, 561

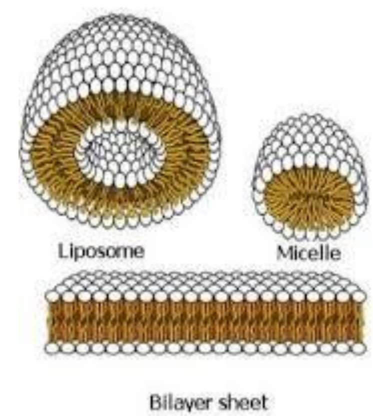
# Wide vs small angle scattering

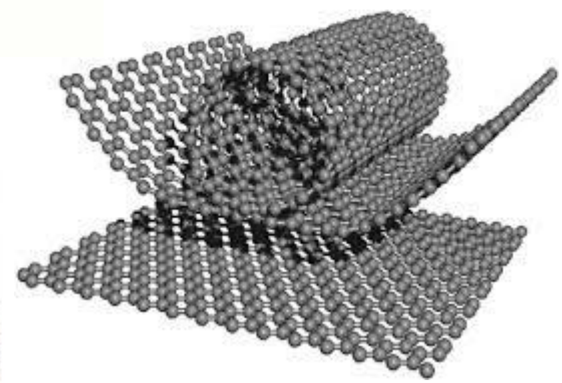
Wide Angle Scattering < $10^{-9}$ m









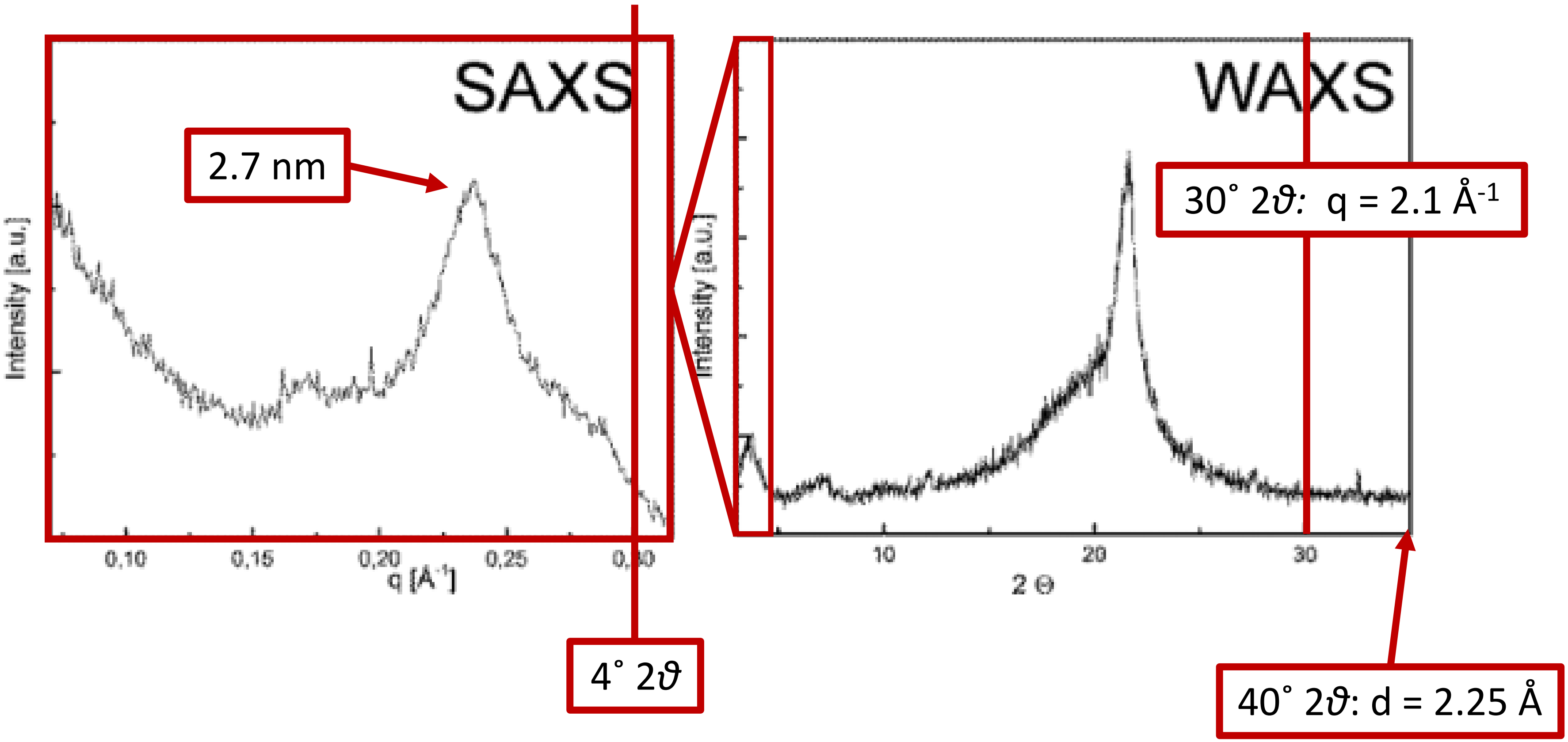



Small Angle Scattering > $10^{-9}$ m

# Wide vs small angle scattering

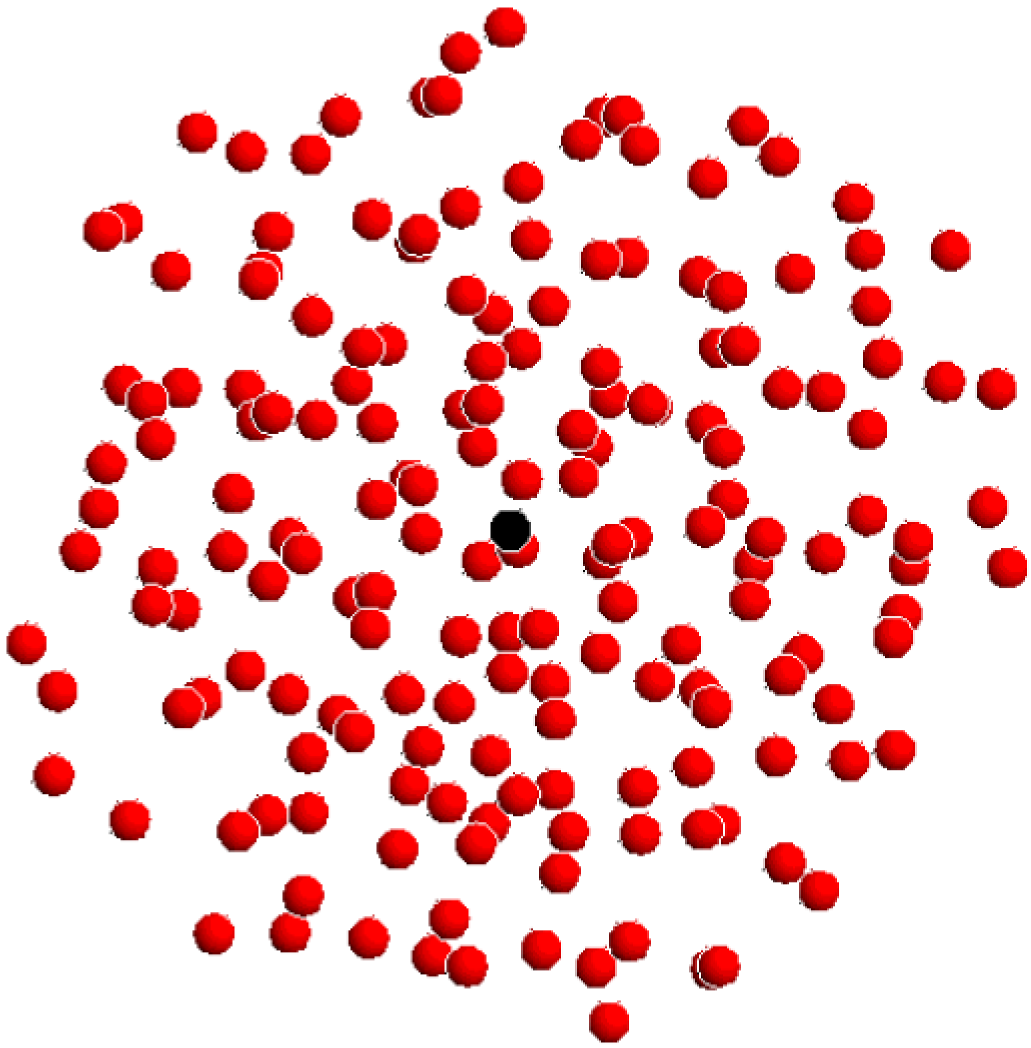
$$q = \frac{4\pi \sin(\theta)}{\lambda}$$

Amorphous poly(phosphoamidate), data acquired with Cu Kα radiation ($\lambda$ = 1.54 Å)

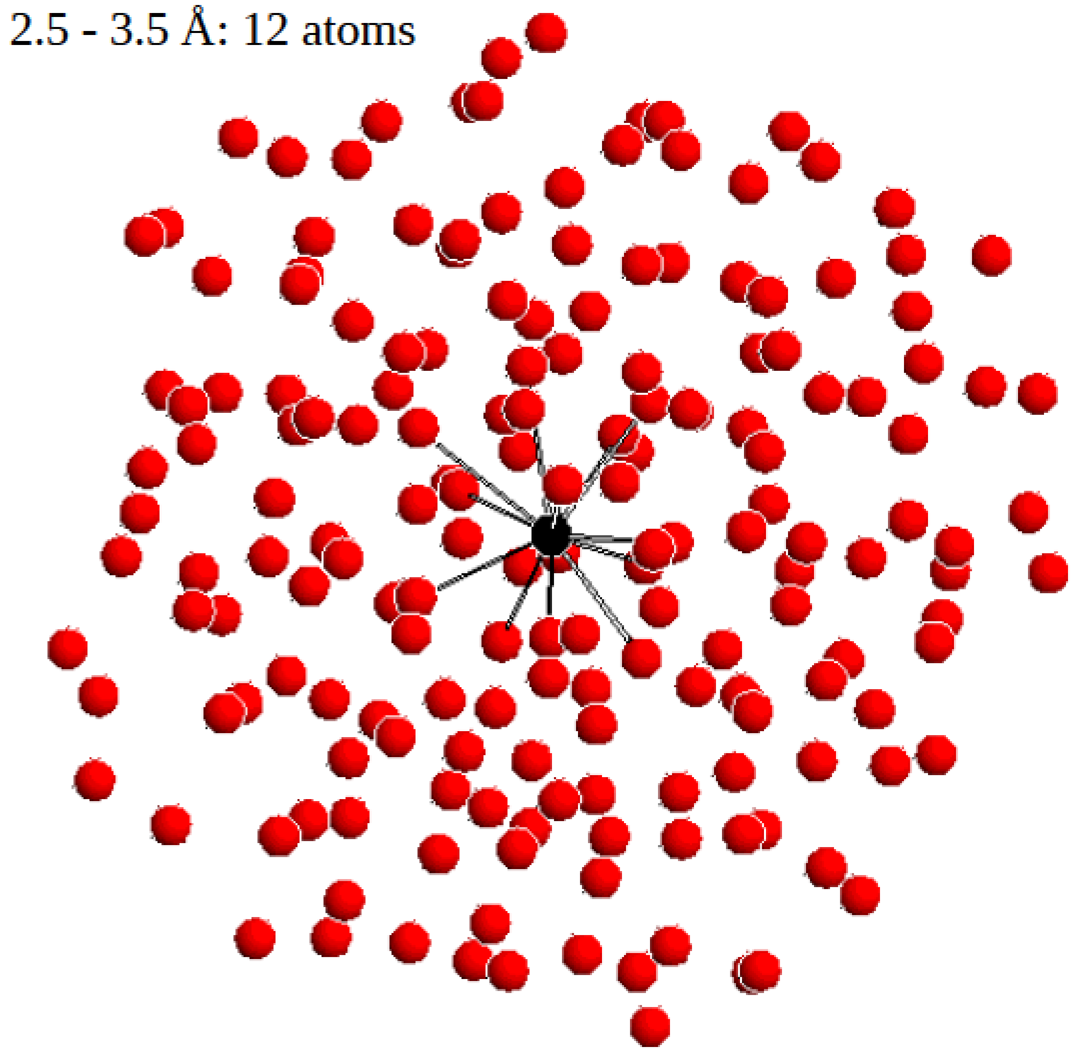



Polym. Chem.,2016, 7, 5004–5010

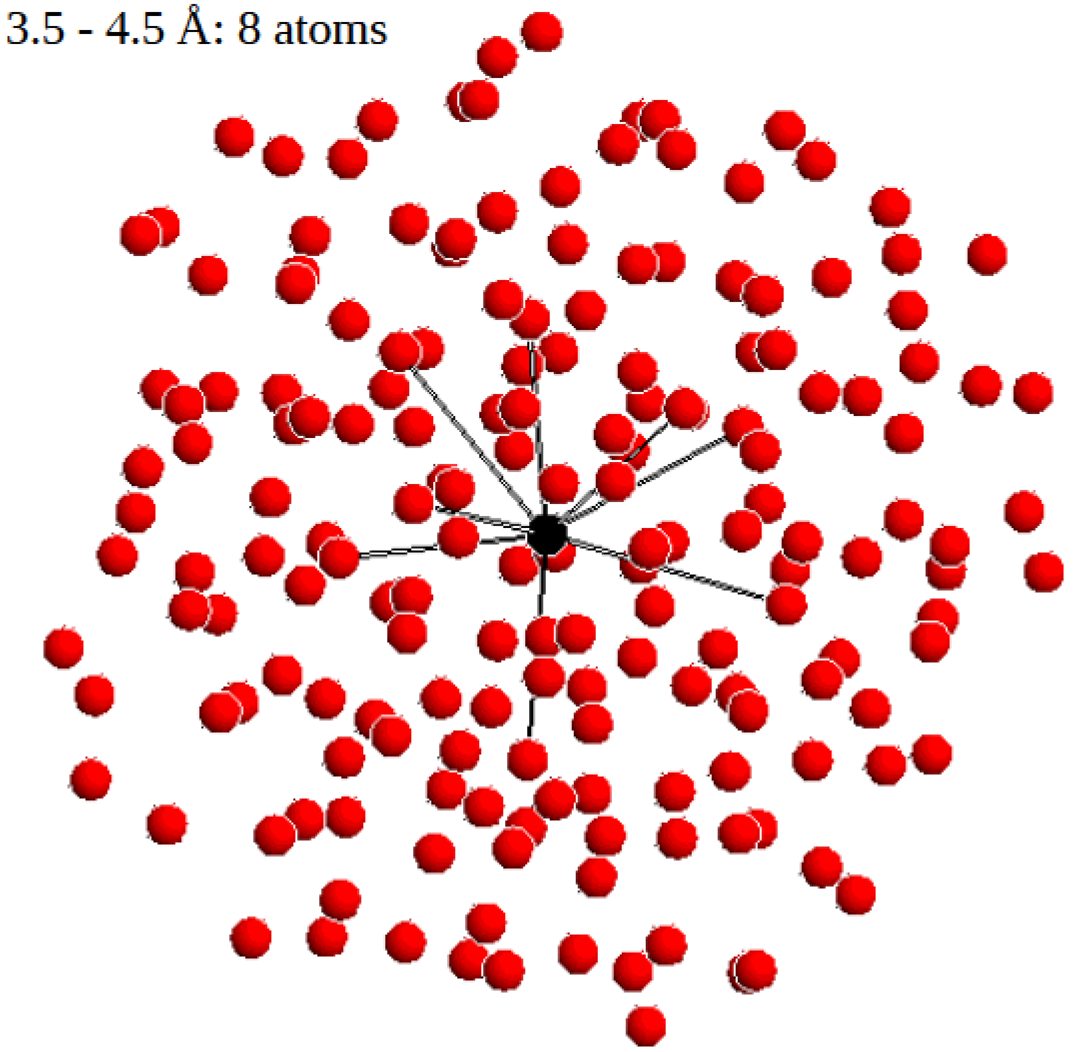
# Pair distribution function



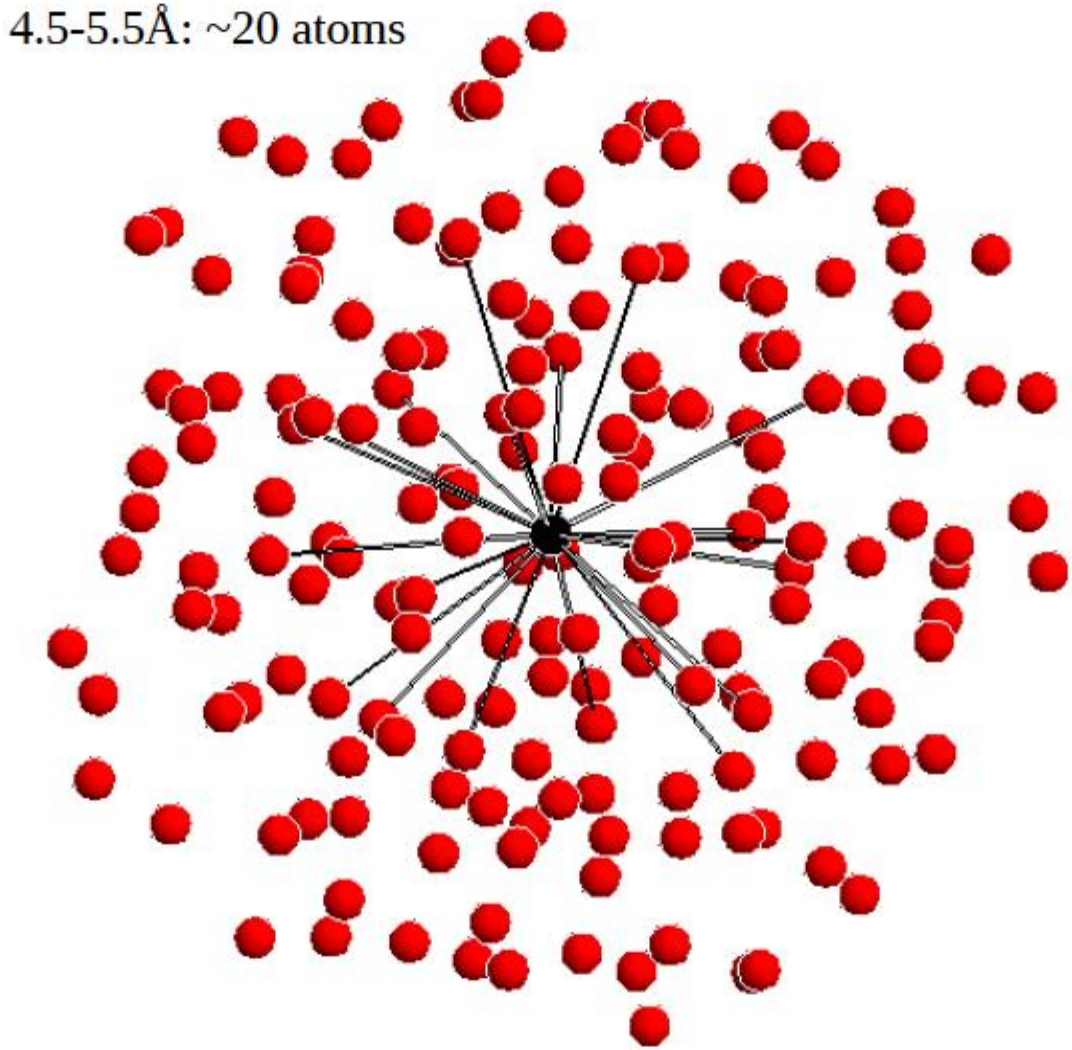
# Pair distribution function



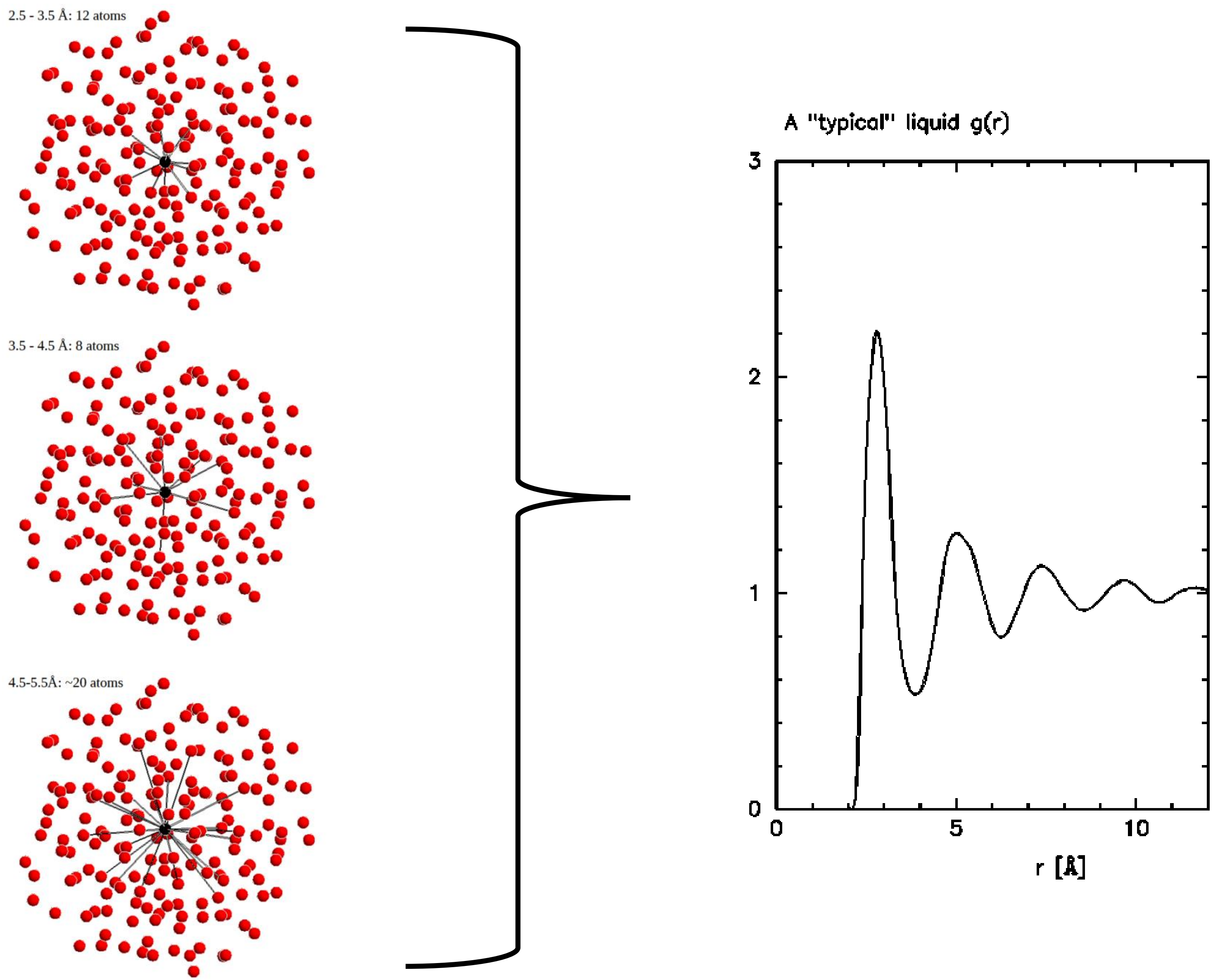
# Pair distribution function



# Pair distribution function



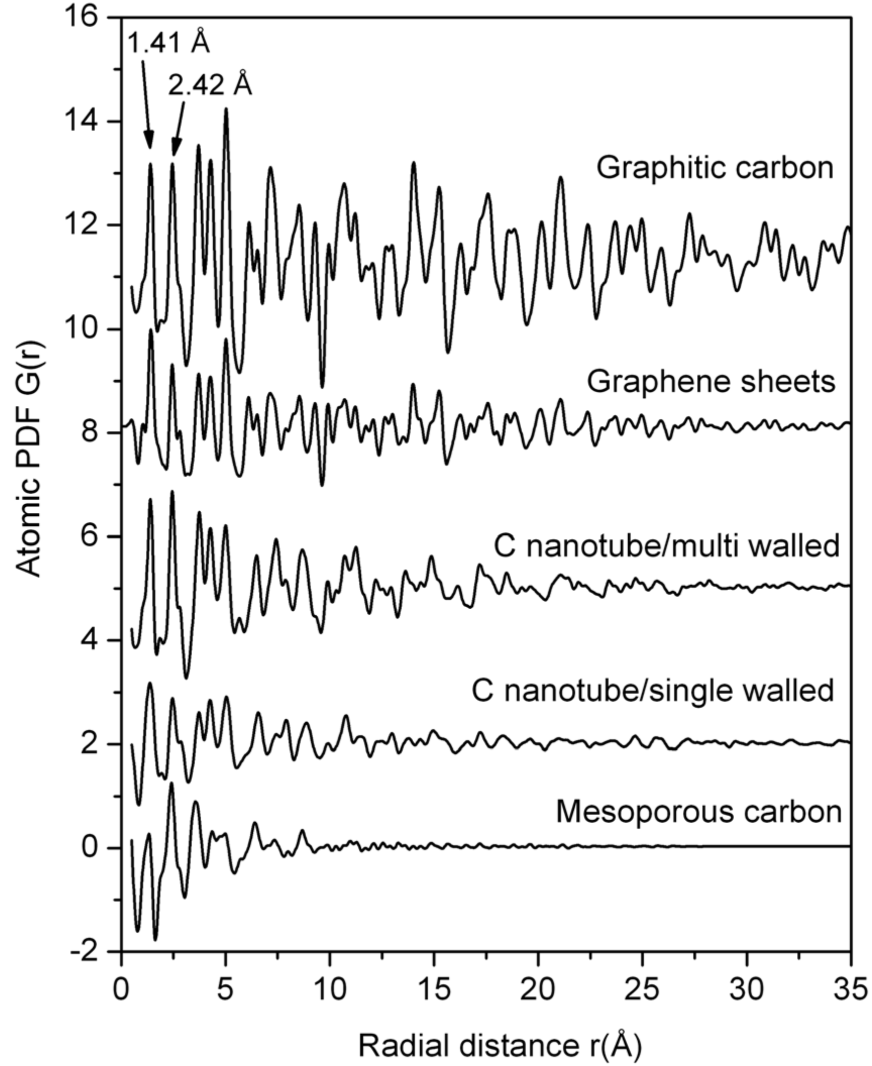
# Pair distribution function



# Pair distribution function

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

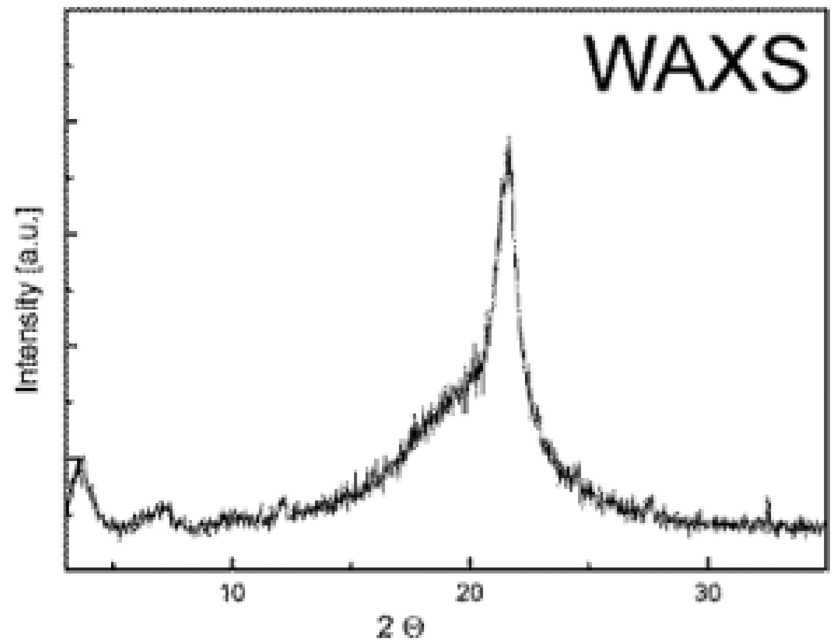
$$= V\frac{N-1}{N}(\delta(r - r_1)$$



# Pair distribution function

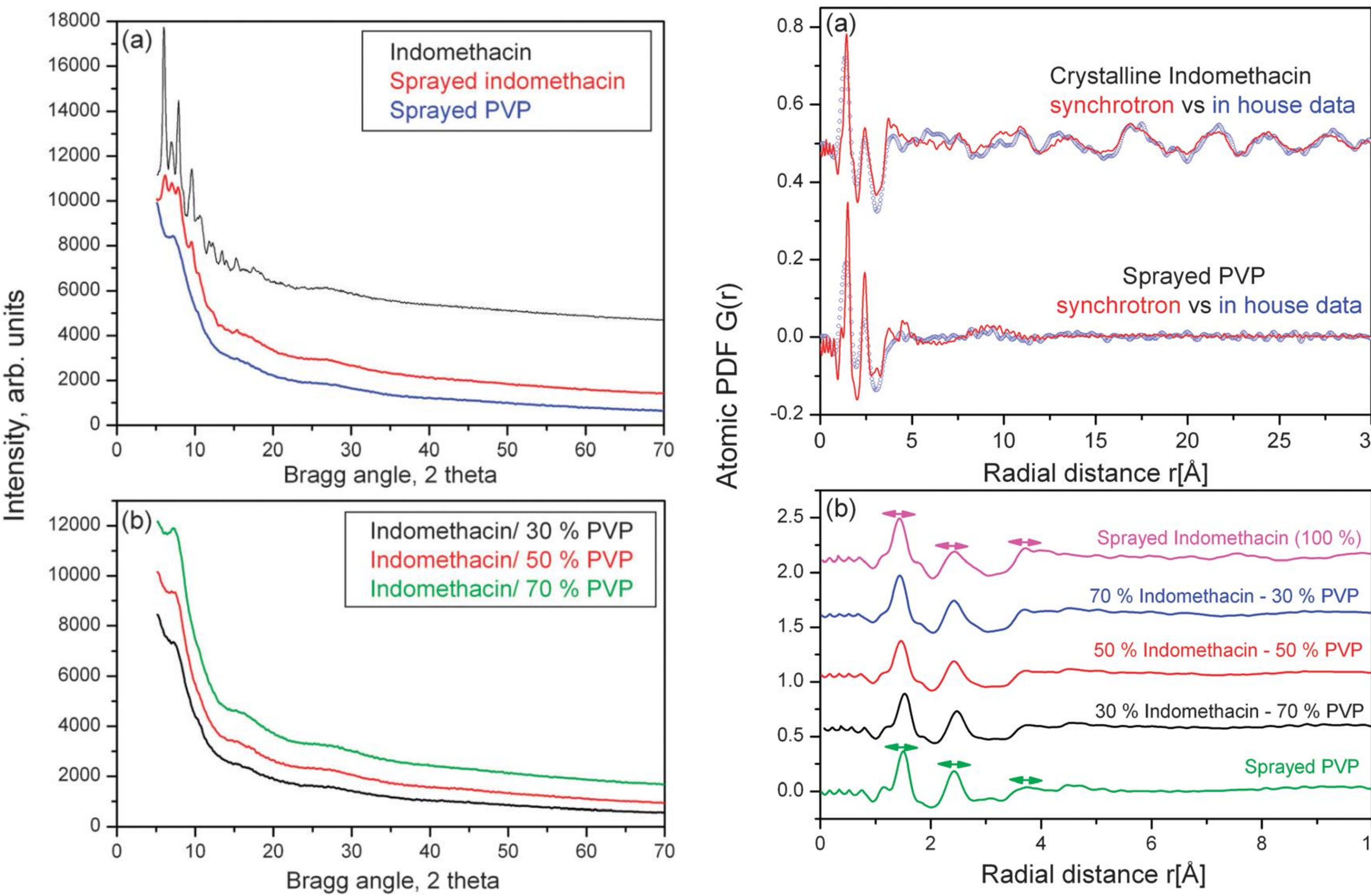
Measurement in reciprocal space gives structure factor $S(\mathrm{q})$

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



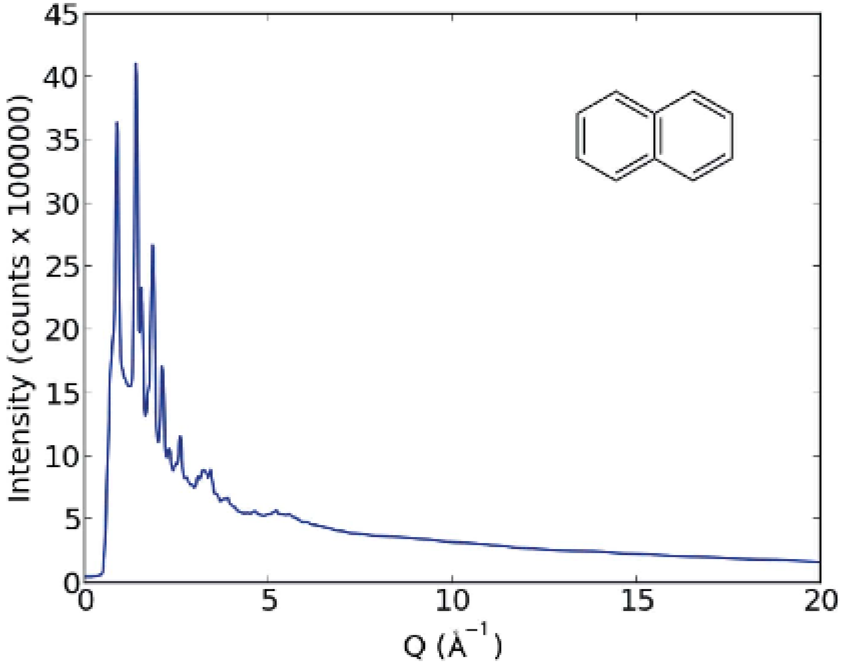

$S(\mathrm{q})$ is related to $g(r)$ by Fourier Transform

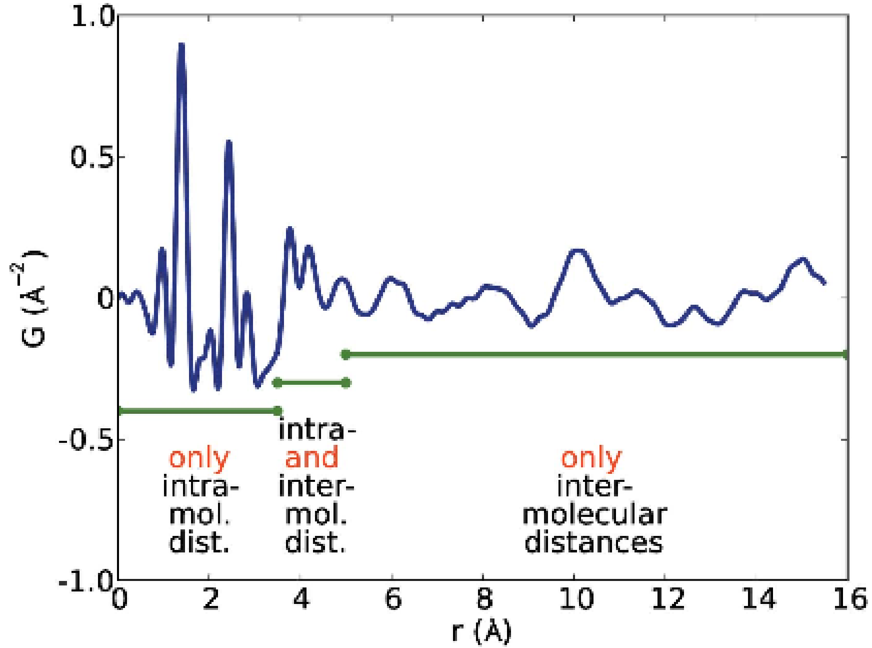
# Indomethacin in polymer




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

# Structure solution from WAXS

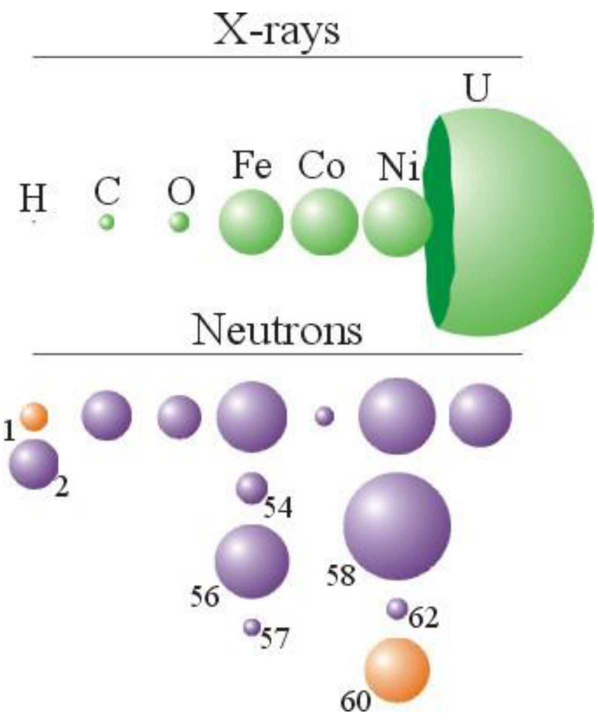


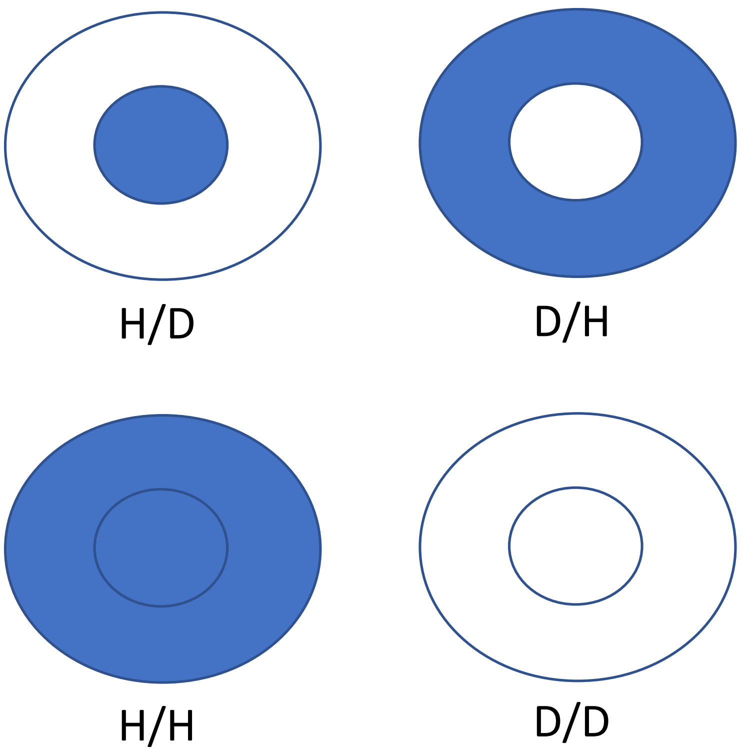




**Problem: fitting of too many parameters to one structure factor!**

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

# Wide-angle neutron scattering



# WANS

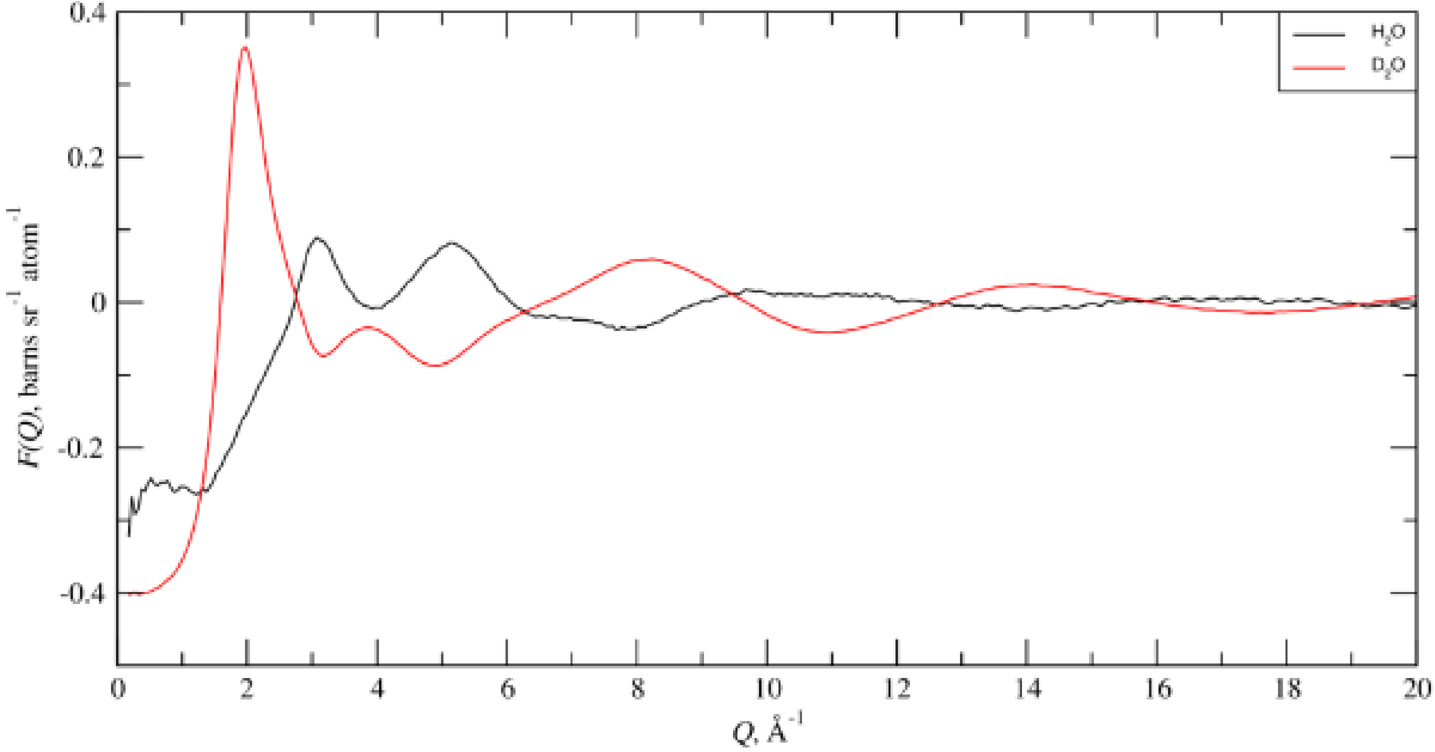
**Water**

| $i$ | $j$ | $c_i$ | $c_j$ | $b_i$, 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**

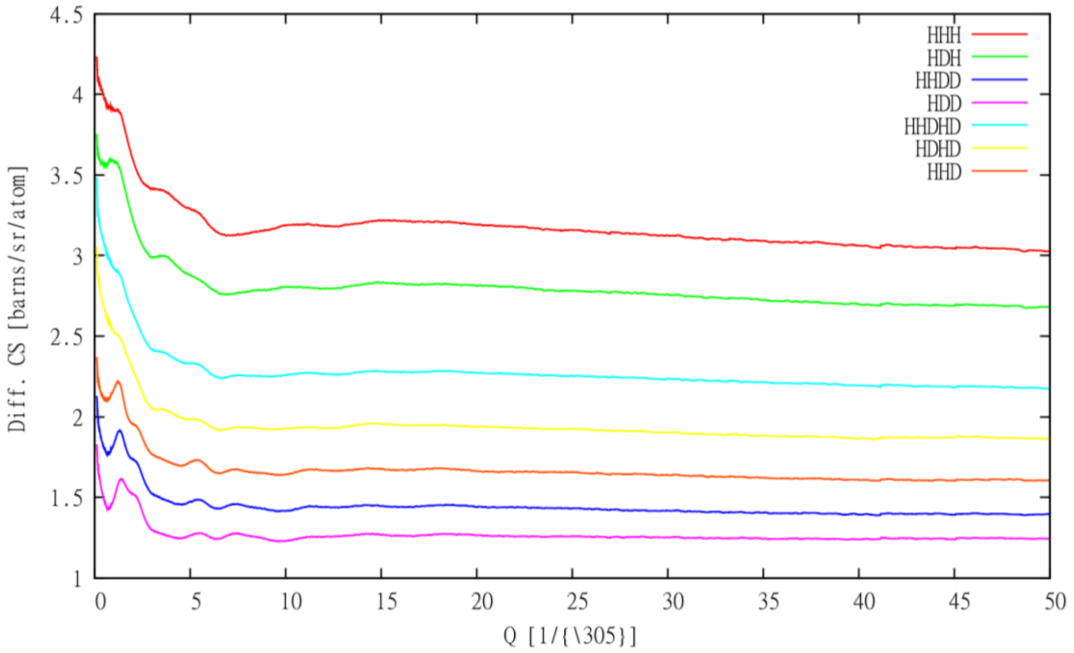
| $i$ | $j$ | $c_i$ | $c_j$ | $b_i$, fm | $b_j$, fm | $c_i c_j b_i b_j = w_{ij}$, fm |
|---|---|---|---|---|---|---|
| O | O | 1/3 | 1/3 | 0.5804 | 0.5804 | 0.0374 |
| O | D | 1/3 | 2/3 | 0.5804 | 0.6674 | 0.0861 |
| D | D | 2/3 | 2/3 | 0.6674 | 0.6674 | 0.1980 |

# 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

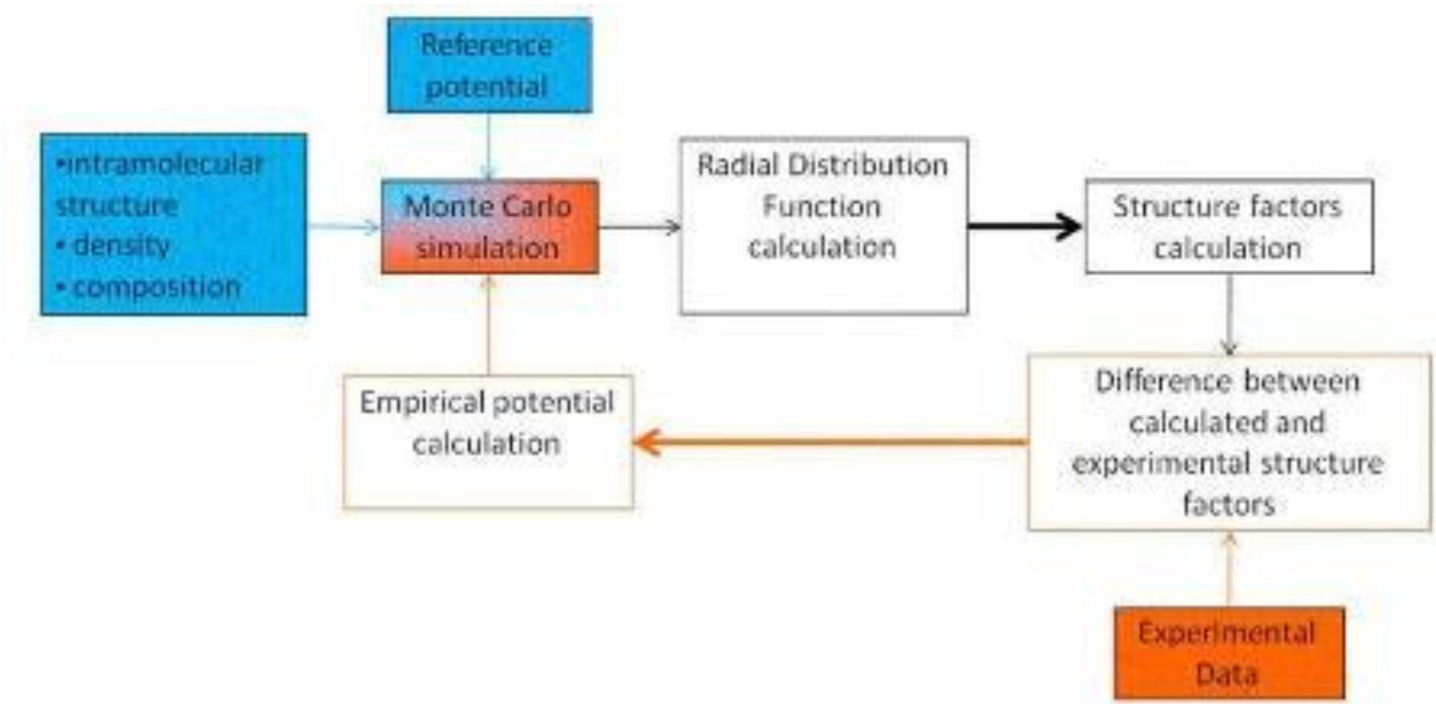



- Each isotopic mixture gives one structure factor
- Different correlations can be extracted from each structure factor

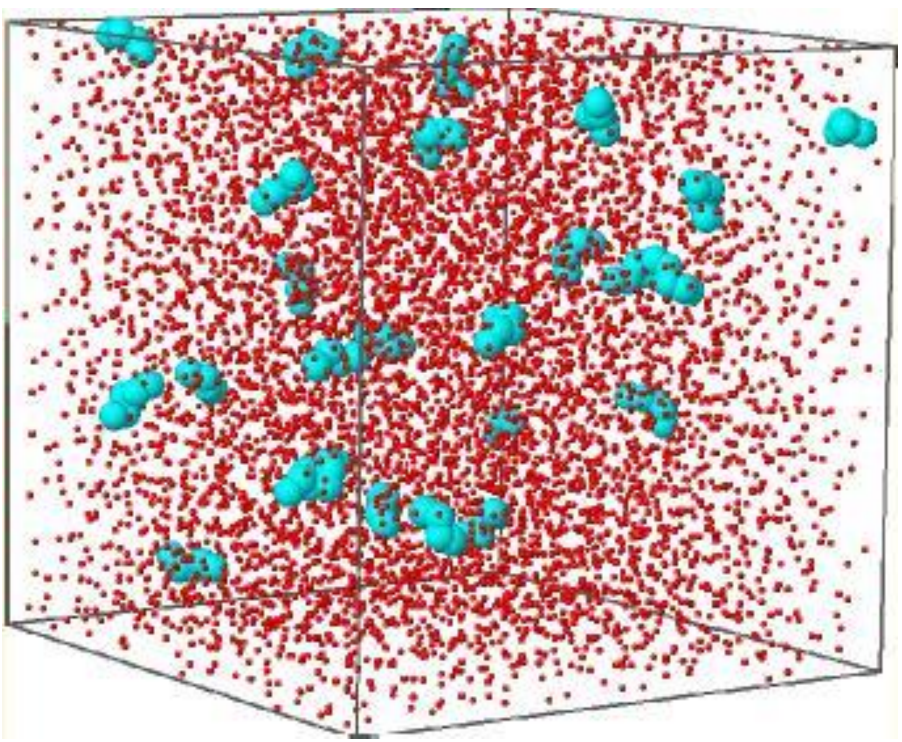
https://www.isis.stfc.ac.uk/OtherFiles/Disordered%20Materials/DM%20Isotopic%20Substitution%20Experiments%20v1.0.pdf

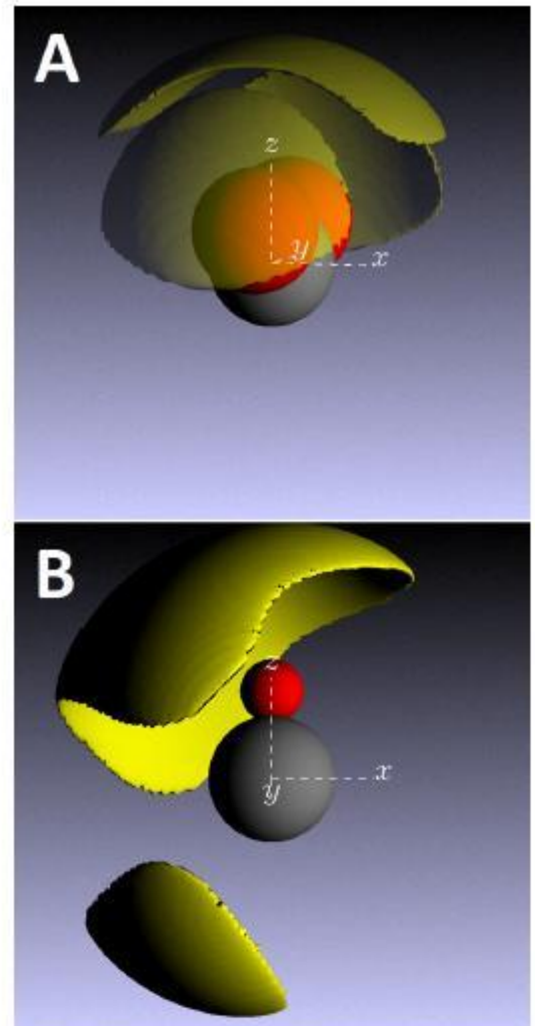
# Generation of structural models

## EPSR (empirical potential structure refinement)



# Generation of structural models

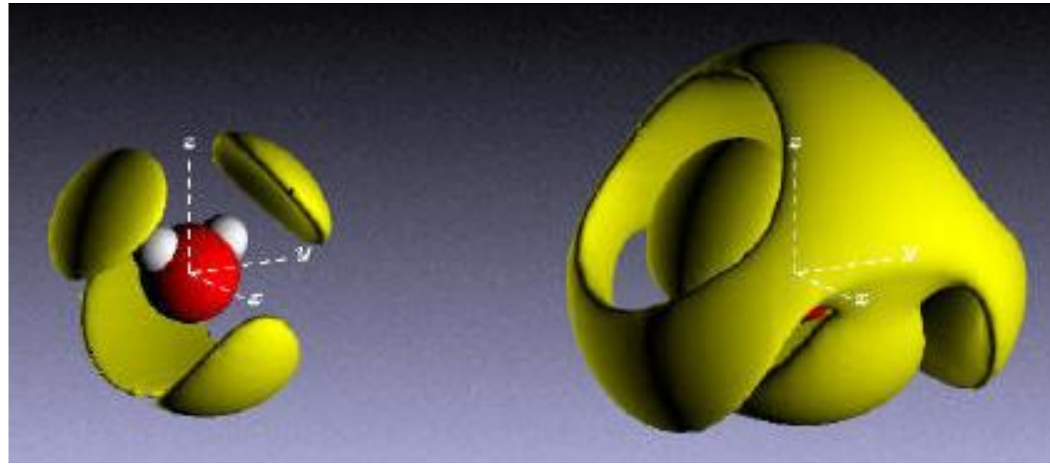


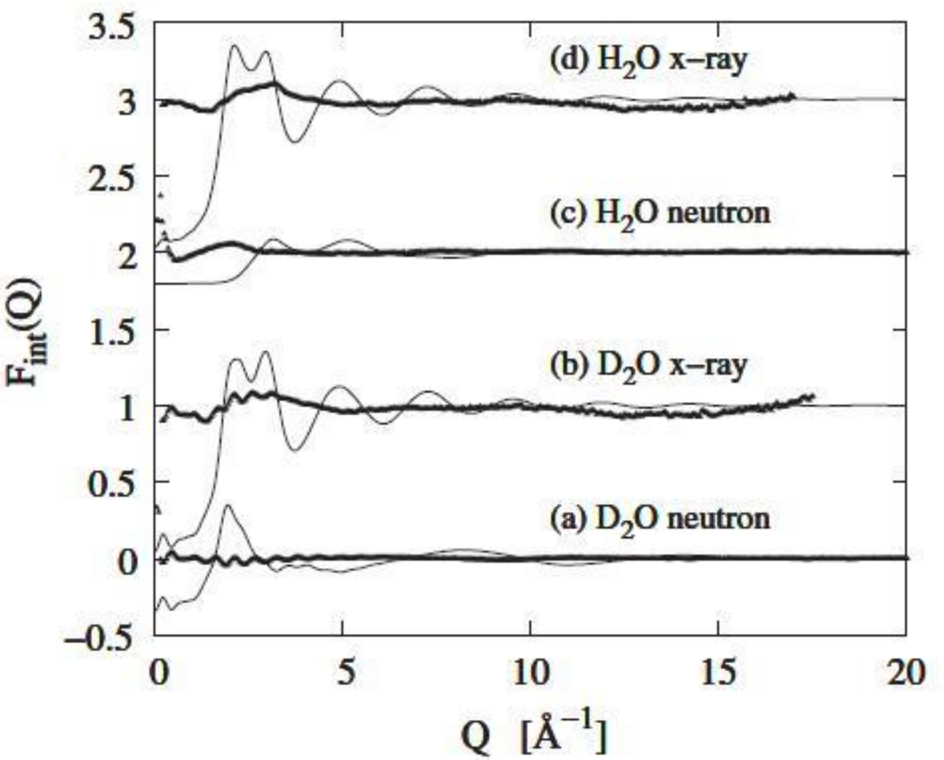


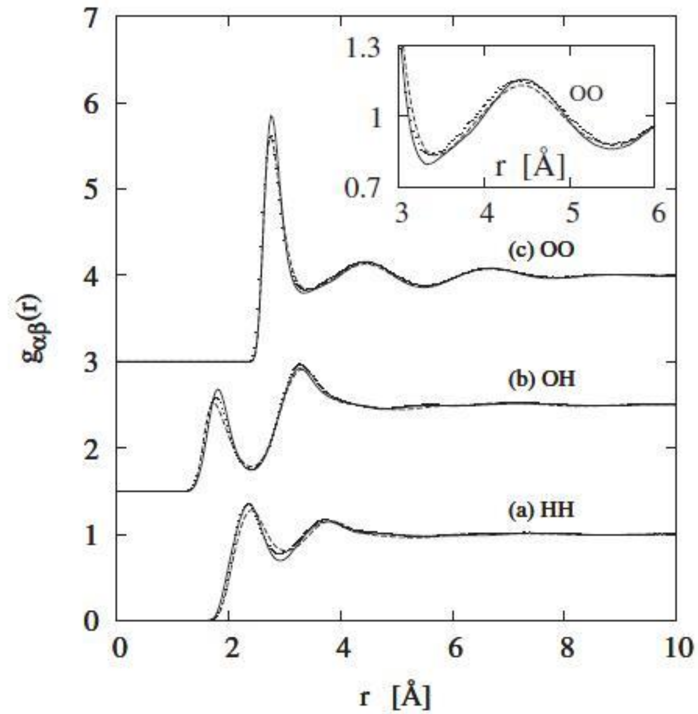

N.H. Rhys, A.K. Soper, L. Dougan, *J. Phys. Chem. B*, 2012, **116**, 13308

# Applications

# Water

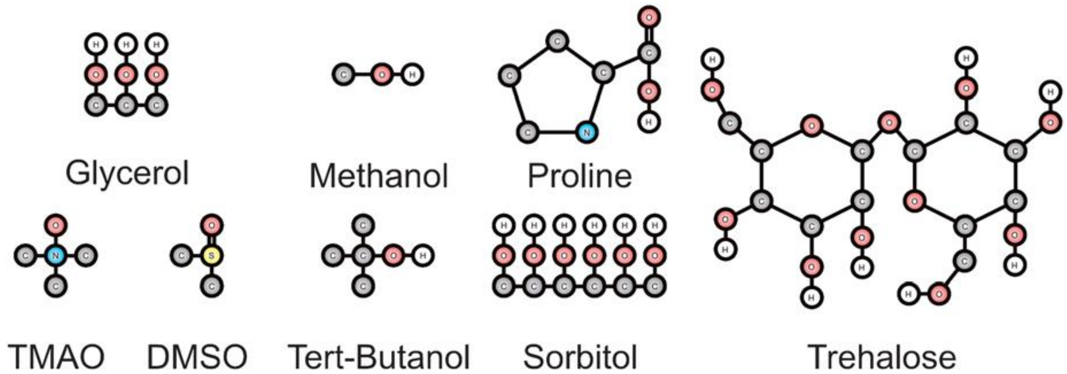


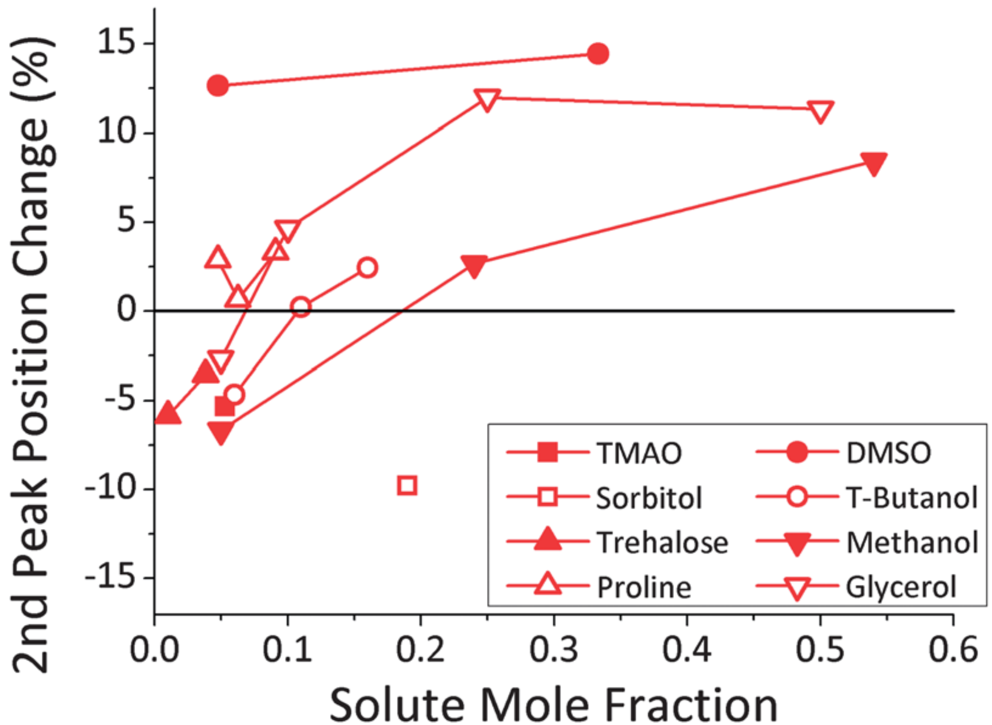


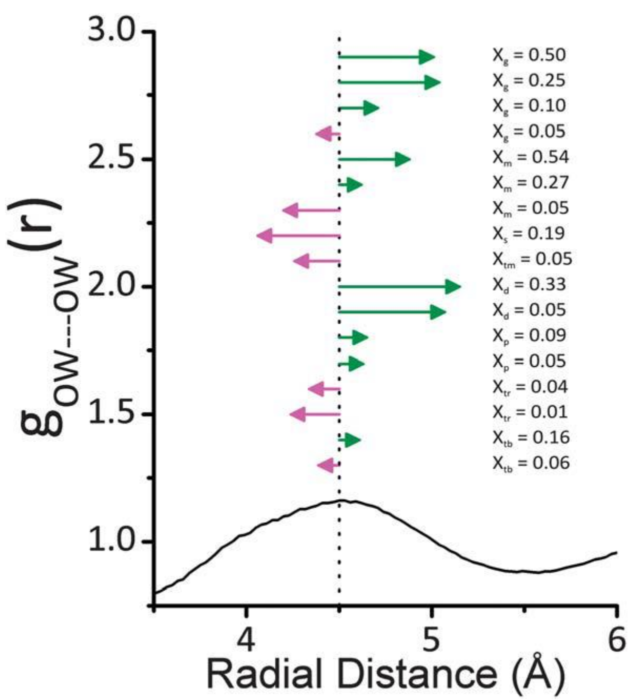




A. Soper, C.J. Benmore, *Phys. Rev. Lett.*, **101**, 065502

# Antifreeze effect

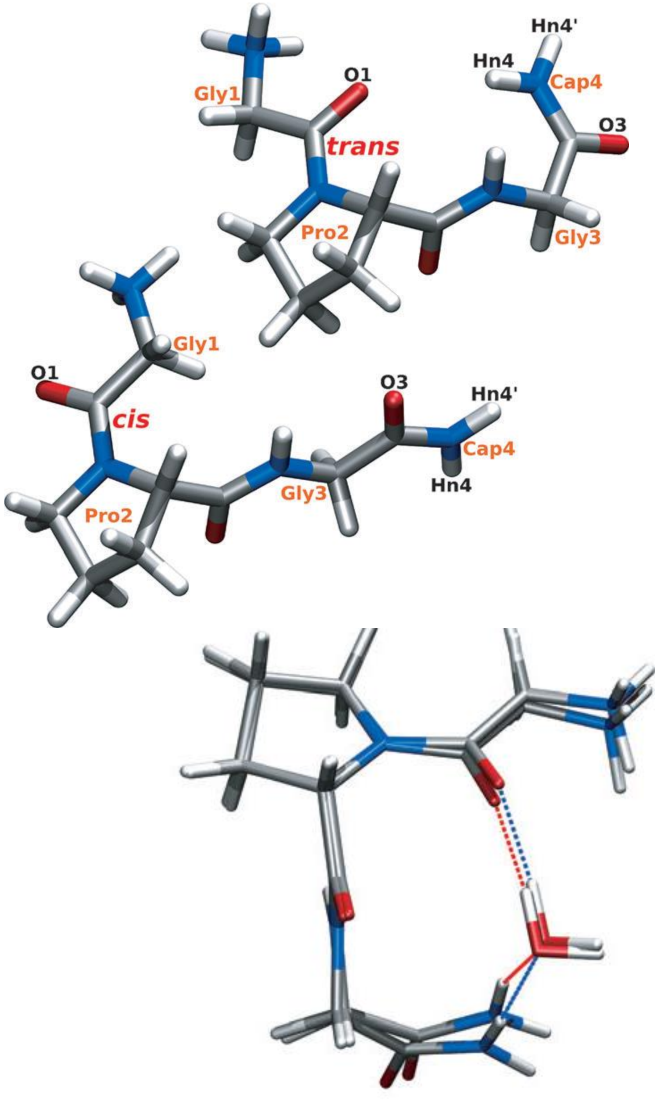


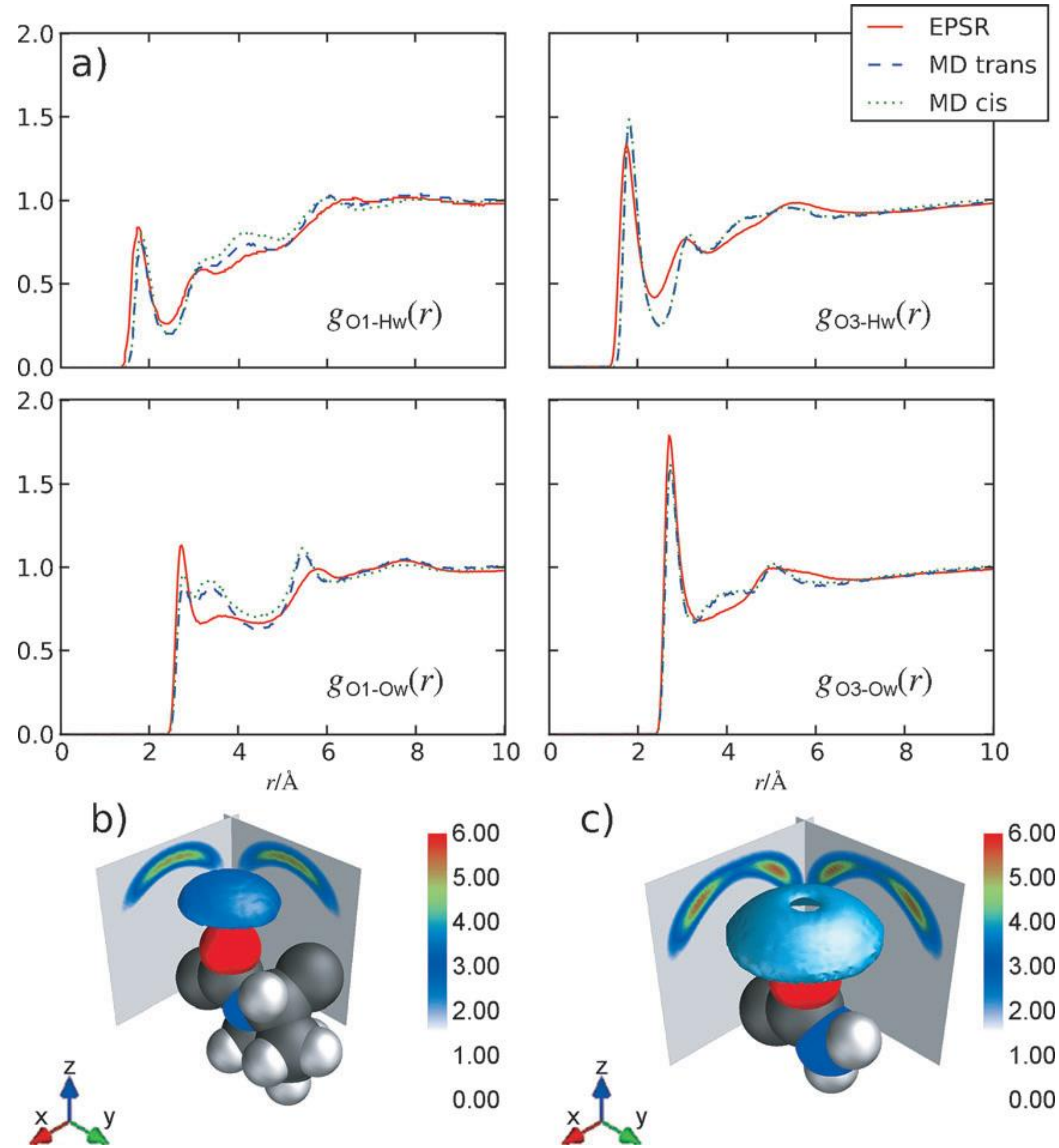




J.J. Towey, A.K. Soper, L. Dougan, *Faraday Disc.* 2013, DOI 10.1039/c3fd00084b

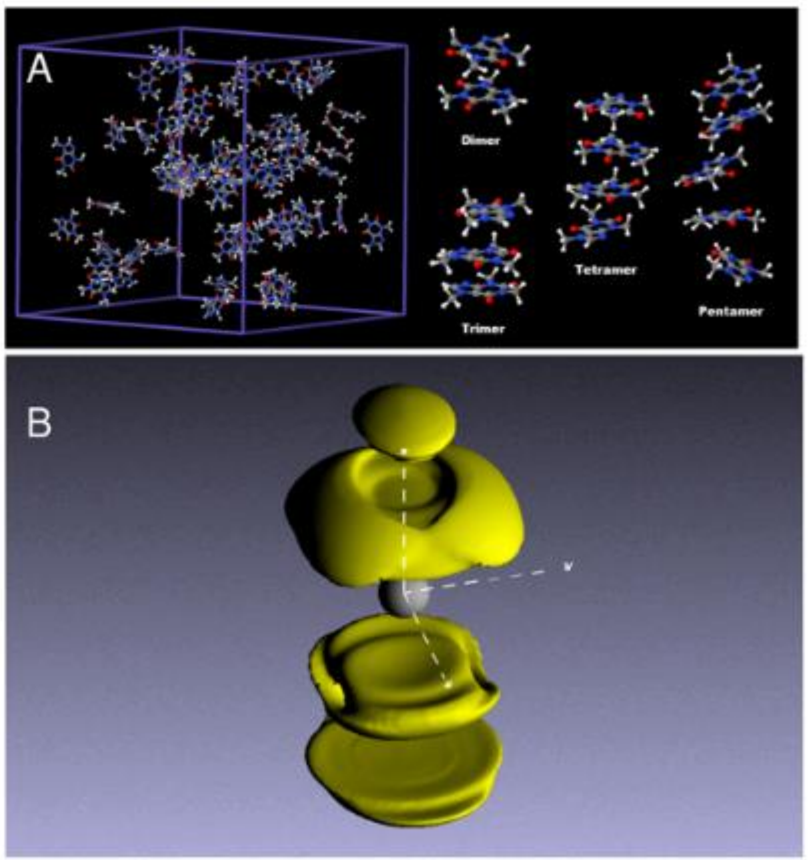
# Small peptides

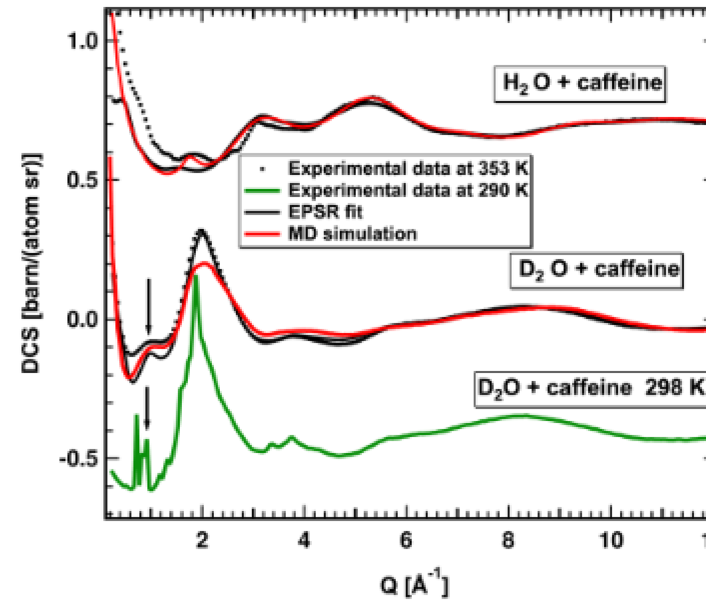


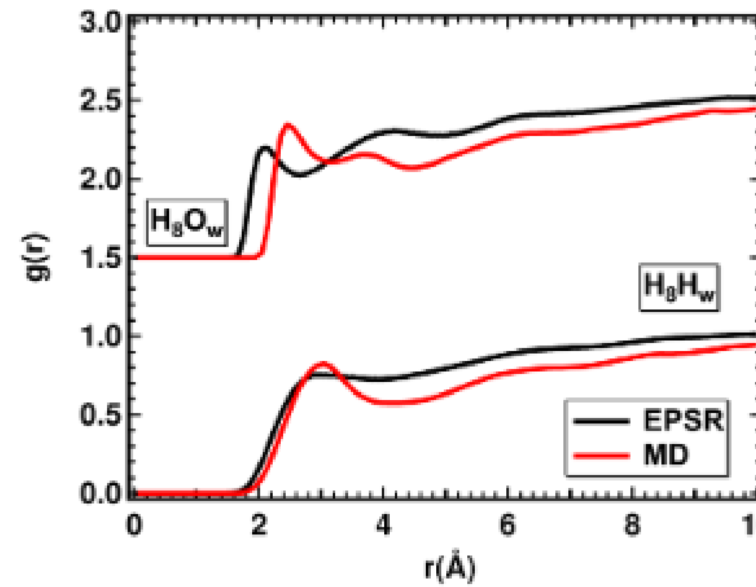




S. Busch, C.D. Bruce, C. Redfield, C.D. Lorenz, S.E. McLain, *Angew. Chem. Int. Ed.*, 2013, **52**, 1

# Drug compounds

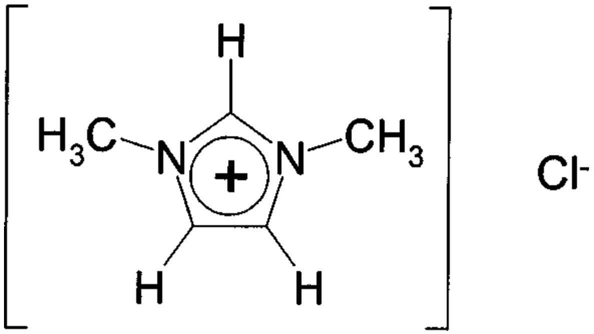


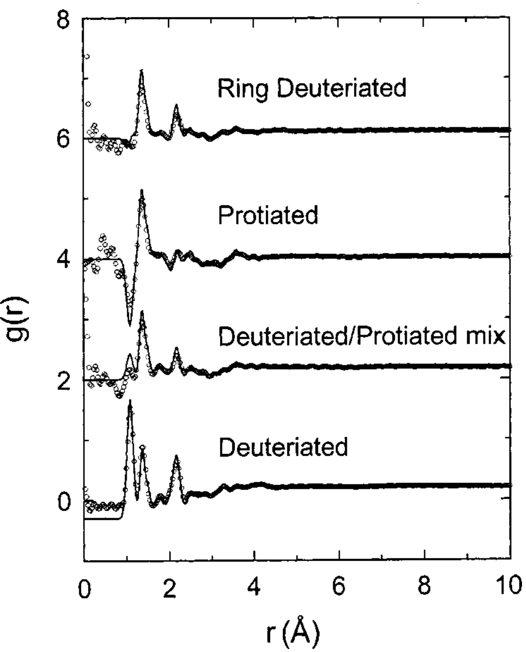



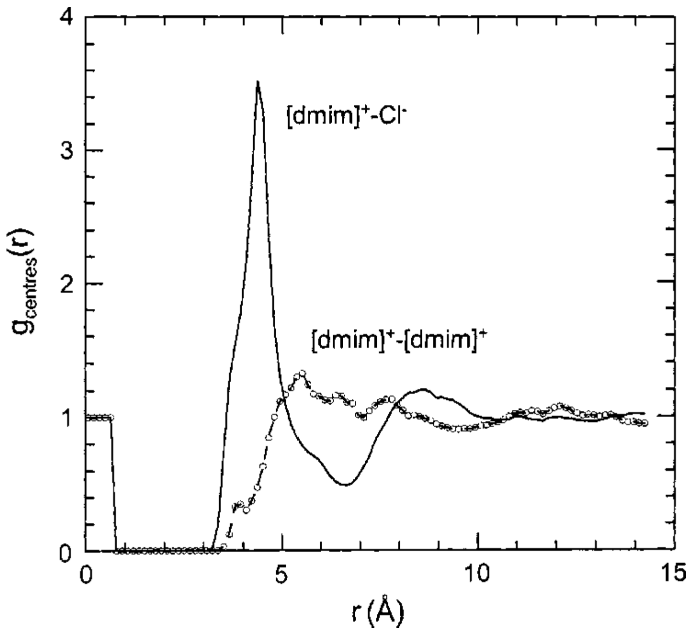



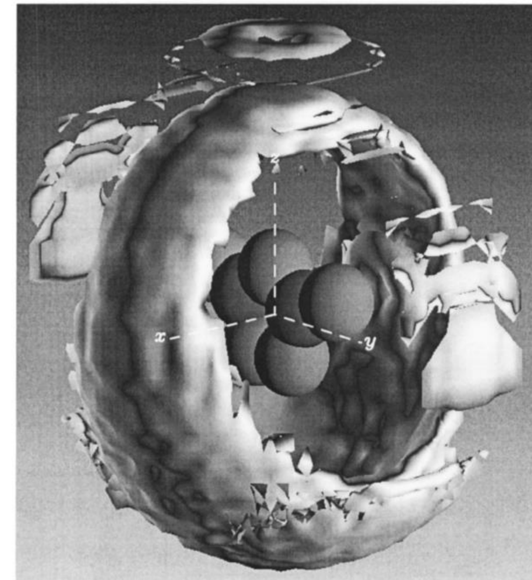

L. Tavagnacco, J.W. Brady, F. Bruni, S. Callear, M.A. Ricci, M.L. Saboungi, A. Cesaro, *J. Phys Chem. B*, 2015, **119**, 13294

# Ionic liquid/ salt melt

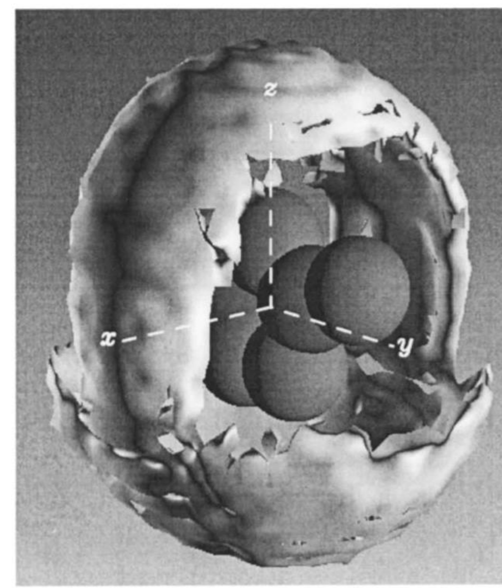


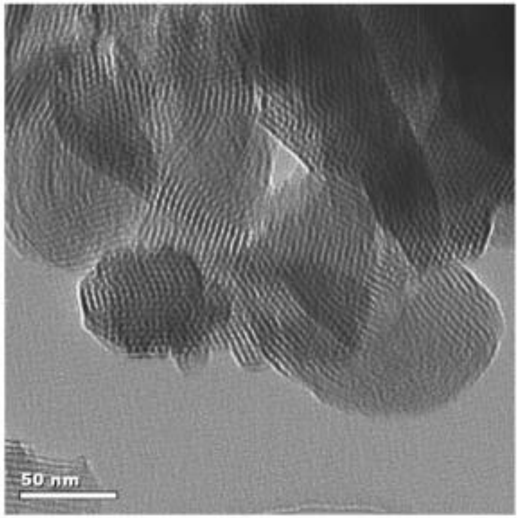

Imidazol-Imidazol Abstand

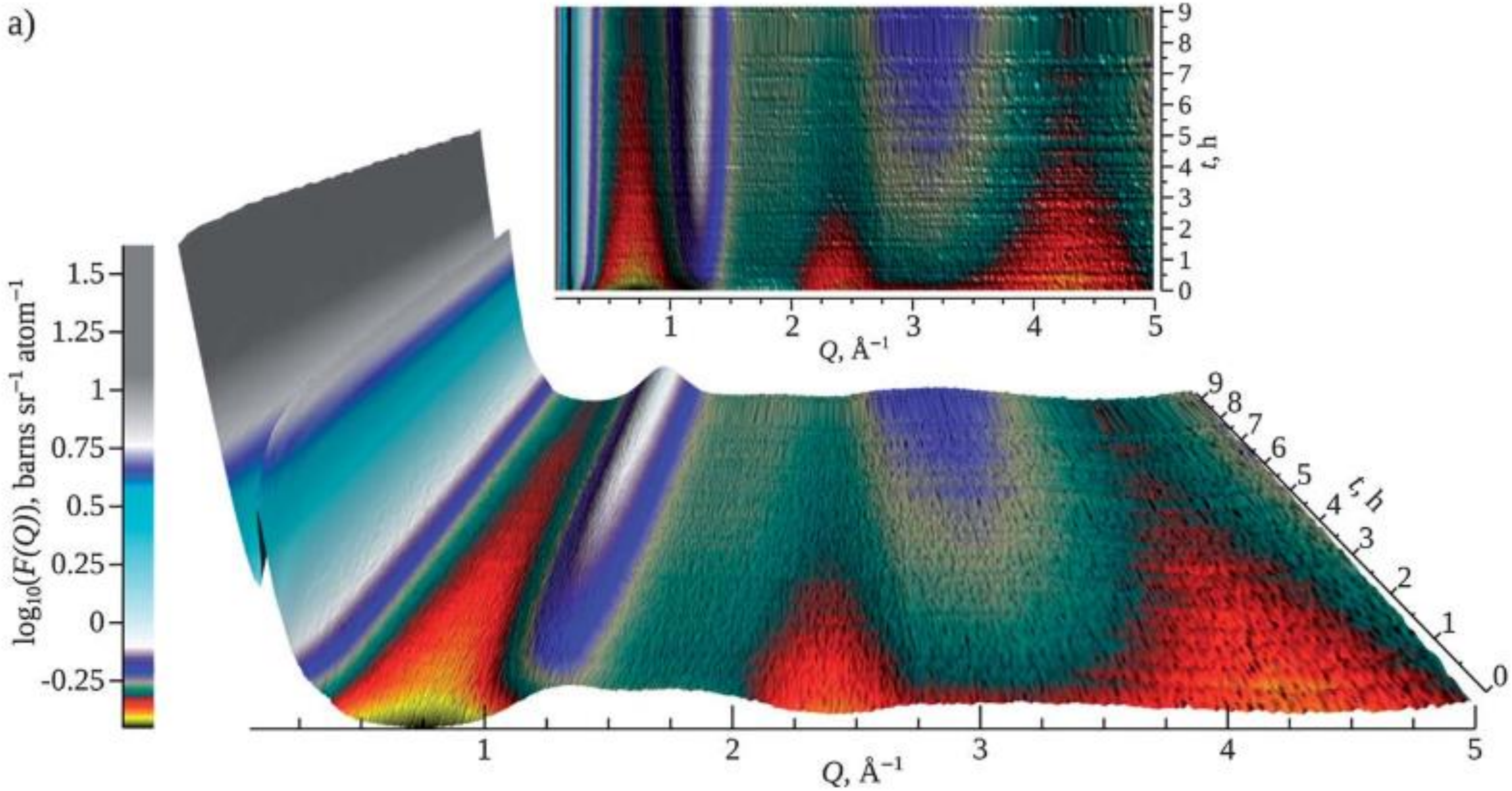



Imidazol-Chlorid Abstand

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