

# Hybrid reverse Monte Carlo modelling

T. C. Petersen<sup>1,2</sup>

<sup>1</sup>Monash Centre for Electron Microscopy, Monash University,  
Clayton, 3800, Victoria, Australia.

<sup>2</sup>School of Physics and Astronomy, Monash University, Clayton,  
3800, Victoria, Australia.



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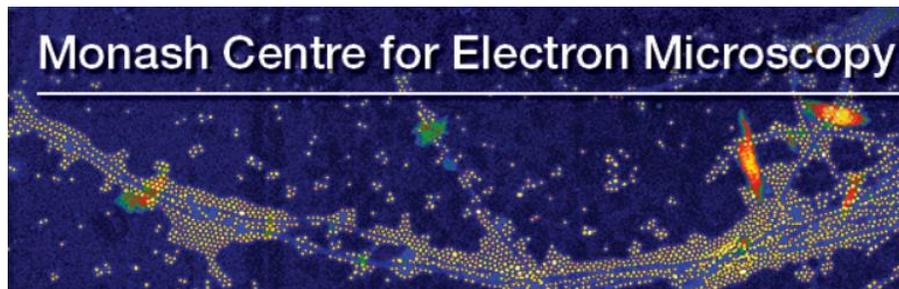
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Molecular & Materials  
Modelling

# Disordered solids

Many solids are non-crystalline with atomic structures that challenge crystallography.

Examples of technological importance include silica, chalcogenide and metallic glasses; ion-irradiated amorphous solids; polymers, chars, activated and non-graphitizing carbons; glassy and jammed colloidal systems; chemically disordered alloys etc.

The disorder is *valuable* – materials can be more homogenous, isotropic, tough, wear-resistant, corrosion resistant, formable, hierarchically porous, desirably metastable, or simply *different* from crystalline counterparts.



Crucibles and Boats made of glassy carbon SIGRADUR®.

# Atomic modelling of disordered solids

Disordered solids with short range order extending to 1 nm can require many atoms for modelling.

Ab-initio/quantum chemistry simulations are limited to ~200 atoms.

Classical molecular dynamics with accurate empirical potentials can be used if synthesis pathways are known – a good example is rapidly quenched diamond like carbon [1].

An alternative is to constrain atomic models to agree with experiment – the C<sub>70</sub> structure is an early example in electron microscopy [2]. There are now many such algorithms for disordered atomic modelling (here are some):

*\*\*reverse Monte Carlo* [R. L. McGreevy and L. Pusztai, Mol. Sim. **1** 359 (1988)].

*\*\*empirical potential structure refinement* [A. K. Soper, Chem. Phys. **202**, 295 (1996)].

*\*\*reverse Monte Carlo with molecular mechanics method* [H. Morita et al. J. Mol. Liq. **147** 182 (2009)]

*\*\*experimentally constrained structural relaxation* [Borisenko et al. Acta Materialia **60**, 359 (2012)].

*\*\*ab initio force enhanced atomic refinement* [A. Pandey et al., Sci. Rep. **6** 3371 (2016)]

[1] N. A. Marks, D. R. McKenzie, B. A. Pailthorpe, M. Bernasconi, and M. Parrinello, Phys. Rev. Lett., **76** 768 (1996).

[2] D. R. McKenzie, C. A. Davis, D. J. H. Cockayne, D. A. Muller, and A. M. Vassallo, Nature **355** 622 (1992).

# The hybrid reverse Monte Carlo algorithm (HRMC)

In McGreevy and Pusztai's reverse Monte Carlo (RMC) algorithm [1], the sum-squared ( $\chi^2$ ) difference between experimental data and that calculated from a model is iteratively minimized using the Metropolis accept/conditional-reject Monte Carlo algorithm.

Data can comprise structure factors  $S(q)$ , radial distribution functions  $g(r)$ , coordination statistics (such as from EXAFS) and average bond angles (Raman) etc., producing weighted contributions to  $\chi^2$ .

The hybrid algorithm (HRMC) [2] adds an empirical many-body potential energy to  $\chi^2$ , weighted by the Boltzmann temperature factor, as in standard MC. Simulated annealing ensures efficient  $\chi^2$  minimization.

For covalently bonded solids, high quality potentials are required, such as the silicon Environment Dependent Interaction Potential (EDIP) [3], adapted for carbon by Marks [4].

[1] R. L. McGreevy and L. Pusztai, *Molecular Simulation* **1**, 359 (1988).

[2] G. Opletal, et al., *Mol. Sim.* **28**, 927 (2002).

[3] A. Z. Bazant, E. Kaxiras, and J. F. Justo, *Phys. Rev. B* **56**, 8542 (1997).

[4] N. A. Marks, *Phys. Rev. B* **63**, 035401 (2001).

# HRMC is a hybrid of Metropolis-Hastings MC and RMC

In HRMC, Monte Carlo moves are iteratively accepted with a conditional probability of the form (where the  $A_j$  are fitting weights for the  $j^{\text{th}}$  constraint):

$$P = \prod_{j=1}^N e^{-\frac{(A_j \chi_{OLDj}^2 - A_j \chi_{NEWj}^2)}{N}} e^{\frac{(E_{OLD} - E_{NEW})}{kT}}$$



Conventional RMC (McGreevy and Pustzai)



Hybrid RMC (Opletal et al. [1], see also [2])

$E/kT$  is a Boltzmann-weighted many-body interaction potential and the diffraction constraints are given by ( $\sigma$  is the standard error):

$$X_{\text{sq OLD}}^2 = \sum_i^M \frac{[S(q_i)_{\text{EXP}} - S(q_i)_{\text{OLD}}]^2}{\sigma(q_i)^2} \quad X_{\text{gr OLD}}^2 = \sum_i^M \frac{[g(r_i)_{\text{EXP}} - g(r_i)_{\text{OLD}}]^2}{\sigma(r_i)^2}$$

Download HRMC here: <https://research.csiro.au/mmm/hrmc/>

# RMC non-uniqueness

Many different RMC models can fit the same diffraction data.

RMC uniqueness was recently tested [1] by trying to reproduce a 240 atom model of a  $\text{Ge}_{6.25}\text{As}_{32.50}\text{Se}_{61.25}$  glass, which came from *ab-initio* molecular dynamics (liquid quench, DFT/VASP).

Many RMC simulations were performed with up to five constraints: av. bond length BI, bond angle distribution g3, bond fraction of atomic pairs Bn, coordination Cn and the PDF g2.

DFT energies and network statistics were calculated to compare input and output models. *Bond angle* constraints in particular produced low energy structures and close matches with the input model. Note that low energy structures can still contain incorrect multi-component structural unit populations (SUPs).

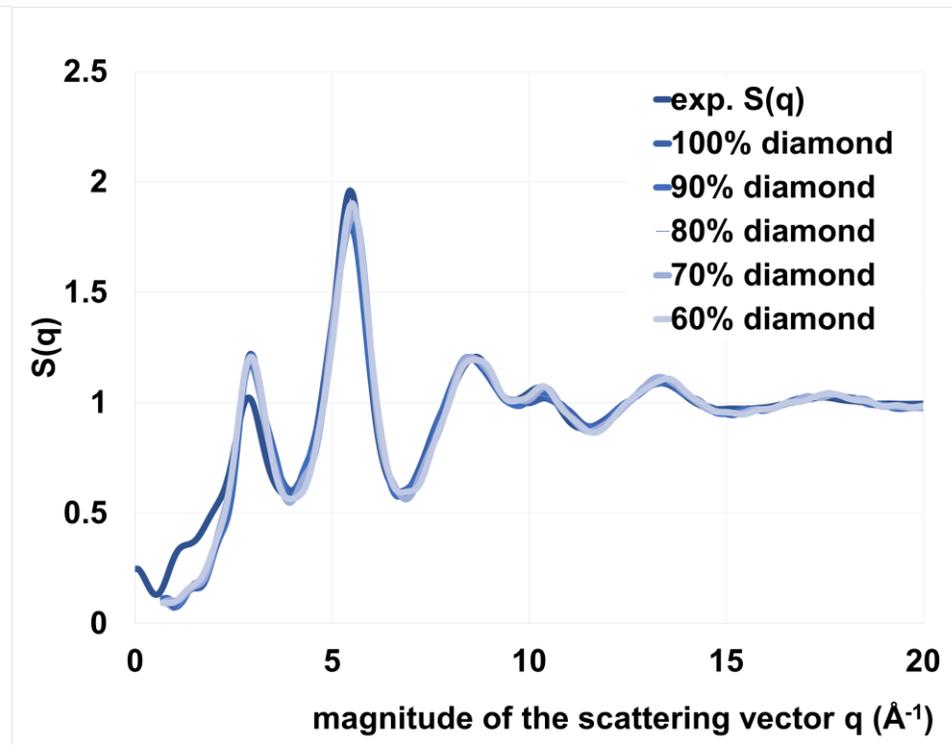
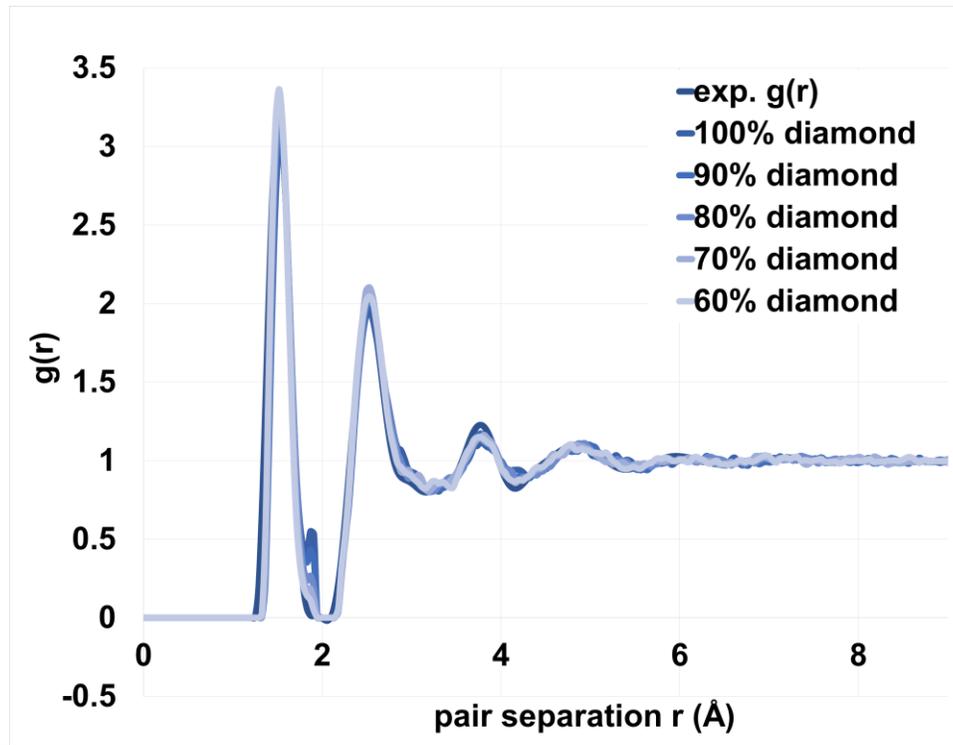
Title	$\Delta$ Energy	$\Delta$ Rings	$\Delta$ SUP	3Rings
Bl	0.708	52	0.788	32
BnBl	0.663	57	0.533	39
g2	0.645	45	0.800	33
g2Bl	0.622	49	0.800	37
g2R	0.589	20	0.817	3
Bn	0.565	15	0.483	7
g3	0.564	21	0.904	0
g2BnBl	0.555	28	0.550	23
Cn	0.543	31	0.971	14
CnBl	0.539	26	1.017	14
g3Bl	0.534	19	0.875	0
g3Bn	0.530	23	0.608	0
g3g2	0.510	17	0.846	0
g2Bn	0.500	23	0.471	14
CnBnBl	0.497	18	0.292	8
g3g2Bl	0.485	18	0.763	1
CnBn	0.485	26	0.146	10
g2CnBl	0.455	33	0.942	19
g2Cn	0.434	28	1.000	17
g2CnBnBl	0.407	27	0.400	15
g3BnBl	0.399	9	0.333	0
g2CnBn	0.395	19	0.171	3
g3g2CnBl	0.370	10	0.908	0
g3Cn	0.367	16	0.925	1
g3g2BnBl	0.357	19	0.458	3
g3g2Bn	0.345	12	0.383	0
g3CnBl	0.342	10	0.808	0
g3CnBnBl	0.341	9	0.333	0
g3g2Cn	0.332	8	0.979	2
g3CnBn	0.307	4	0.088	0
g3g2CnBn	0.279	10	0.229	0
g3g2CnBnBl	0.263	12	0.292	0
g3g2CnBnBl*	0.215	3	0.104	0

[1] G. Opletal, T. C. Petersen, A. S. Barnard and S. P. Russo, J. Comp. Chem. **38** 1547 (2017).

# Embracing non-uniqueness: HRMC of diamond like carbon

Thin films of diamond like carbon (DLC) was synthesized using a plasma-biased cathodic arc [1]. For the high density 2.9 g/cc specimen, wide-angle energy-filtered electron diffraction data [2] accurately matched previous neutron diffraction data for similar tetrahedrally bonded amorphous films [3].

5 different HRMC calculations using the EDIP potential produced consistency with experiment, whilst bond and coordination constraints were imposed.

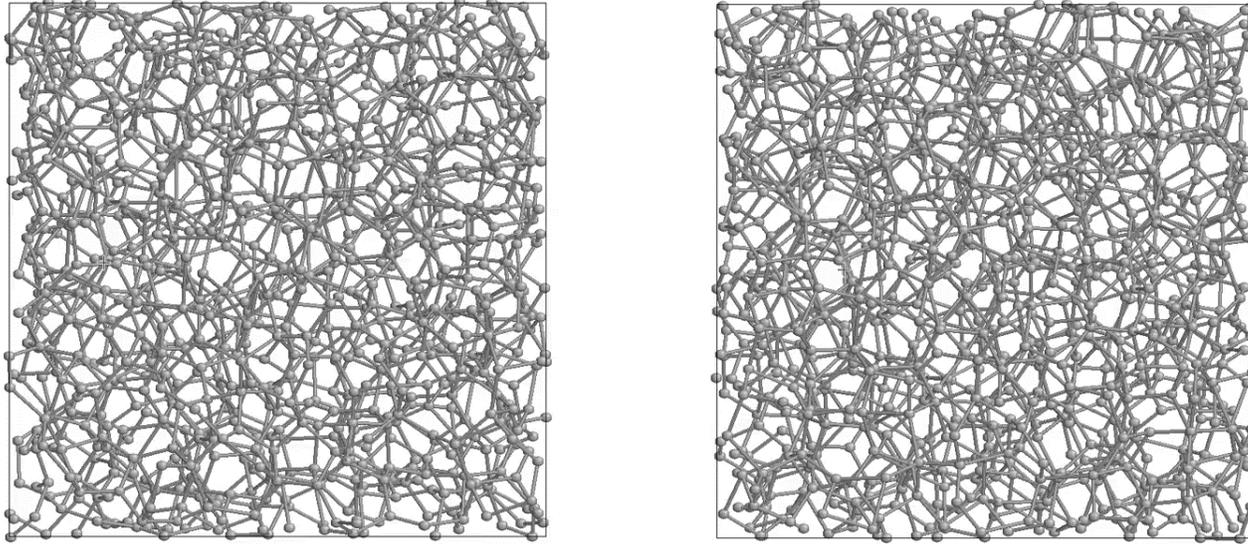


[1] A. Anders, N. Pasaja, S. H. N. Lim, T. C. Petersen, V. J. Keast, Surf. Coat. Tech. **201** (2007) 4628.

[2] D. R. G. Mitchell and T. C. Petersen, Microsc. Res. Tech. **75**, 153 (2012).

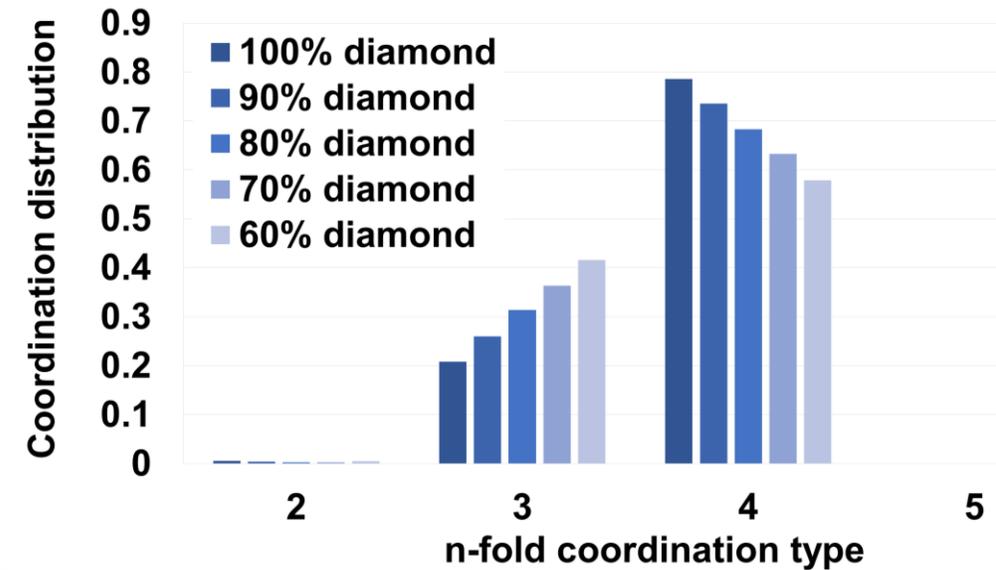
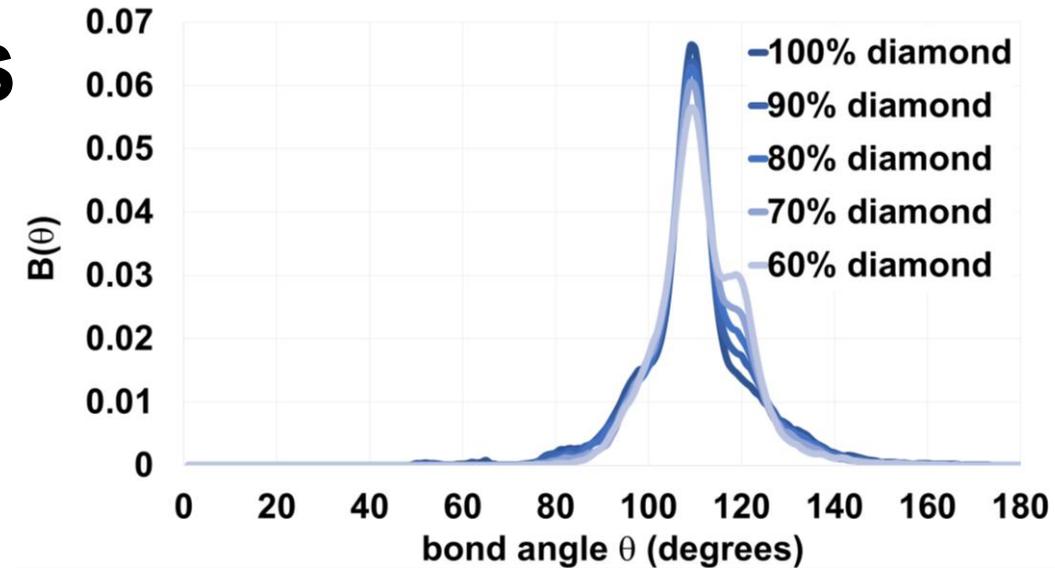
[3] P. H. Gaskell, A. Saeed, P. Chieux and D. R. McKenzie, Phys. Rev. Lett. **67** 1286 (1991).

# Biasing the DLC network statistics



**Above:** 60% diamond (left) & 100% diamond (right) atoms.

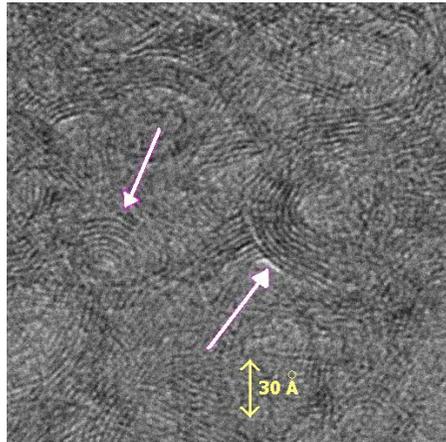
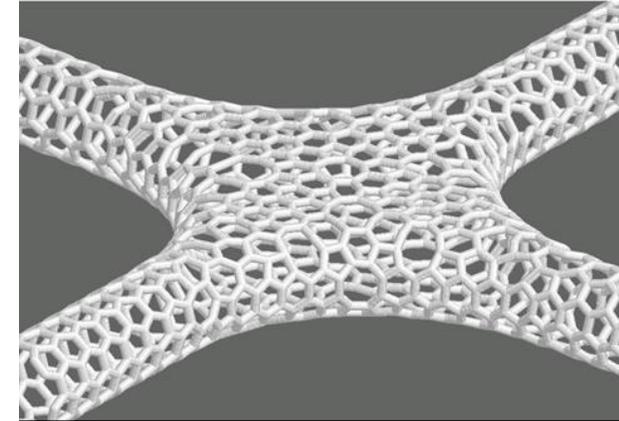
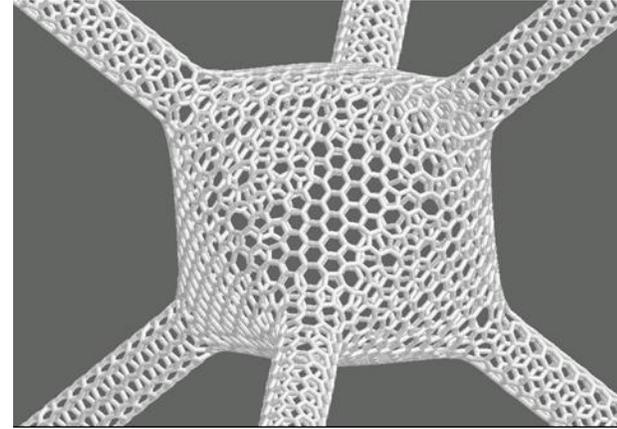
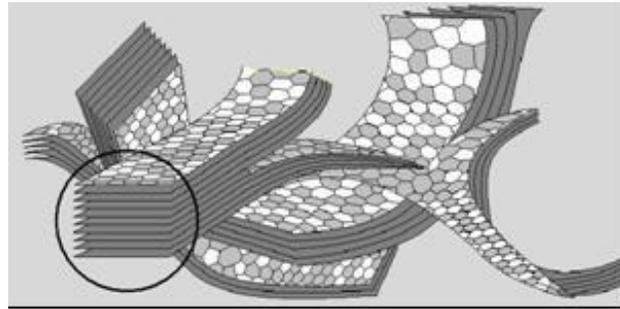
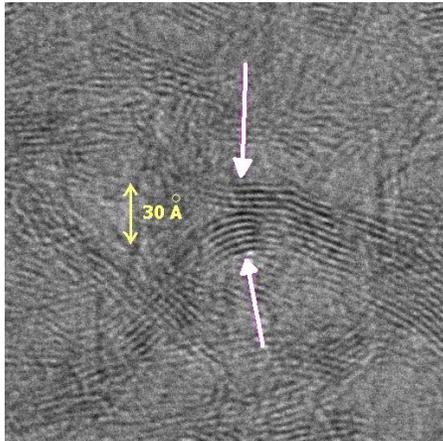
All 5 models fit the diffraction data equally well, yet contain differing blends of diamond/graphite-like network geometry & topology, by design. The models can be used to test diffraction physics theories for how to measure high-order correlations [1].



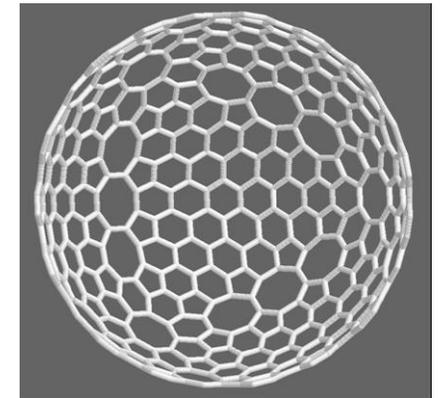
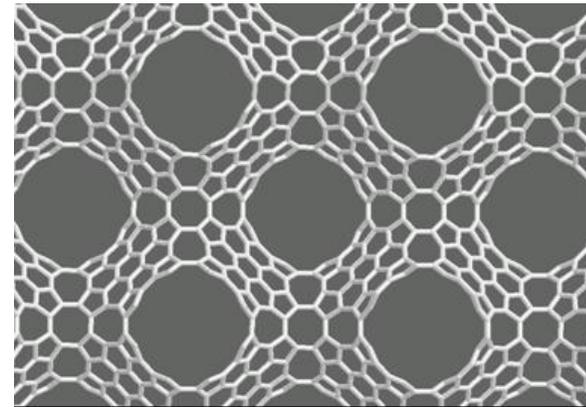
[1] A. V. Martin, IUCrJ **4**, 24 (2017).

# Embracing non-uniqueness: nanoporous glassy carbon

Fullerene models of glassy carbon were proposed in the early 2000s [1].



To try and create such models (above), consistent with HRTEM (left) & diffraction, the HRMC algorithm was modified to simulate atomic diffusion and interaction on periodically tiled manifolds (right) [2].



[1] P. J. F. Harris, A. Burian, and S. Duber, *Phil. Mag. Lett.* **80** 381 (2000).

[2] T. C. Petersen, I. K. Snook, I. Yarovsky, and D. G. McCulloch, *Phys. Rev. B* **72** 125417 (2005).

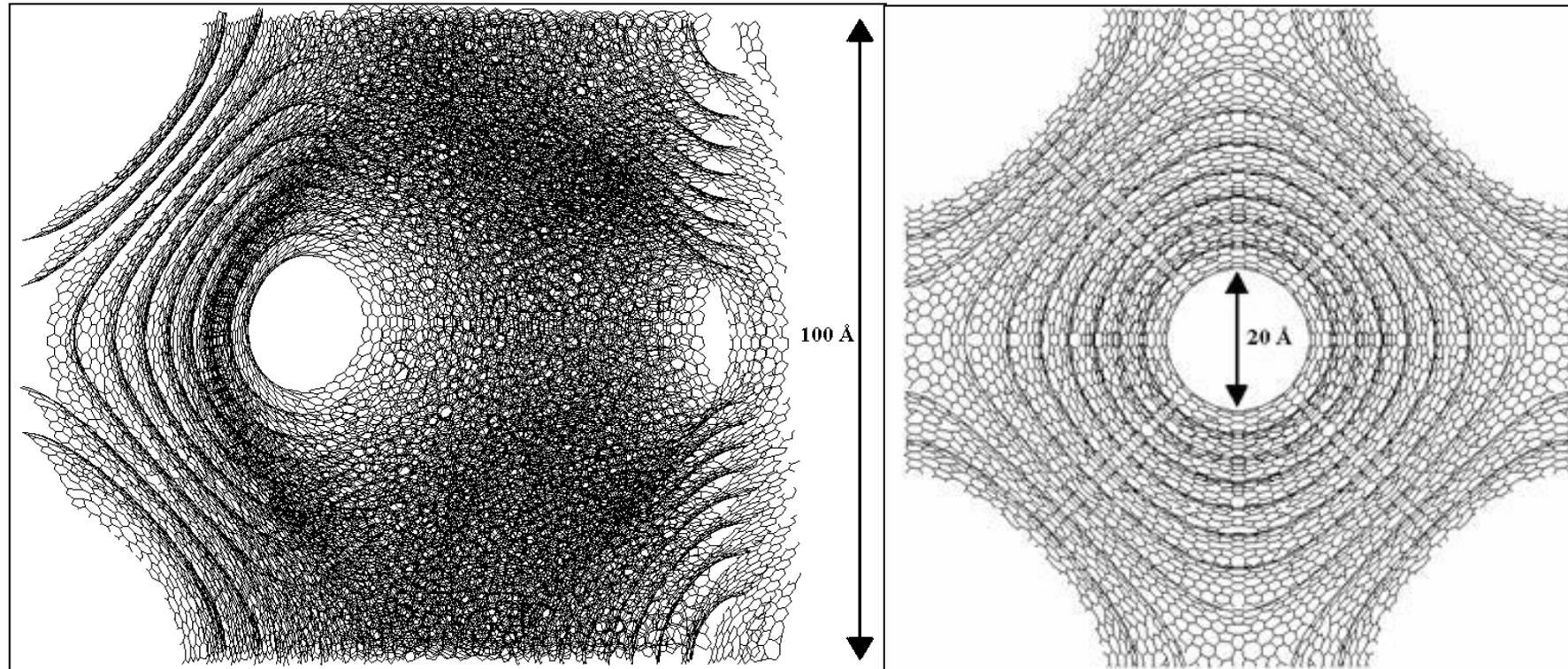
[3] See also the Fring3D algorithm, Fernandez-Alos et al. *Comb. & Flame* **158** 1807 (2011).

# HRMC example: nanoporous glassy carbon

Large closed-pore glassy carbon models of concentric fullerenes (below) with porosity matching bulk-measurements were created using this surface-diffusion based HRMC. Open-pore parallel-surface models were also modelled and similarly matched to experiment [1].

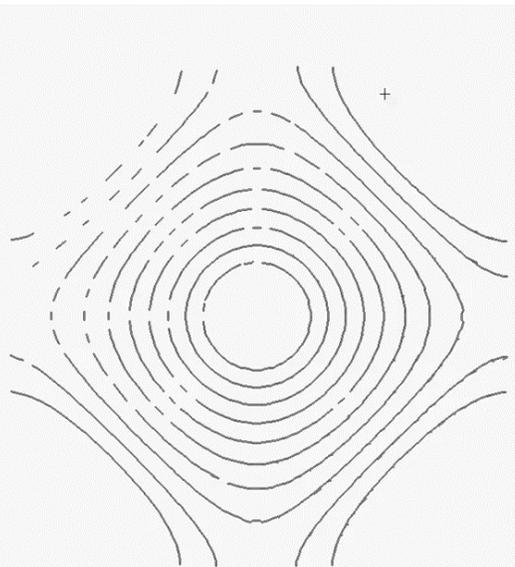
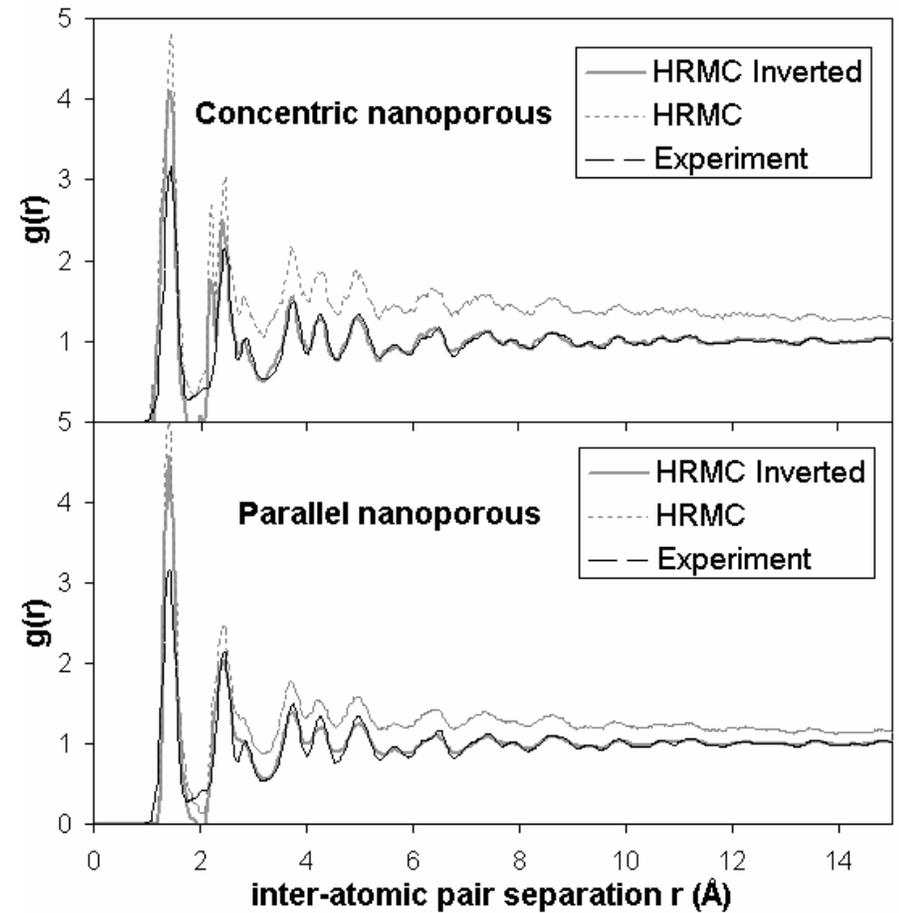
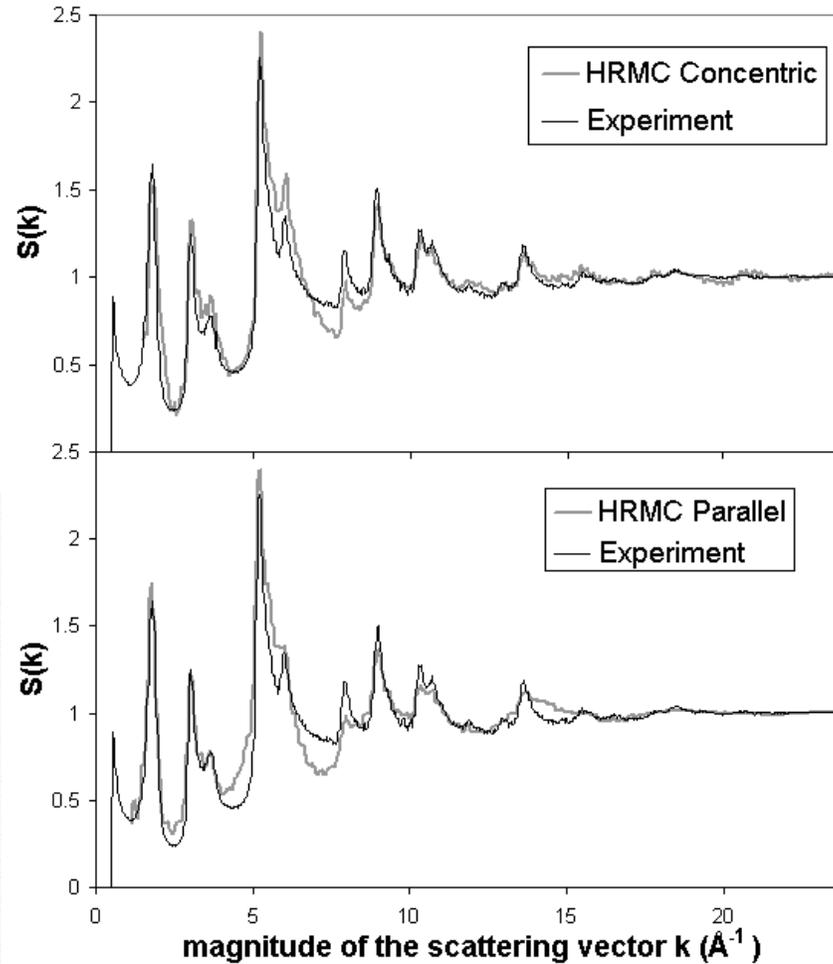
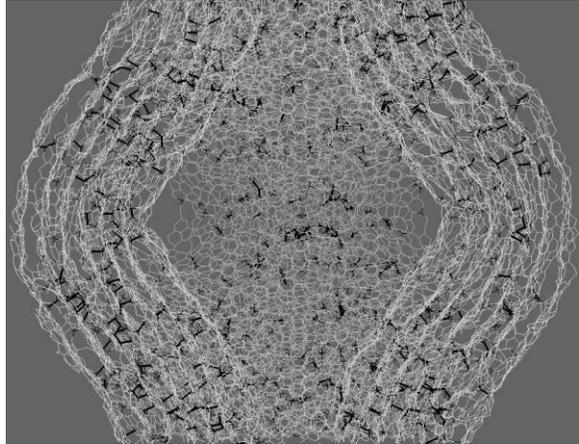
The images on the right show atomic structure prior to HRMC minimization of diffraction constraints.

Standard assumptions used to compute pair correlations such as  $g(r)$  are violated by models such as these.

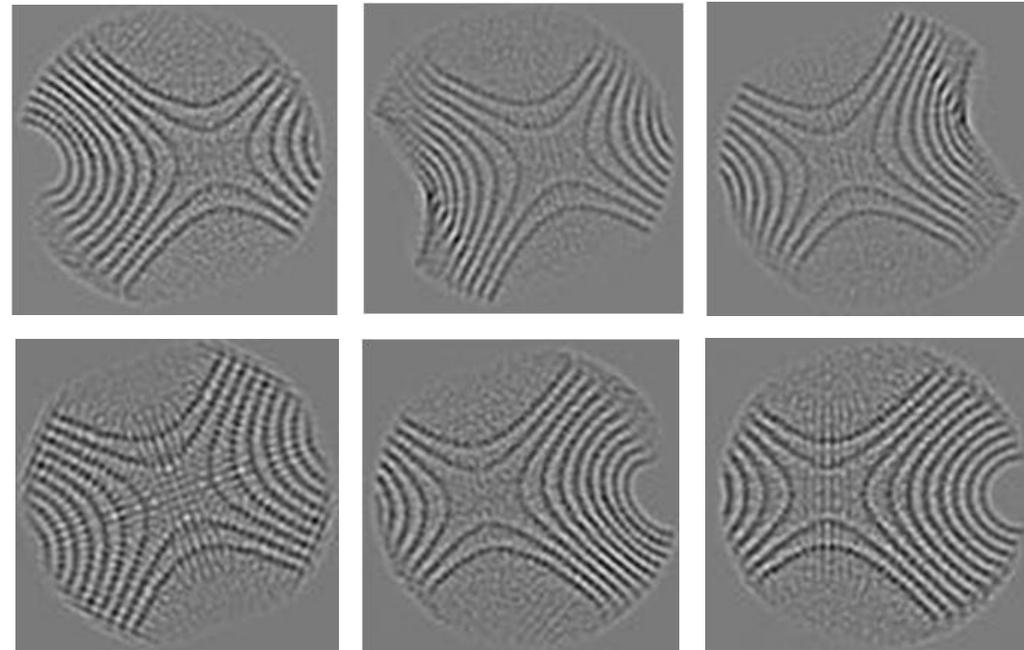
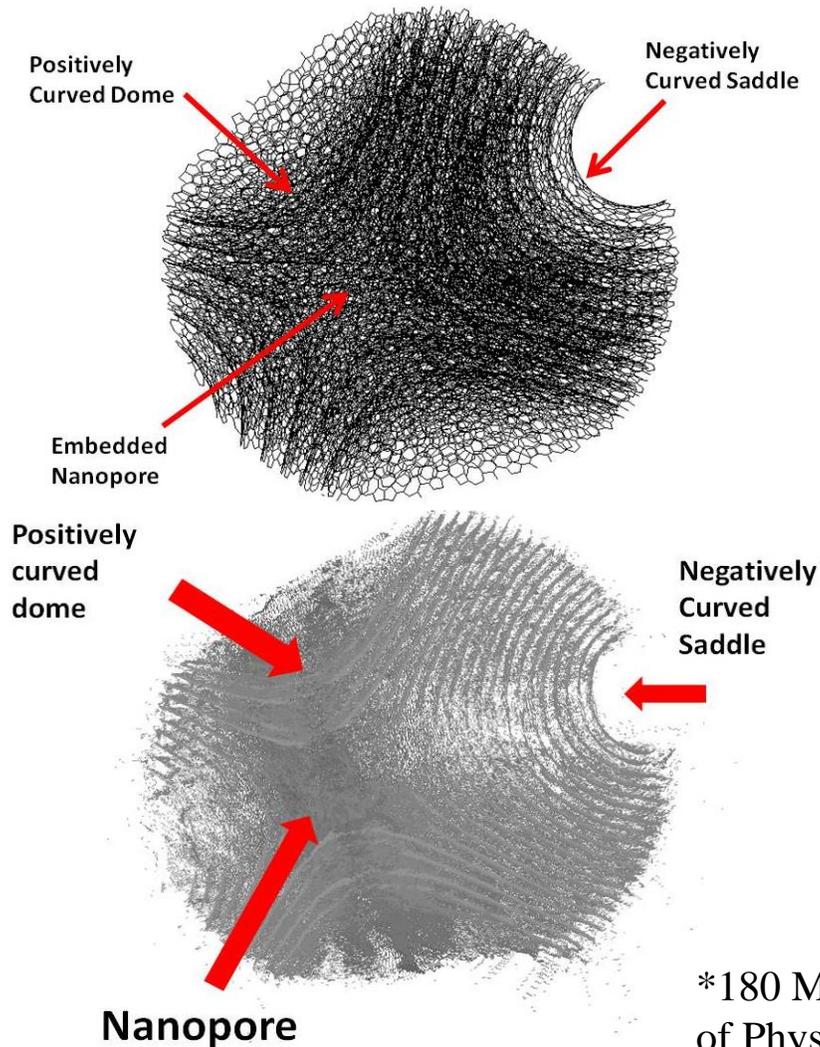


[1] T. C. Petersen, I. K. Snook, I. Yarovsky, D. G. McCulloch, and B. O'Malley, *J. Phys. Chem. C* **111** 802 (2007).

# HRMC example: nanoporous glassy carbon



# Nanoporous glassy carbon: testing tomography theory

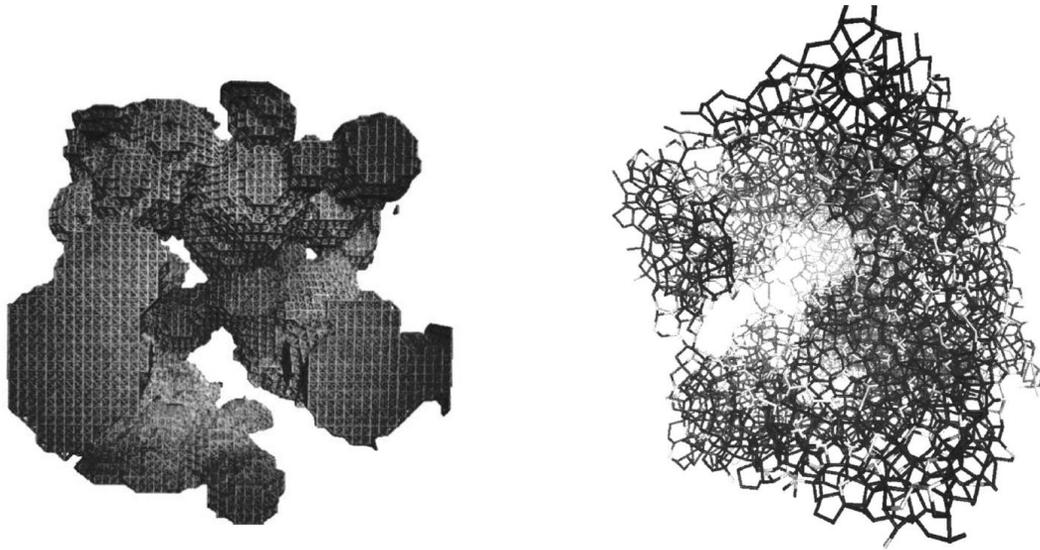


Above: multi-slice HRTEM image simulations of a tomographic tilt-series.

Left: model compared to a 'local tomography' reconstruction (fullerene layers double-counted)

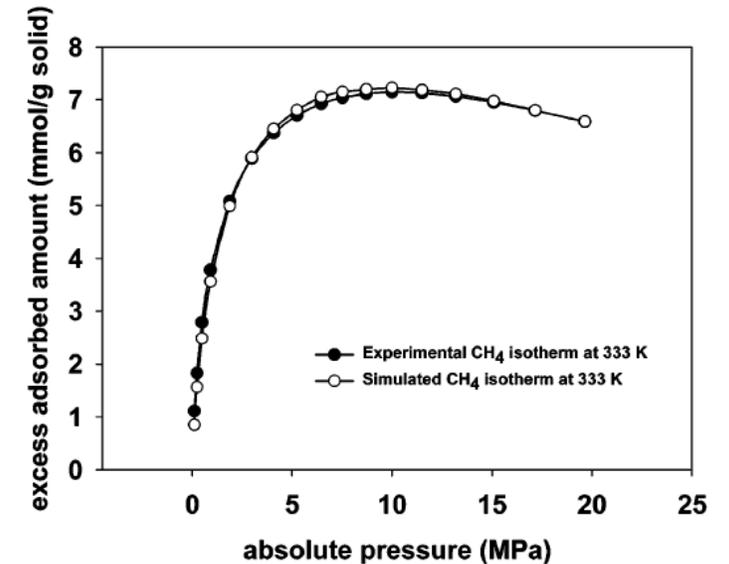
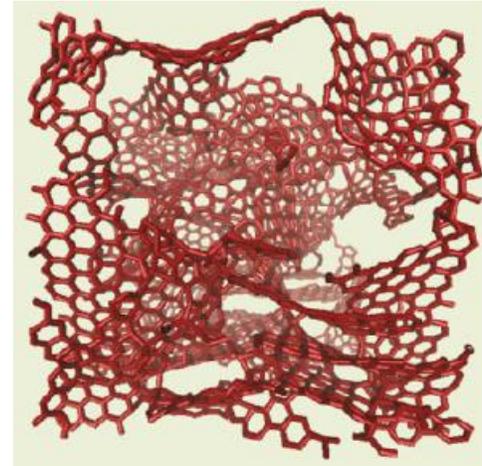
\*180 Multi-slice calculations performed by Vicente Araullo-Peters (School of Physics, University of Sydney) using SimulaTEM software [V = 200kV, Cs = 0.25mm, slice width 0.2nm, -25nm defocus, 3.8nm defocus spread]. See: [A. Gomez-Rodriguez, et al. Ultramicroscopy 110 \(2010\) 95.](#)

# HRMC example: more general nano-porosity



The HRMC code [1] was further developed by Opletal et al. [2] to constrain atomic models with pores of specified volume and surface area.

Above (left) shows an example of the porous constraint for amorphous silicon (above/right).



The porosity constraint in HRMC was used with small- and high-angle neutron diffraction data to model activated carbon. Roughly 5 billion atomic moves and ~3000 atoms produced consistency with diffraction and agreement with experimental adsorption isotherms, providing functional insight [3].

[1] DATA61. CSIRO. Software Collection <http://doi.org/10.4225/08/59dab19e0c3d8>

[2] G. Opletal, T. C. Petersen, I. Snook, and D. G. McCulloch, *J. Chem. Phys.* **126** 214705 (2007).

[3] A. H. Farmahini, G. Opletal, and S. K. Bhatia, *J. Phys. Chem. C* **117** 4081 (2013).

# HRMC with electrons: beyond pair correlations

Pair correlations are measured by volume-averaged diffraction intensities.

Higher order structural correlations can be probed by measuring higher order diffraction statistics, such as the variance in dark-field images [1-3].

Fluctuation electron microscopy [1] (FEM) theory and experiments have shown that the variance is sensitive to medium range order (1nm – 3nm) in disordered solids such as amorphous silicon [4].

FEM data used with experimentally constrained structural relaxation [M. M. J. Treacy and K. B. Borisenko, *Science* **335**, 950 (2012)] has shown that (computationally intensive 4-body correlations) can support the debated existence of paracrystals in amorphous silicon (a-Si).

I performed HRMC simulations to test whether such dense para-crystal networks could be seen using phase contrast images in aberration corrected electron microscopy (next few slides).

[1] M.M.J. Treacy, J.M. Gibson, *Ultramicroscopy* **52** 31 (1993).

[2] J. M. Cowley, *Microsc. Res. Tech.* **46** **75** (1999).

[3] W.E. McBride et al. *J. Non-Cryst. Sol.* **351** 413 (2005)

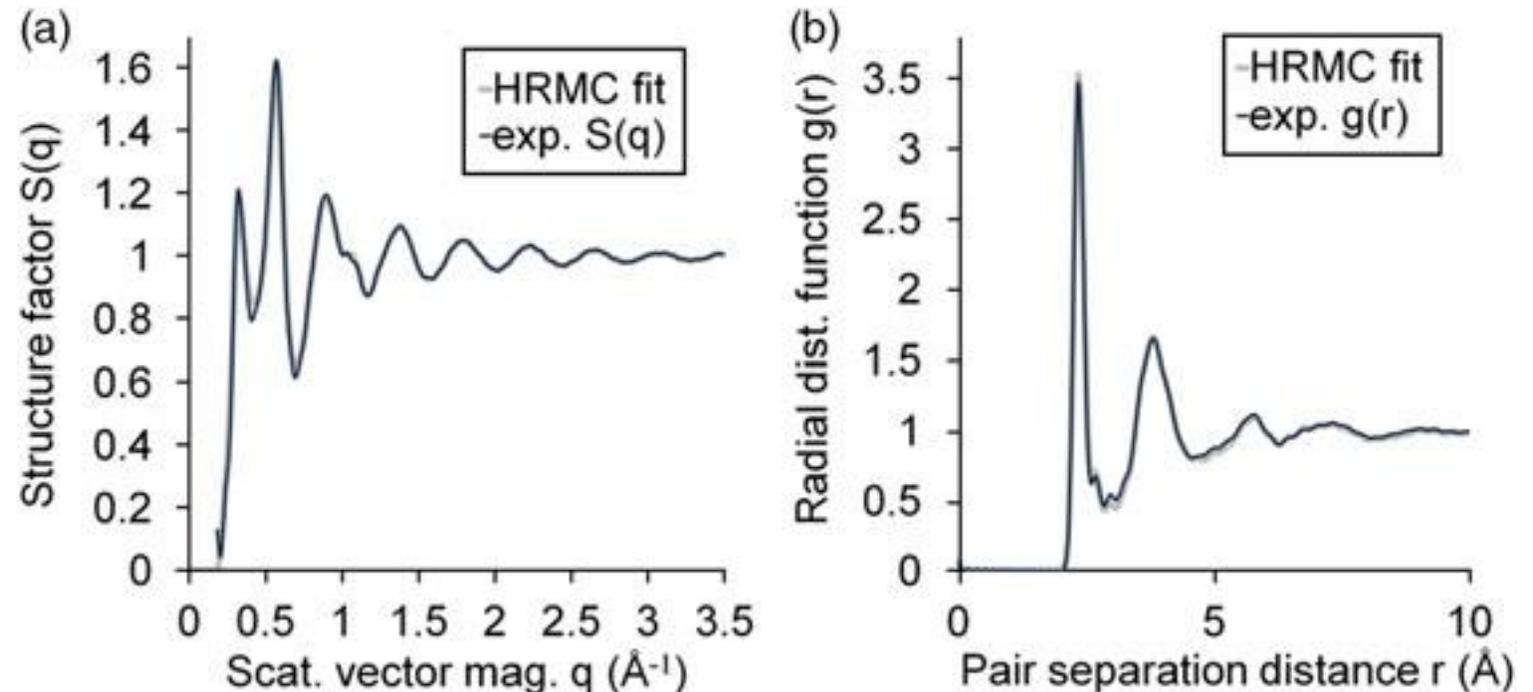
[4] P. M. Voyles, J. E. Gerbi, M. M. J. Treacy, J. M. Gibson and J. R. Abelson, *Phys. Rev. Lett.* **86** 5514 (2001).

# Amorphous silicon networks and paracrystals

HRMC of  $\sim 1700$  atoms created atomic models of self-ion implanted a-Si, consistent with experiment.

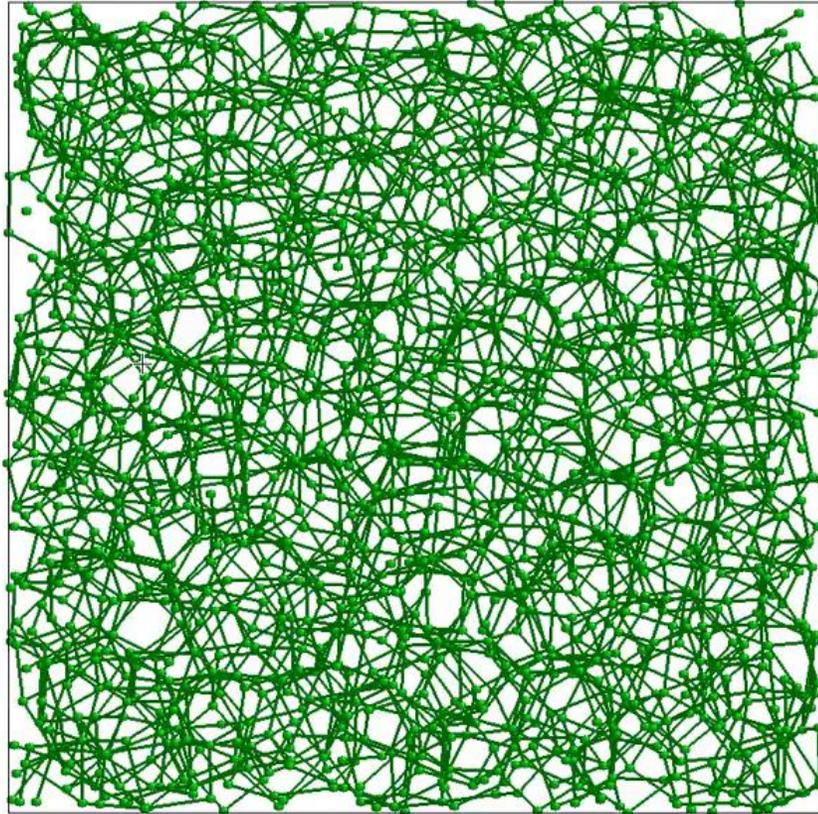
To mimic the Treacy & Borisenko model, a 1 nm sized paracrystal was then inserted into the continuous random network.

Further relaxation in HRMC also produced good agreement with our electron microscopy data (and low potential energy) [1].

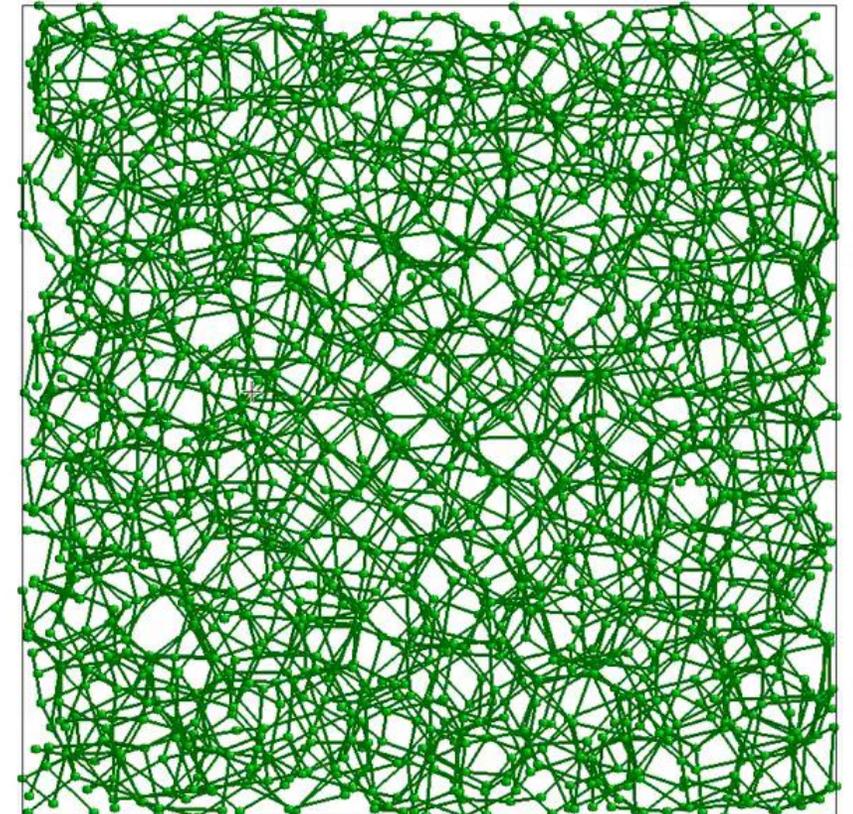


# Amorphous silicon networks and paracrystals

**Left:** HRMC a-Si model without paracrystal

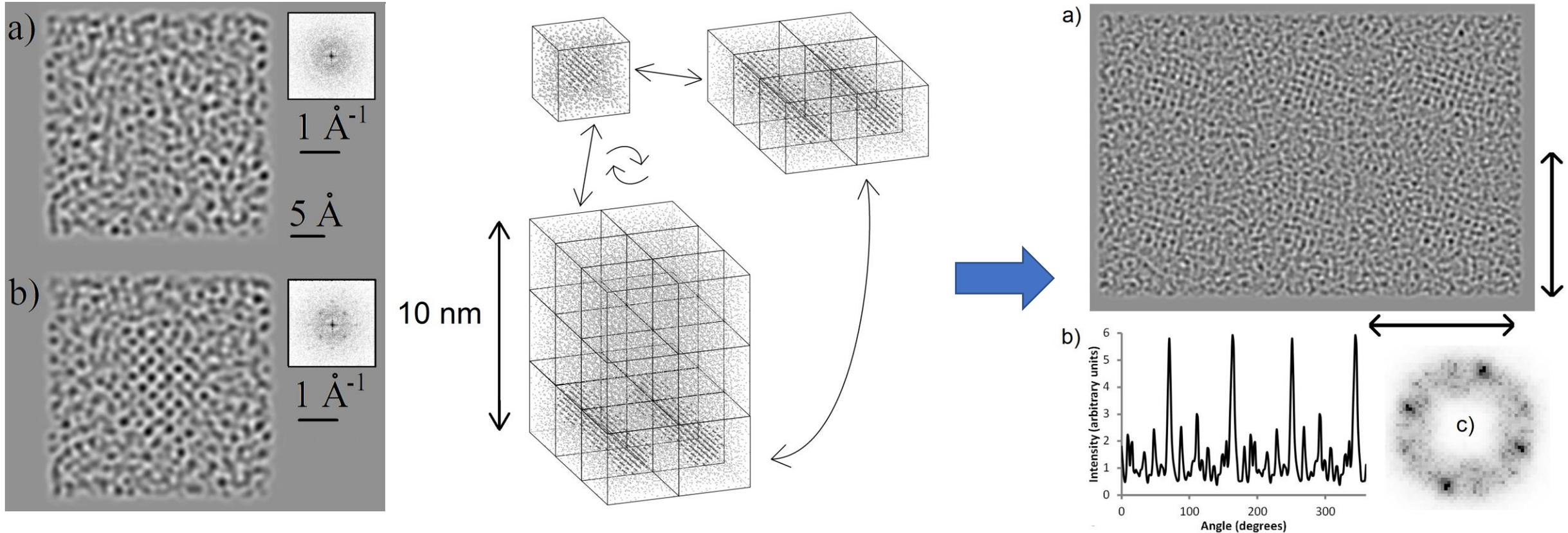


**Right:** HRMC a-Si model with embedded paracrystal [1].



# Amorphous silicon networks and paracrystals

Multi-slice phase contrast images\* and diffraction indeed revealed the paracrystal:



\*200 kV, slice thickness 0.2 nm, Cs 1  $\mu\text{m}$ , defocus spread of 3 nm, beam divergence 0.1 mrad, -7 nm defocus.

A. Gomez-Rodriguez, L. M. Beltran-del-Rio, Ultramicroscopy **110** 95 (2010)

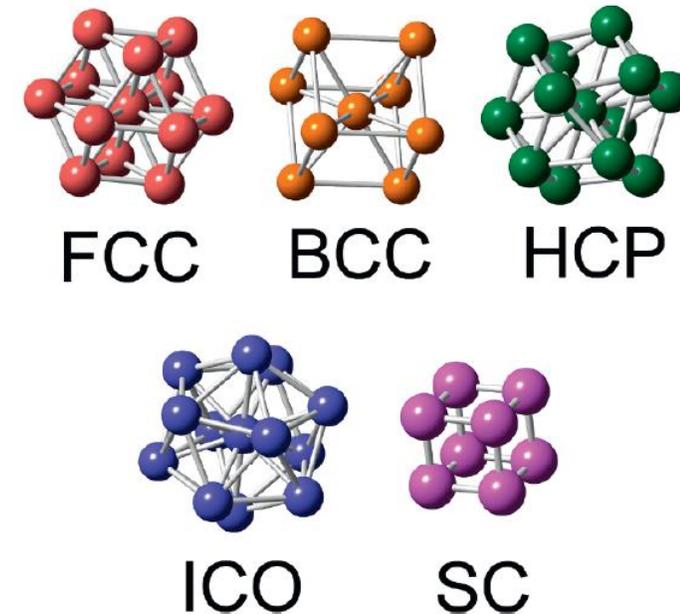
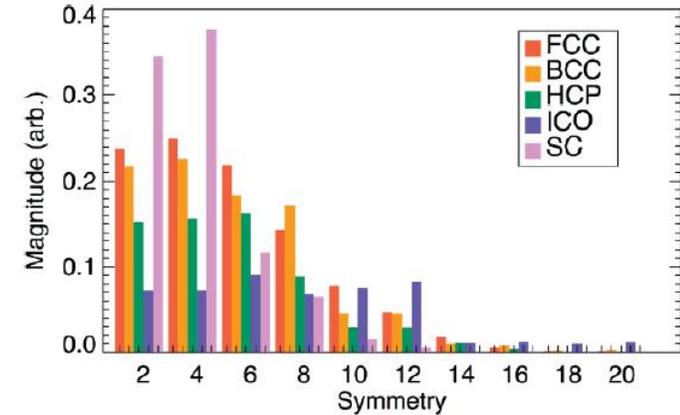
# Beyond pair statistics: nano-beam electron diffraction

In a series of papers [1-4] Amelia Liu has shown subtle *angular correlations* can be revealed, when the size of a scanned diffraction probe is tuned to that of clusters comprising the short range order.

After devising corrections for dynamical scattering in experimental data [2], efficient means for computing angular correlations from archetypal clusters were deduced.

As such, bond orientation order (BOO) parameters [5] appropriate to the projection geometry were tabulated for a variety of structures [4].

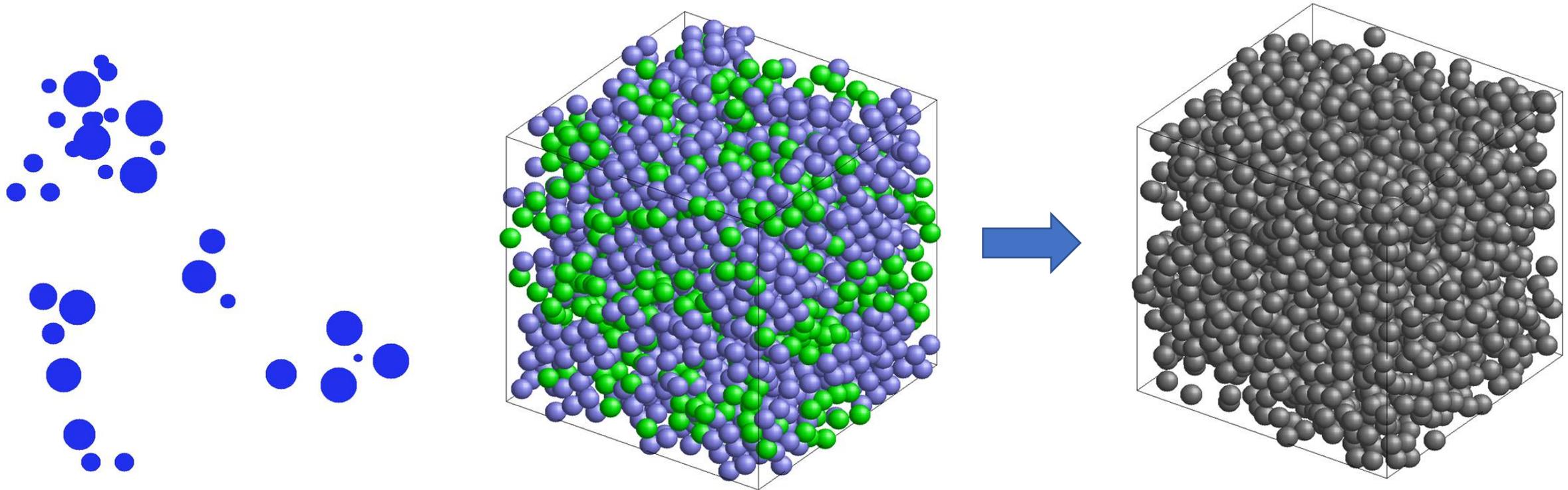
Using synchrotron SAXS scanning diffraction from a colloidal glass of 300nm silica spheres as a test-bed, it was recently shown that the 'cluster spectrum' of these BOO parameters can be measured from experiment by fitting to a basis of the archetypal symmetry magnitudes.



- [1] A. C. Y. Liu et al., Phys. Rev. Lett. **110** 205505 (2013), [2] Acta Cryst. A **71** 473 (2015),  
[3] Phys. Rev. Lett., **116**, 205501 (2016), [4] PNAS **114** 10344 (2017).  
[5] P. J. Steinhardt, D. R. Nelson, M. Ronchetti, Phys. Rev. B **28** 784 (1983)

# Using BOO cluster information in RMC simulations<sup>1</sup>

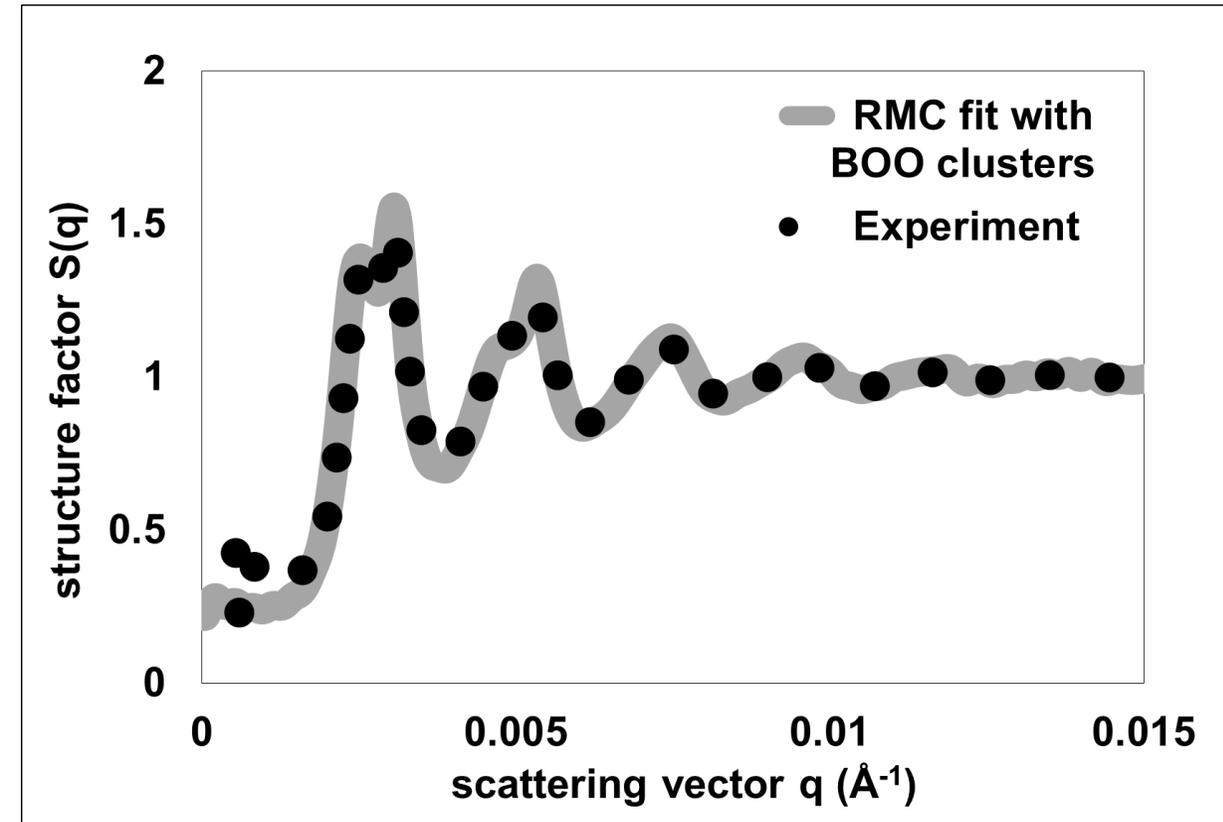
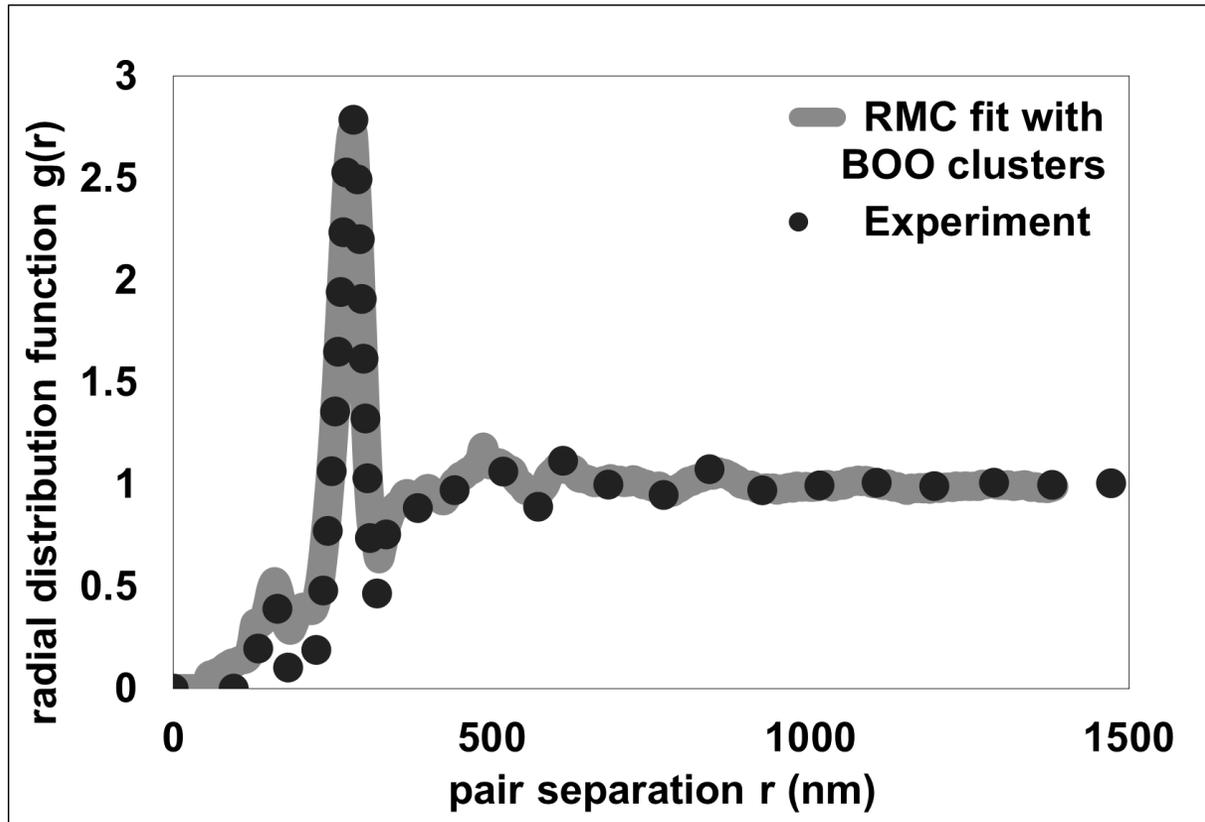
Synchrotron SAXS diffraction data of silica spheres was fitted to a model of 2000 spheres using RMC. Random spherical holes were then carved from the model. BOO clusters of FCC, ICOS and BCC in the experimentally measured proportions were inserted in the holes.



[1] E. D. Bøjesen, T. C. Petersen, A. V. Martin, M. Weyland and A. C. Y. Liu, *J. Phys. Mater.* **3** 044002 (2020).

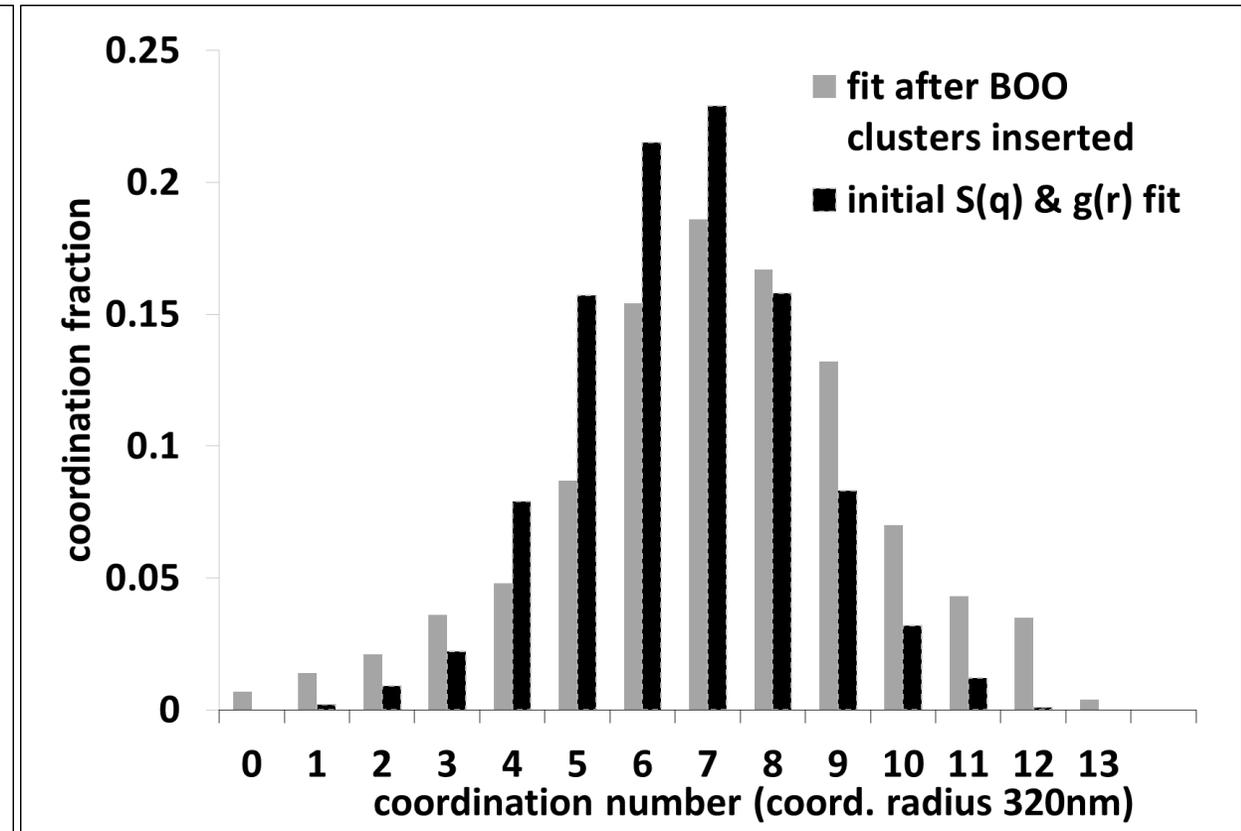
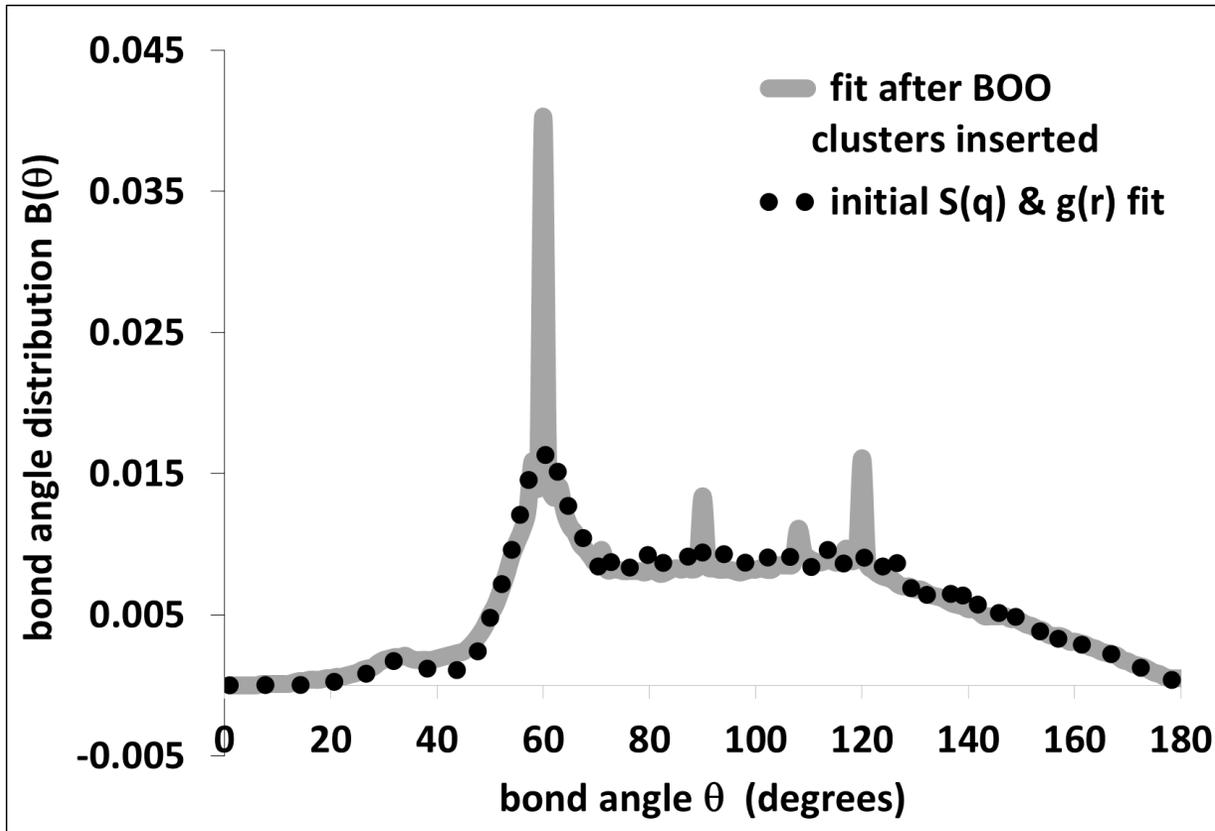
# RMC pair correlations with relaxed BOO clusters

The experimental diffraction data was satisfactorily fitted after inserting the BOO clusters, while including extra bond and coordination constraints derived from the initial insertion model.



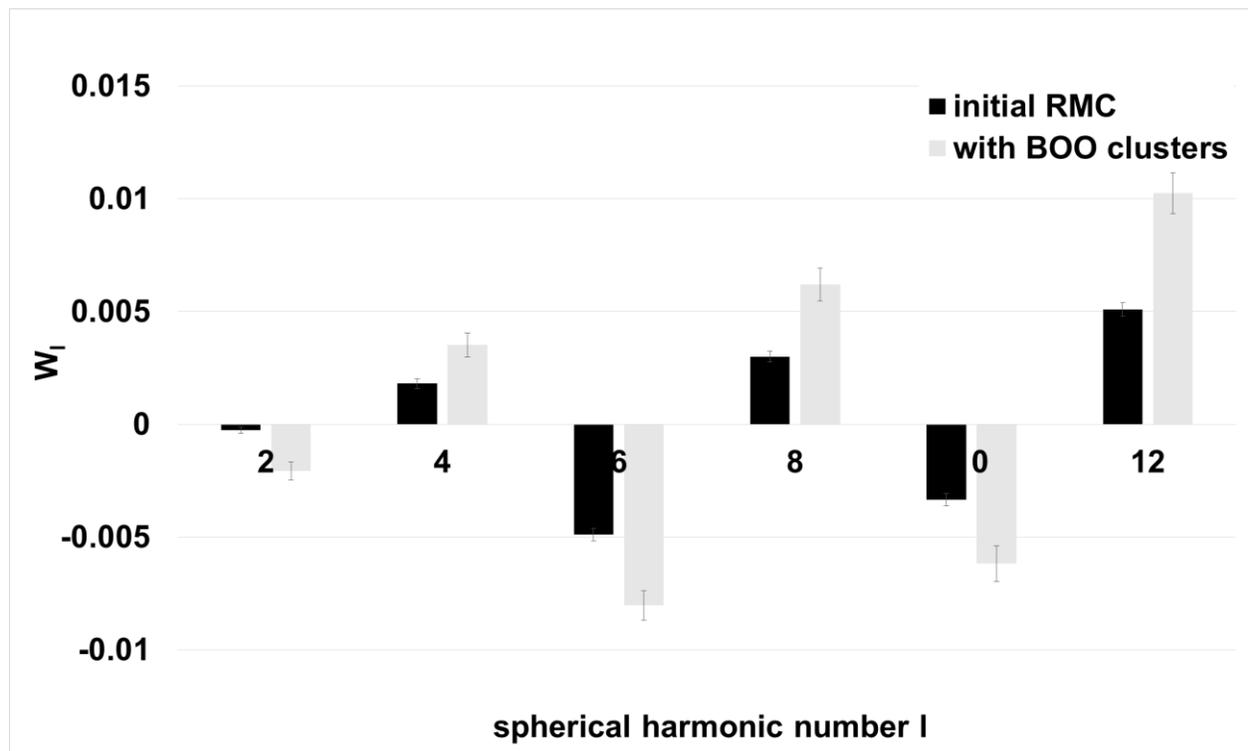
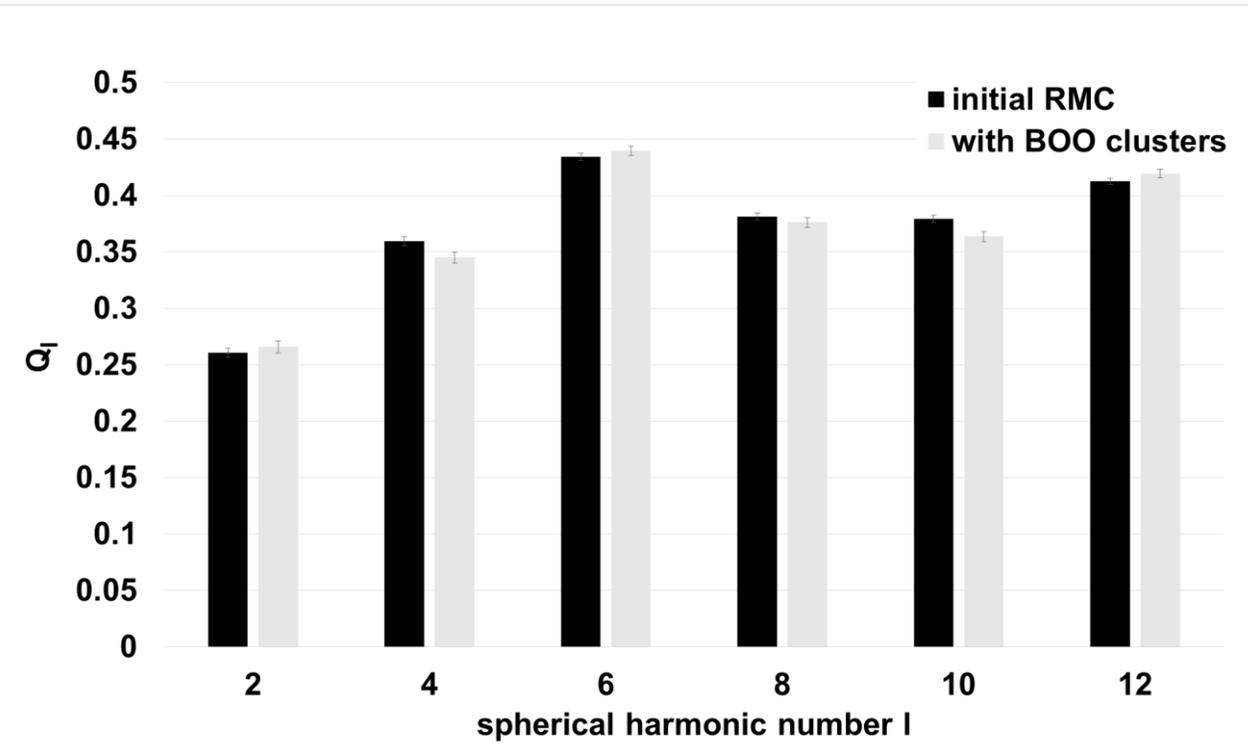
# Colloidal network statistics

Bond angle  $B(\theta)$  and coordination distributions fitted during the RMC relaxation successfully preserved (much of) the orientation order from the inserted BOO clusters.



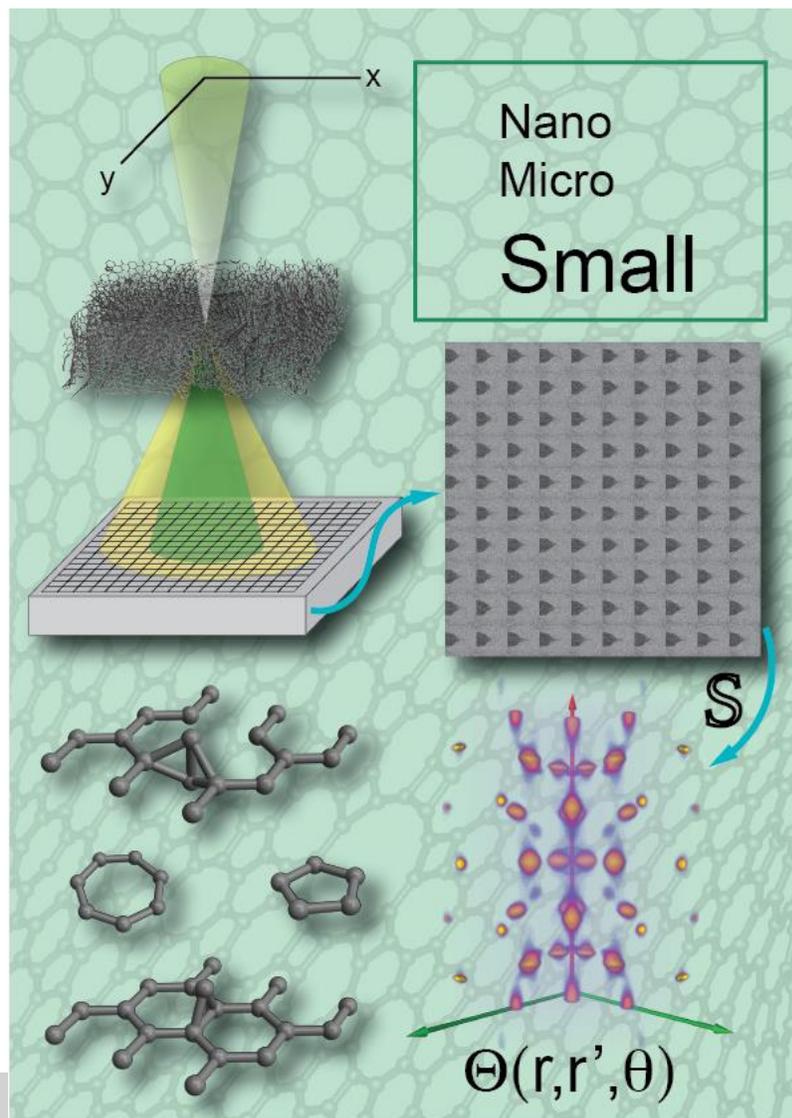
# Spherical harmonic Steinhardt BOO parameters

After RMC relaxation, averaged spherical harmonic bond orientation order parameters also show increased angular correlations [1], indicating preservation of BOO cluster information.



[1] P. J. Steinhardt, D. R. Nelson, M. Ronchetti, Phys. Rev. B **28** 784 (1983)

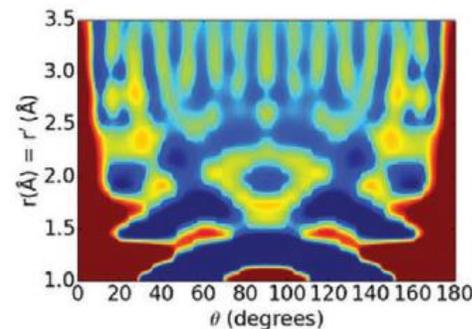
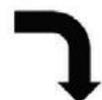
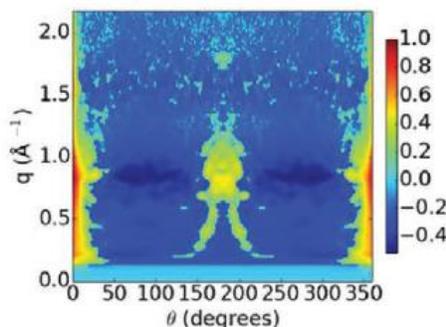
# Bond angle information from activated carbon....



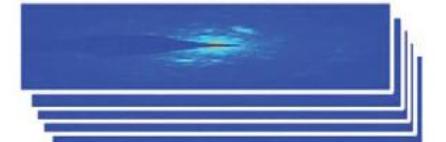
Can scanning electron diffraction data yield  $B(\theta)$  for RMC fitting?

$$\Theta(r, r', \theta) = \tilde{g}_2(r, r' = r, 0) + \tilde{g}_3(r, r', \theta) + \tilde{g}_3(r, r', \pi + \theta) + \tilde{g}_4(r, r', \theta)$$

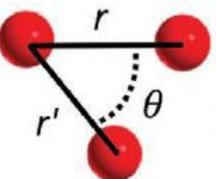
Intensity correlation function



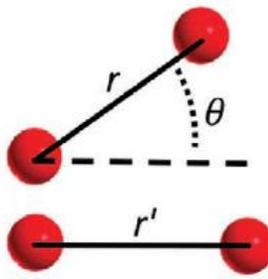
PADF



Ensemble of diffraction patterns



3-body geometry



4-body geometry

The 'pair angle distribution function'  $\Theta(r, r', \theta)$  can be measured to quantify bond angle information:

A. V. Martin, IUCrJ **4**, 24 (2017).

It *may*<sup>1</sup> be possible to extract a symmetrised version of  $B(\theta)$  for fitting in RMC/HRMC:

Martin et al. Small **16**, 2000828 (2020).

# CONCLUSION

Hybrid reverse Monte Carlo modelling can describe a wide range of low-energy structures consistent with experimental observations.

Electron microscopy enables nano-scale spatial sampling of structural inhomogeneity.

RMC simulations can produce non-unique models but more experimentally motivated constraints can improve the structural descriptions of disordered solids. More work is needed to model strong scattering physics unique to electron microscopy, to alleviate stringent experiment constraints.

New diffraction experiments and theory can provide a wealth of valuable information such as medium range order, bond angles and archetypal angular correlations, to provide further insights regarding many-body structural correlations in non-crystalline condensed matter systems.