Introduction to fluctuation x-ray scattering:
A new way to probe disordered structure at advanged light sources

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Outline

- The “structure problem” for disordered materials
- Structure and Scattering
- What is fluctuation scattering and how is it done?
- Recent applications / case studies

1) The structure problem for disordered materials

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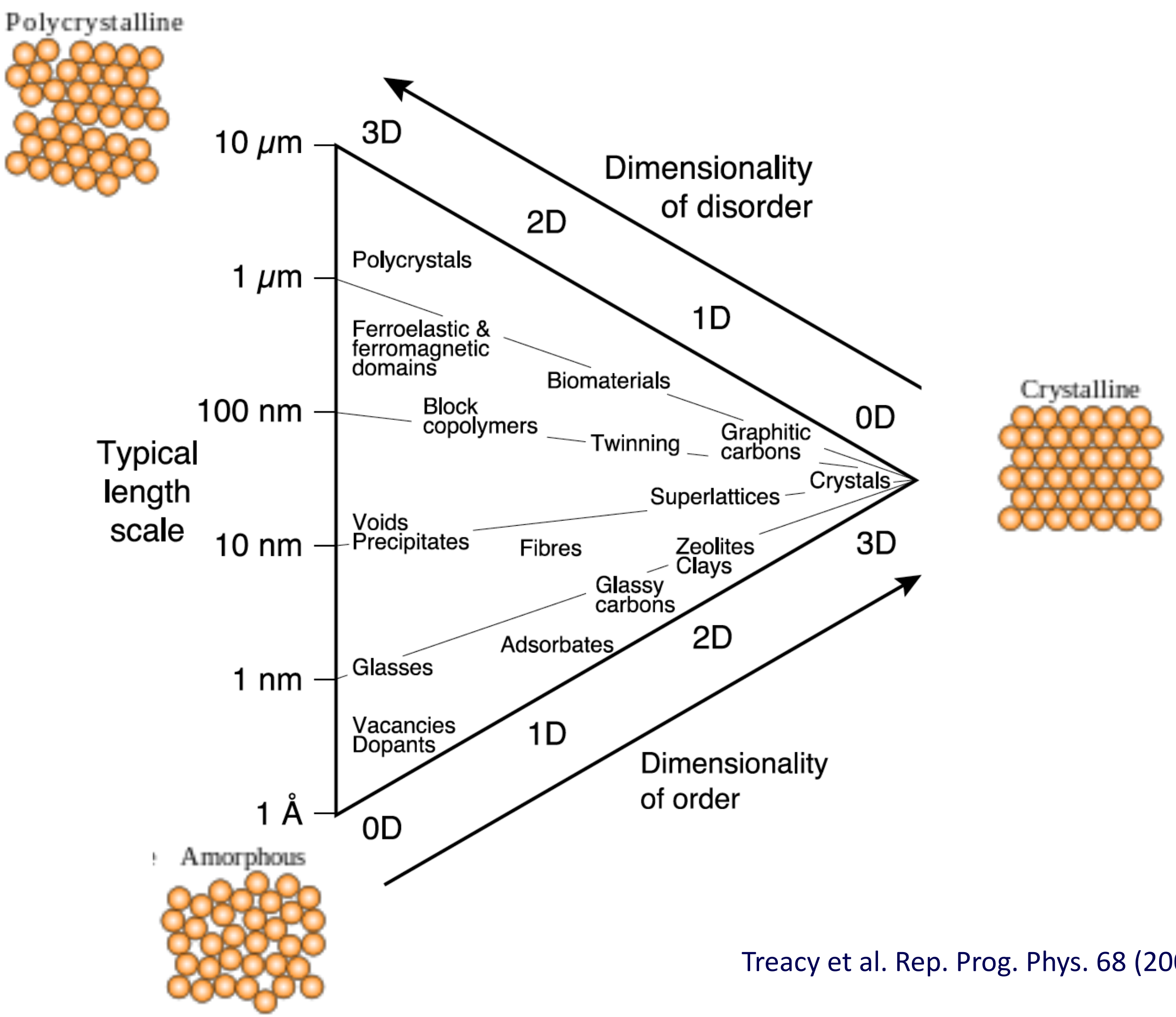
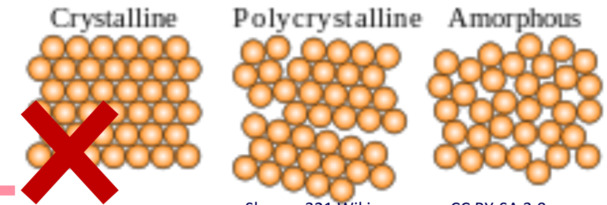
Degrees of order



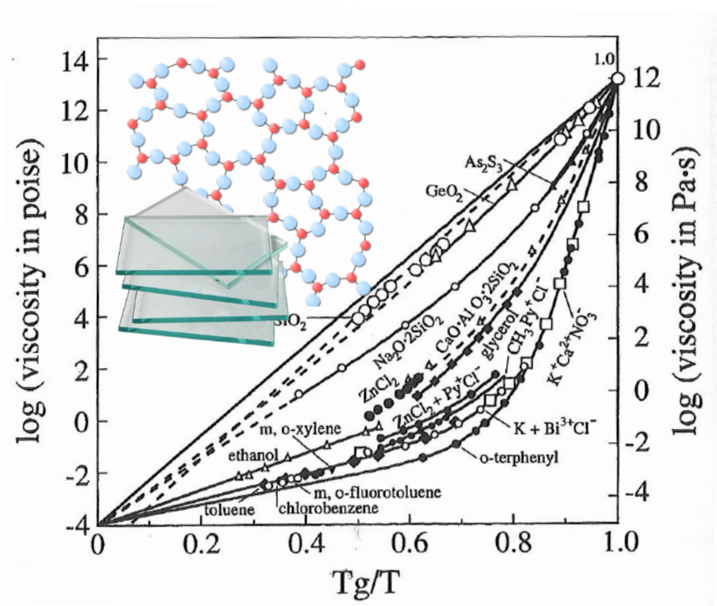
Treacy et al. Rep. Prog. Phys. 68 (2005) 2899

We live in a disordered world!



Sbyrnes321 Wikicommons CC BY-SA 3.0

Mystery of the glass transition



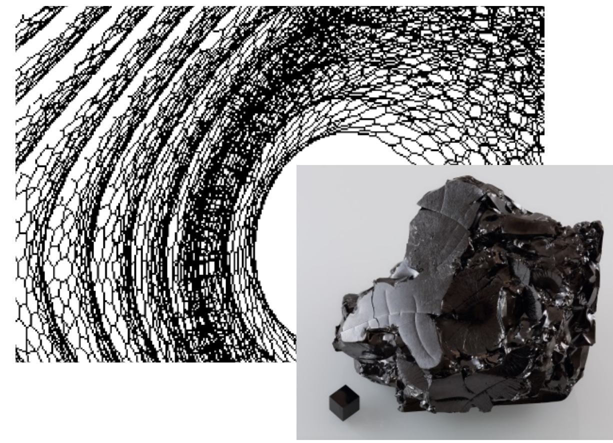
Metallic glass

ABC NEWS 22/8/17

Metallic glass ceiling may be smashed with improved technique to treat contaminated water

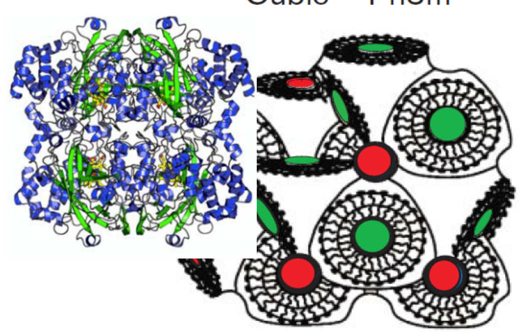
Amorphous Materials

Glassy carbon (High T crucibles; electrochemistry)



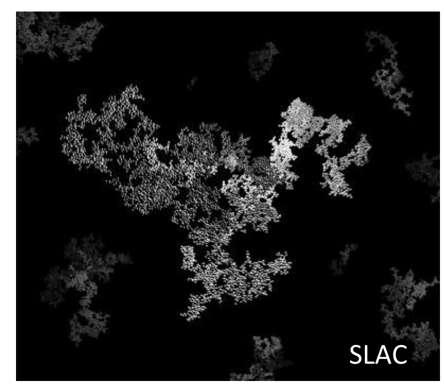
Lipidic membrane materials /Proteins

Cubic – Pn3m



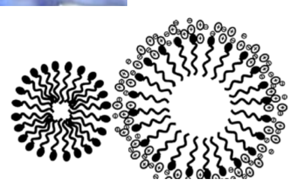
Airborne particles (soot)

(pollution/respiratory health)



Liquids

Ionic Liquids



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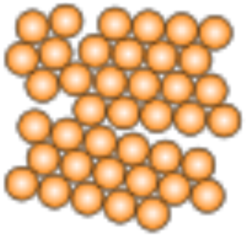
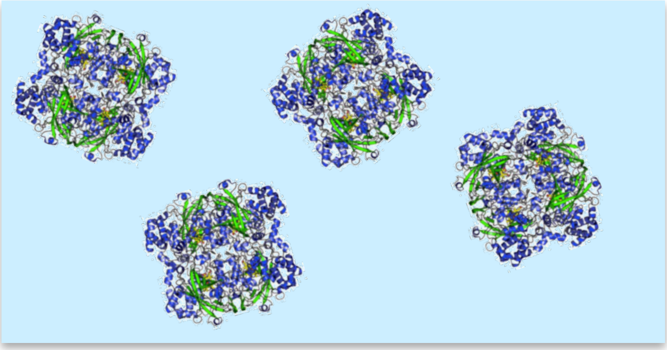
Orientation vs Structural disorder

Orientation disorder
of ordered particles/crystal domains

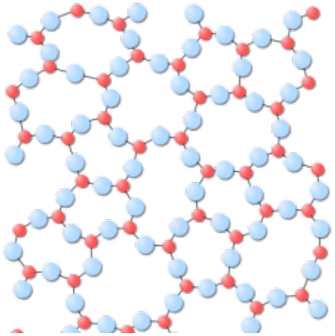


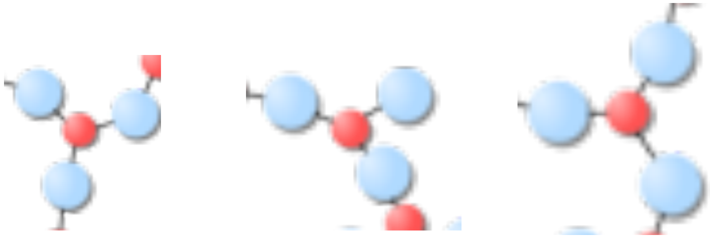
polycrystal



Particles in solution

Structural Heterogeneity
(+ orientational disorder)

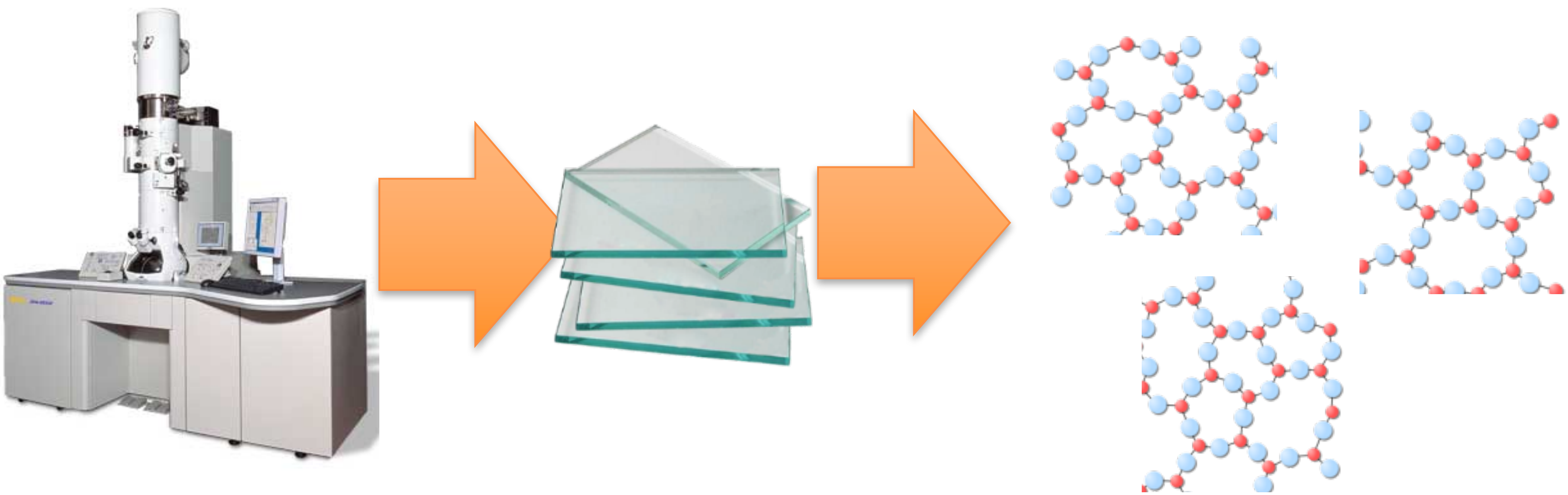




A thought experiment

Imagine you had an amazing microscopy technique that could measure all the atoms in a disordered structure in 3D.

A 3D image of all the atoms should tell you everything, *right*?



<u>BUT every time you put in a new sample of the same material you see a different structure!</u>

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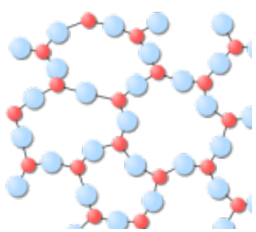
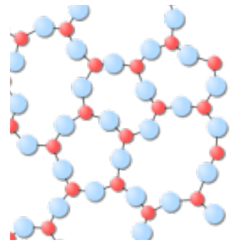
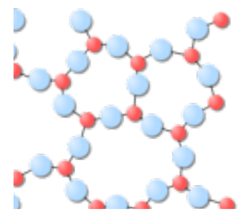
So what would we do with the images?







Common structural information:

- Same density
- Same bond distances

- Close neighbors have certain angles

- *n*-particle correlation functions $g^{(n)}(\boldsymbol{r}_1, \dots, \boldsymbol{r}_n)$

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2) Structure & Scattering

Structure and scattering

Non-periodic Particle   Crystal

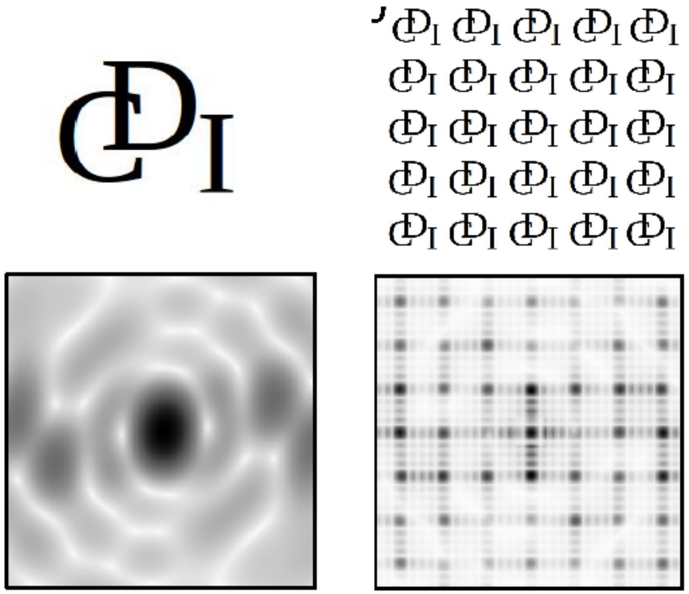
Electron density $\rho(\boldsymbol{r})$

Fraunhoffer diffraction
(Fourier transform)

Scattering factor $F(\boldsymbol{q})$

$\rho(\boldsymbol{r})$

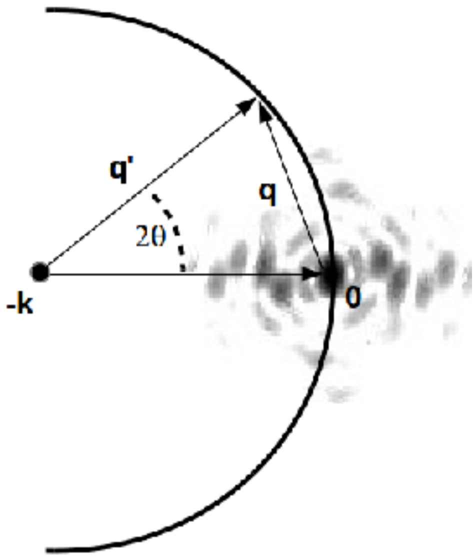
$|F(\boldsymbol{q})|^2$

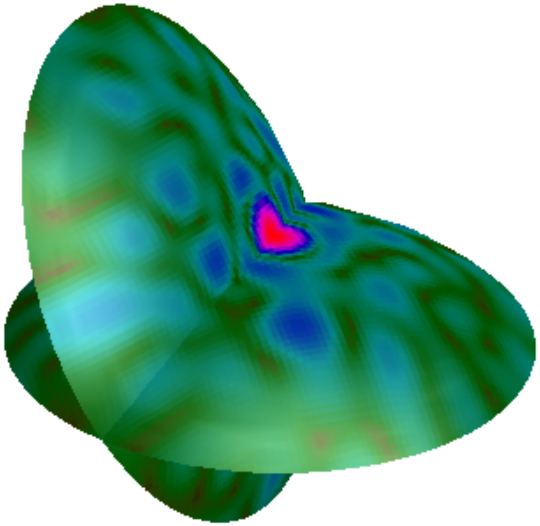


Structure and scattering in 3D

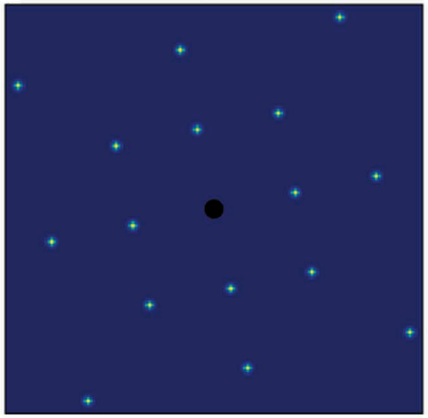
Intensity measured on the detector is a curved slice through $|F(\boldsymbol{q})|^2$ (Ewald sphere)

Depends on sample orientation

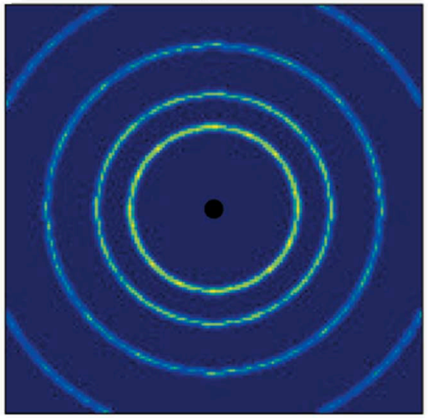




Crystals and powders

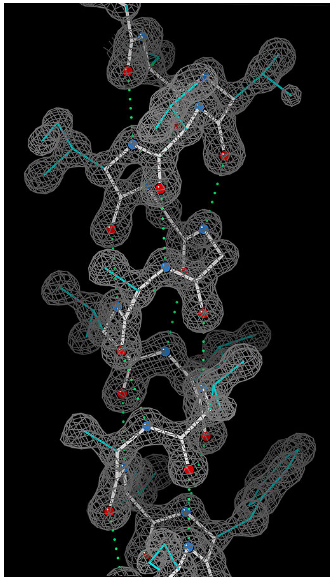


Crystallography

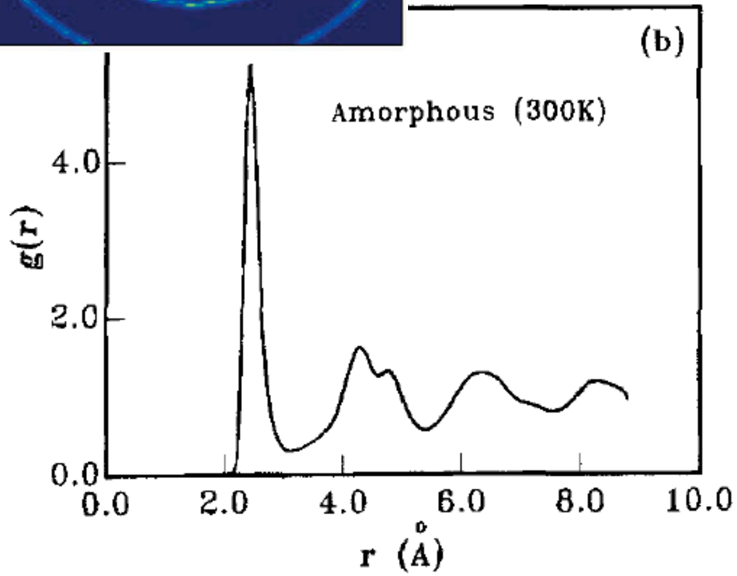


Powder diffraction

Small/Wide angle x-ray scattering (SAXS/WAXS)



Electron Density $\rho(r)$



Pair distribution function $g^{(2)}(r)$

Overview of scattering techniques

Techique	Sample	output
Crystallography	Large well-ordered single crystal	3D electron density
Powder diffraction	Ensemble of small well-ordered crystals	Atomic model
Powder diffraction	Disordered crystals	Pair distribution
SAXS/WAXS	Proteins, liquids, soft matter, colloids	Particle size, Pair-distribution mesoscale lattice parameters
Electron microscopy		

“The structure problem” revisited

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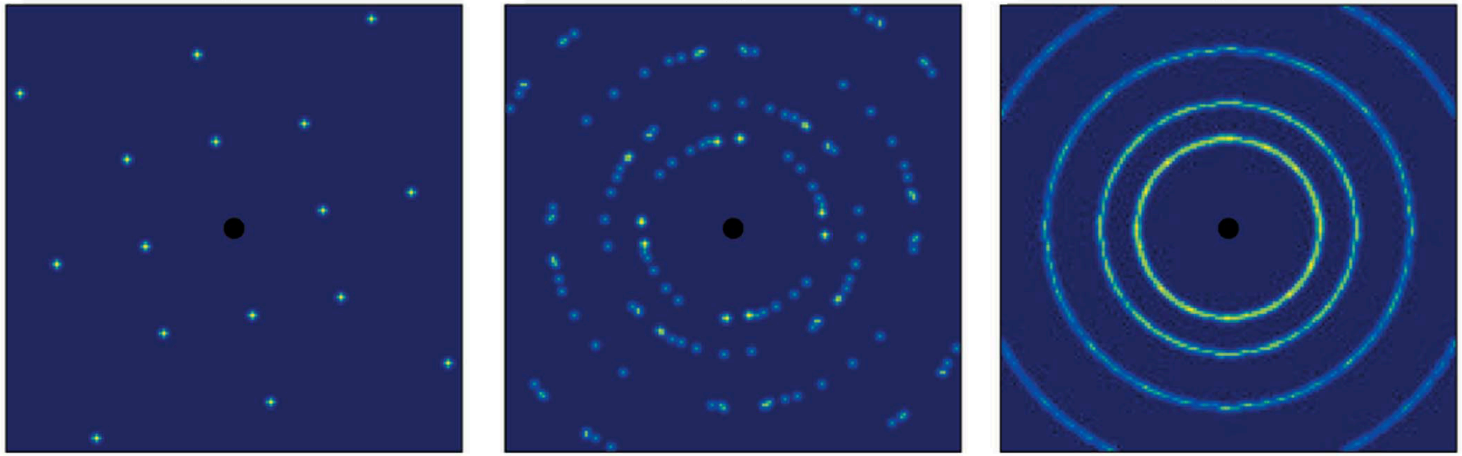
Crystals and powders



Crystal→ 3D structure

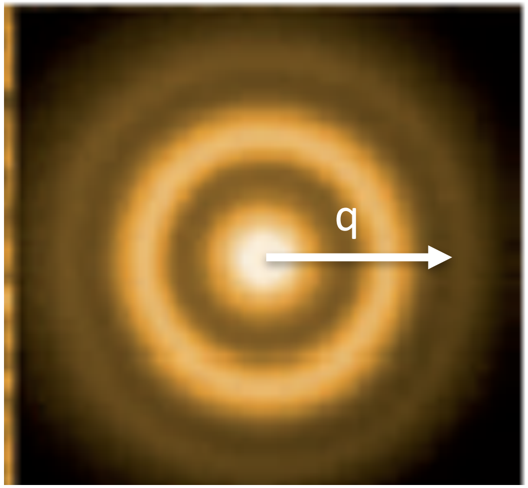
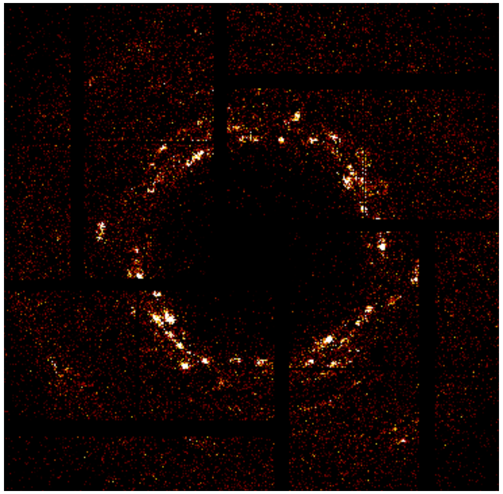
?

Powder
→ 1D pair distribution

$< I(\boldsymbol{q}) > \propto N$ (Number of domains in the beam)

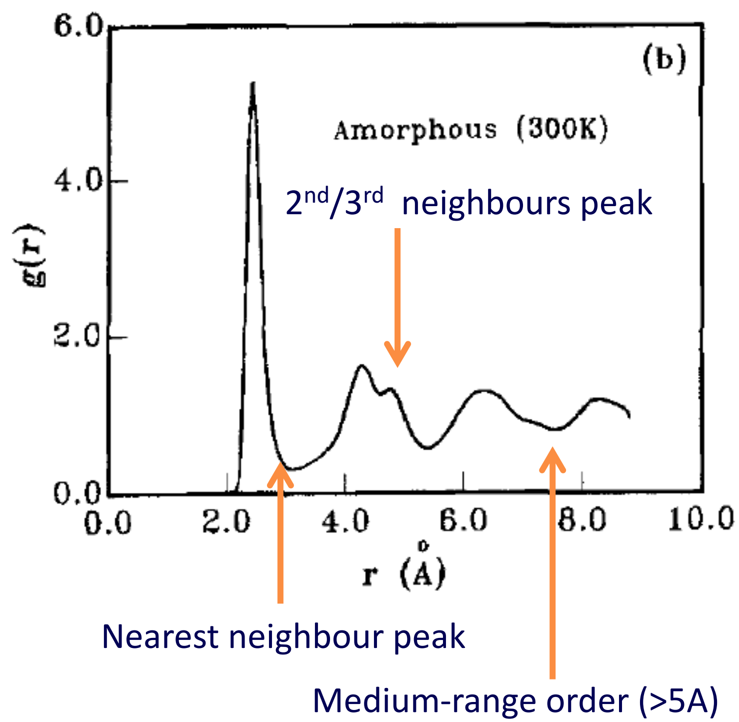
$\sqrt{\delta I^2(\boldsymbol{q})} \propto \sqrt{N}$

The real experiment: Diffraction

Large beam	Small beam at position α
	
Fourier Transform	Fourier Transform
$\propto g^{(2)}(r)$	$\propto g_{\alpha}^{(2)}(\boldsymbol{r})$
Bond distance only	Bond distance & orientation

! But also sample orientation & not ensemble statistics

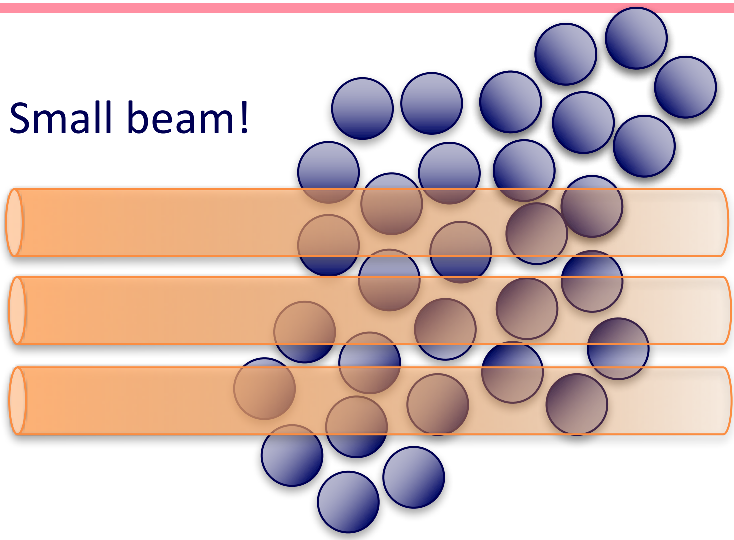
Pair-distribution function (PDF) - $g^{(2)}(r)$

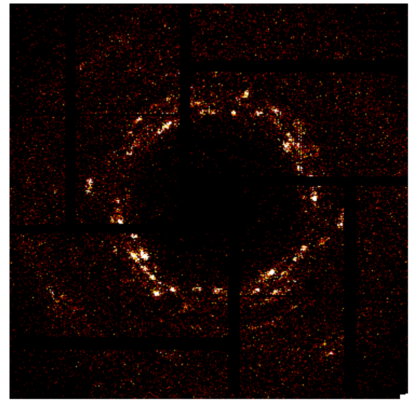


2) Structure & Scattering

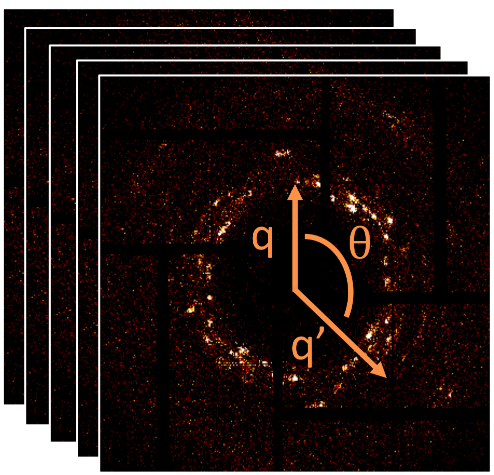
Fluctuation x-ray scattering

Small beam!





Angular variations in intensity



From an ensemble of data (typically 1000s)
→ Angular intensity correlation function

$$C(q,q',\theta) = \int d\phi \, \langle I_\alpha(q,\phi+\theta) I_\alpha(q',\phi) \rangle_\alpha$$

What does a correlation measure?

$$\rho(\boldsymbol{r}) = \sum_{i=0}^{N} \rho_i(\boldsymbol{r}) \qquad F(\boldsymbol{q}) = \sum_{i=0}^{N} f_i(\boldsymbol{q}) e^{i\boldsymbol{q}\cdot\boldsymbol{R}_i}$$

Sum over atoms

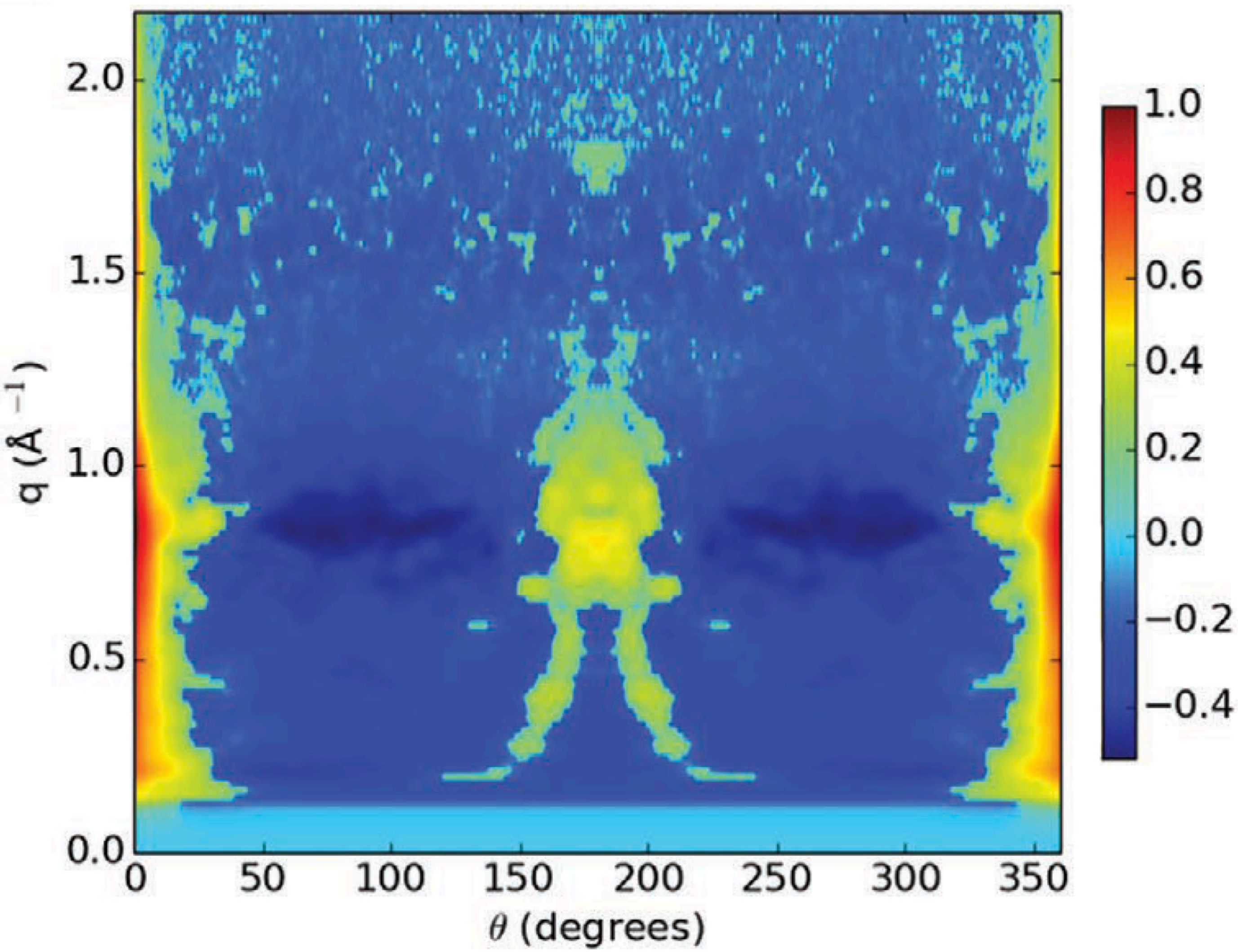
$$I(\boldsymbol{q}) = |F(\boldsymbol{q})|^2 = \sum_{\boldsymbol{i}}^{\boldsymbol{N}} \sum_{\boldsymbol{j}}^{\boldsymbol{N}} \ldots$$

Sum over atom pairs

$$I(\boldsymbol{q})I(\boldsymbol{q}') = \sum_{\boldsymbol{i}}^{\boldsymbol{N}} \sum_{\boldsymbol{j}}^{\boldsymbol{N}} \sum_{\boldsymbol{k}}^{\boldsymbol{N}} \sum_{\boldsymbol{l}}^{\boldsymbol{N}} \ldots$$

Double sum over atom pairs

Example q–space correlation function



History of fluctuation scattering

Fluctuation x-ray scattering

Kam, Z. (1977). *Macromolecules*, **10**, 927–934

$$C(q, q', \theta)$$

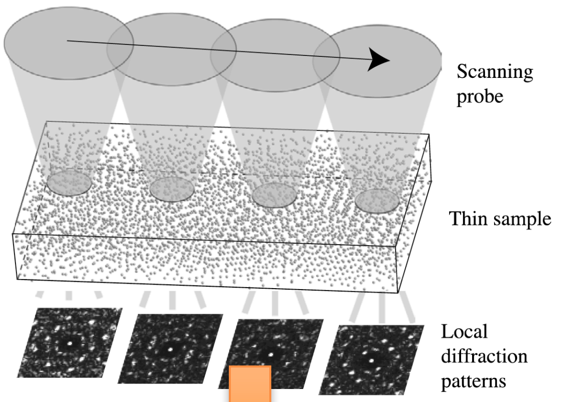
Single particle imaging theory

R. P. Kurta et al., Structural Analysis By X-ray Intensity Angular Cross Correlations, 2016, pp. 1–39.
R. Kirian, J. Phys. B: At. Mol. Opt. Phys. 2012, 45, 223001

$$C(q, q', \theta) \rightarrow \rho(\boldsymbol{r})$$

Fluctuation electron microscopy

M. M. J. Treacy et al., Rep. Prog. Phys. 2005, 68, 2899
M. M. J. Treacy, K. B. Borisenko, Science 2012, 335, 950



Recent growth (2010-present)

Colloids - Wochner, PNAS. 2009, 106, 11511
Liquid crystals Kurta ; Martin
Nanoparticles (Lehmkuler…)

Virus imaging Kurta et al.
Metallic Glasses Liu et al.
Disordered carbons Martin et al.

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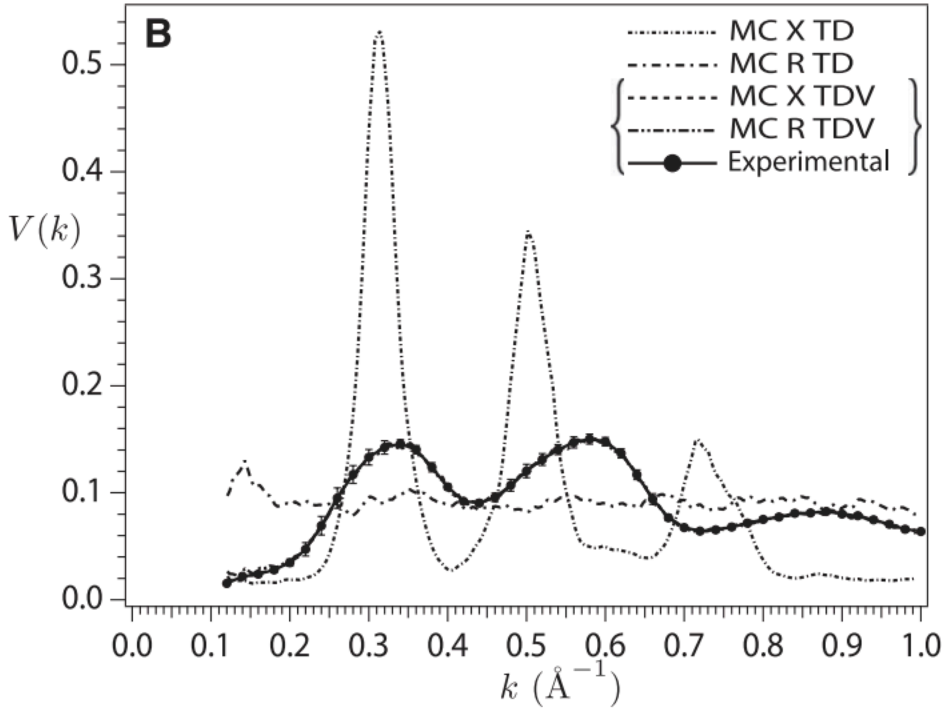
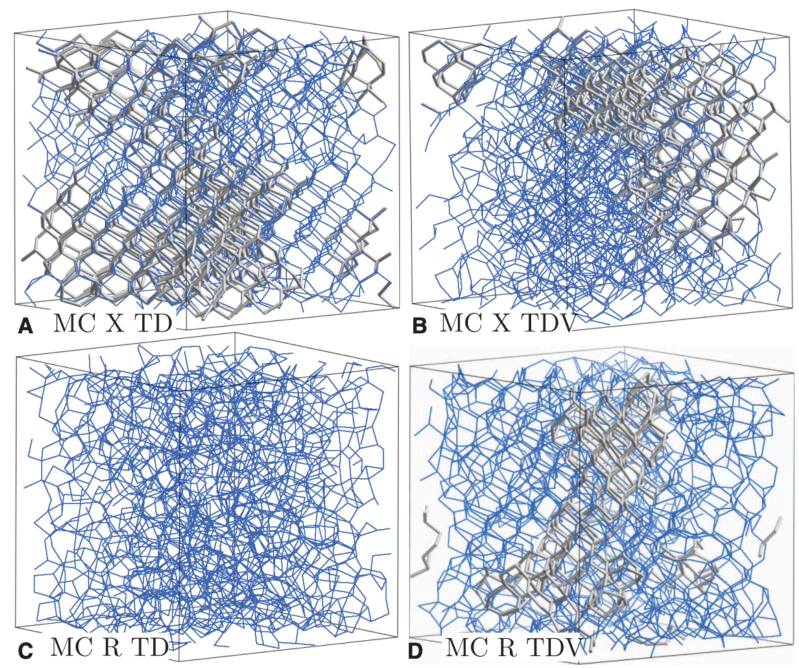
Fluctuation Microscopy

Treacy et al. *Science*, (2012) 335, 950

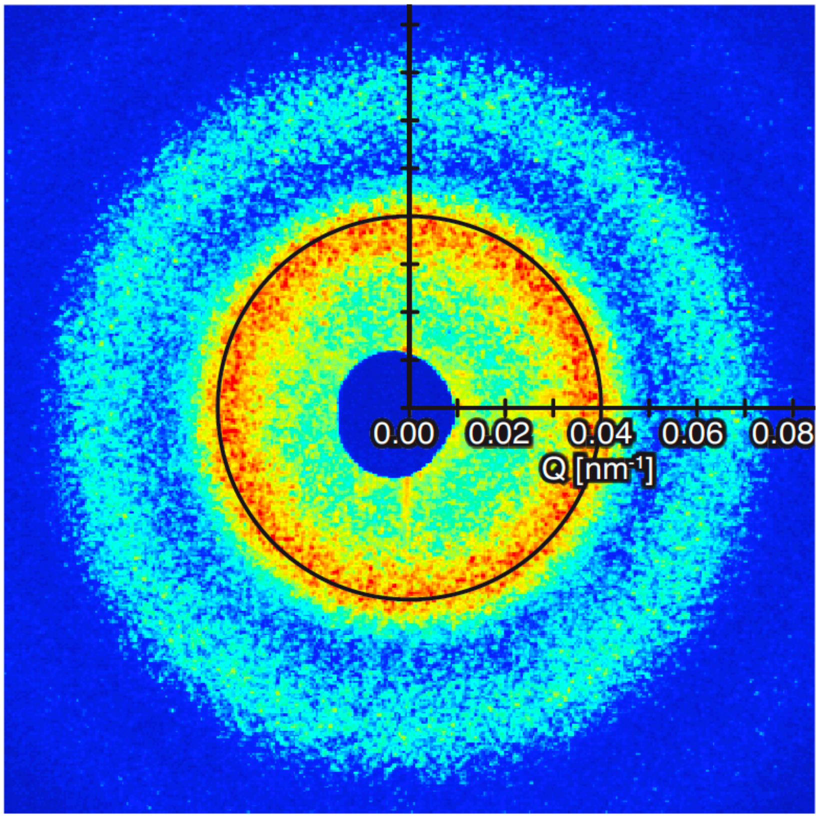
Variance measurements used to constrain disordered structures of amorphous silicon

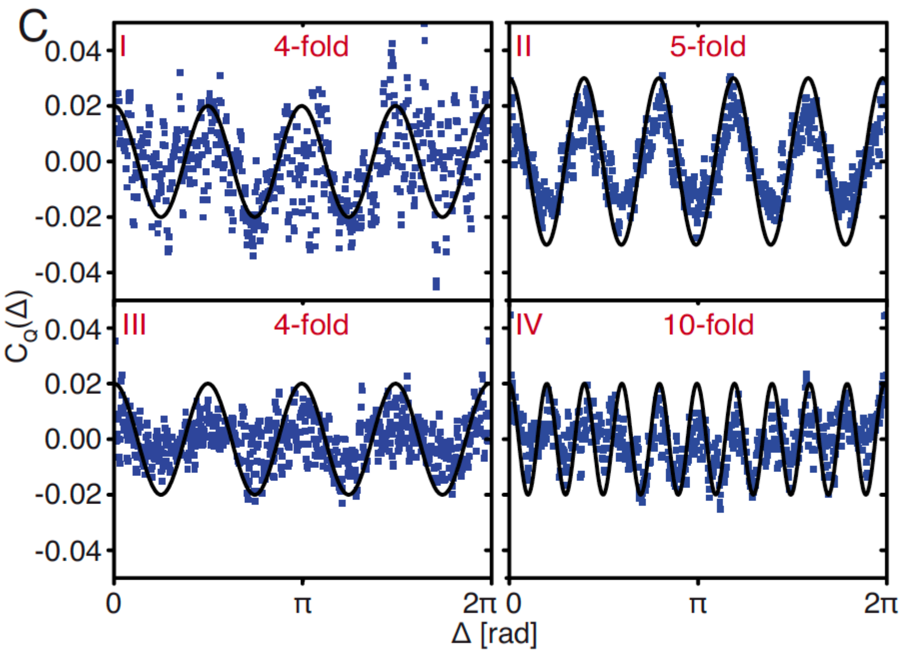




Angular symmetry

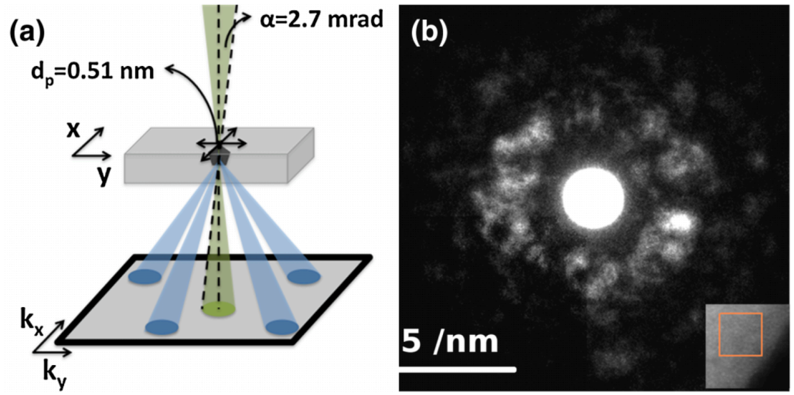
Wochner, PNAS. 2009, 106, 11511

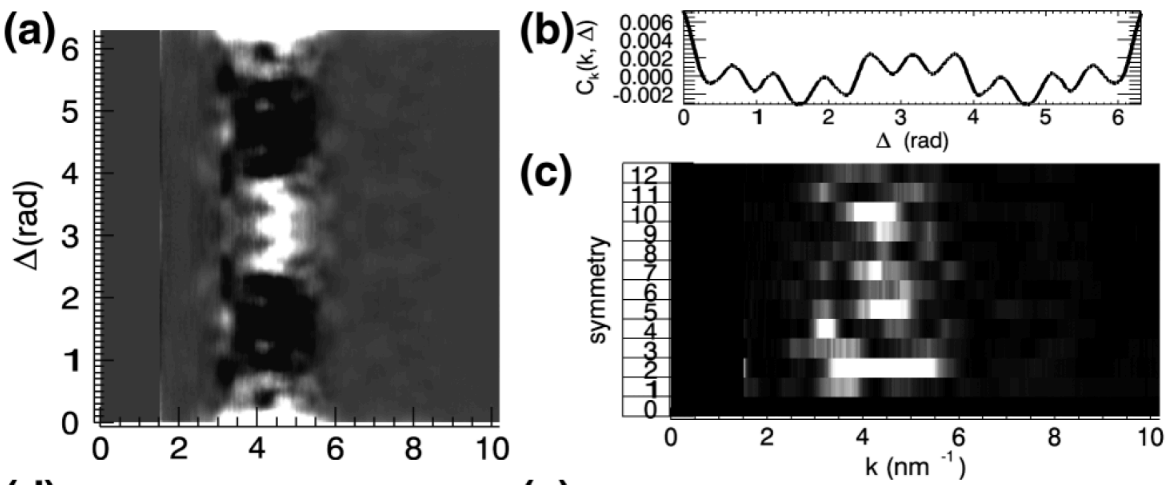




Angular Fourier Analysis - example

Liu et al. PRL 110, 205505 (2013)
Metallic Glasses





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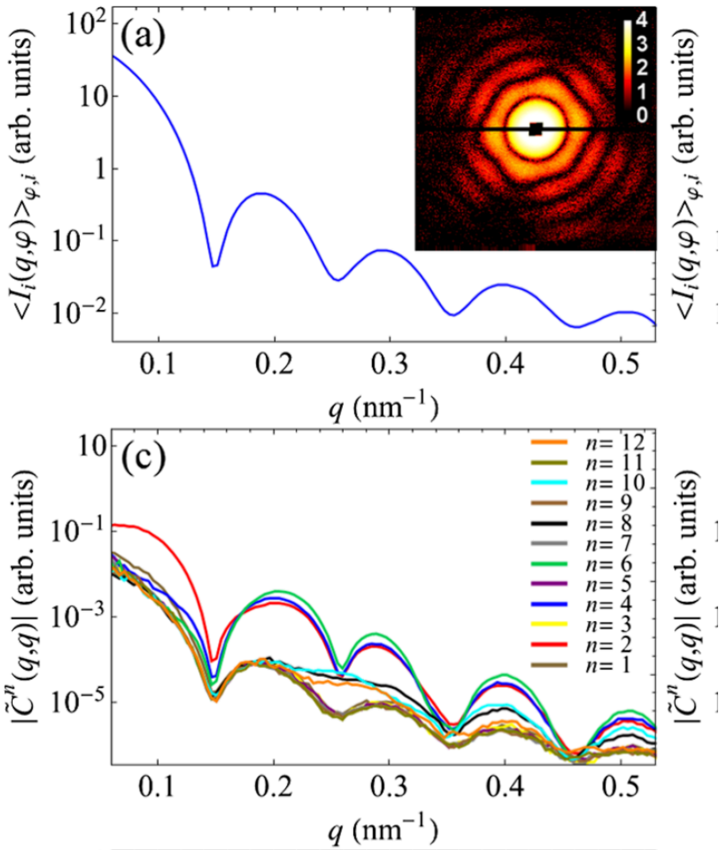
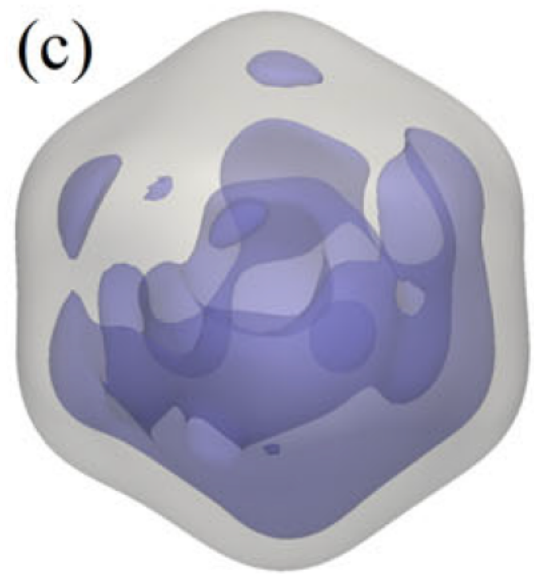
3D imaging

Kurta et al. PRL 119, 158102 (2017)

Donatelli PNAS (2015) 112, 10286–10291 (Theory)





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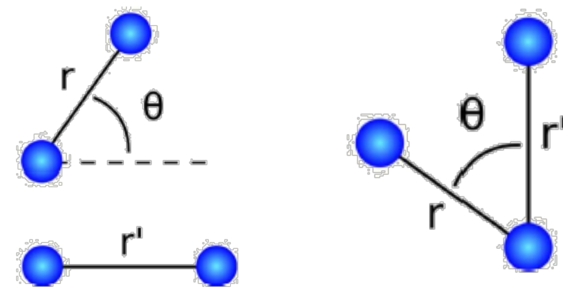
Pair-angle distribution function (PADF)

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

$$C(q,q',\theta) = \int d\phi \, \langle I_\alpha(q,\phi+\theta) I_\alpha(q',\phi) \rangle_\alpha$$

$$\Theta(r,r',\theta) = \tilde{g}^{(2)}(r,r',\theta) + g^{(3)}(r,r',\theta) + g^{(3)}(r,r',\pi-\theta) + g^{(4)}(r,r',\theta)$$



Bulk 3D structure
Assumes sample has no preferred orientation to beam axis

like a "Patterson function" for correlation analysis

Fourier analysis in spherical coordinates

Plane-wave expansion

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \sum_{l=0}^{\infty}(2l+1)i^l j_l(kr)P_l(\widehat{\boldsymbol{k}}\cdot\hat{\boldsymbol{r}})$$

$P_l(x)$ is a Legendre polynomial : $\theta \rightarrow l$

Kam *Macromolecules* (1977) 10, 927

$j_l(x)$ is a spherical Bessel function : $q \rightarrow r$

Lanusse et al. A&A (2012), 540, A92.

Input: $C(q, q', \theta)$

Step 1: $\theta \rightarrow l$

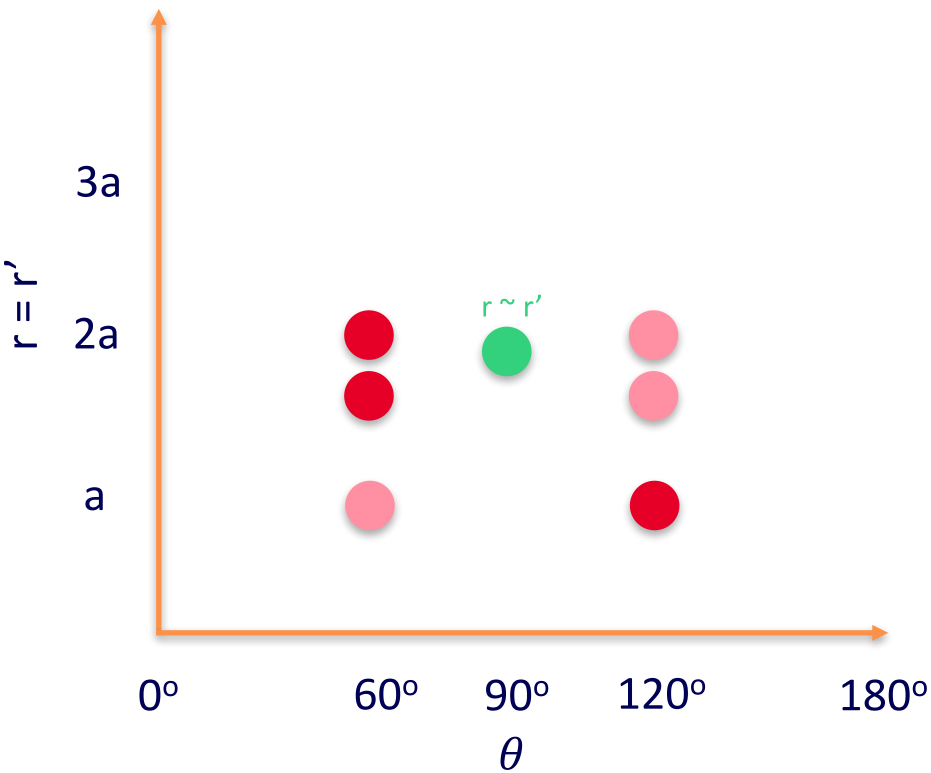
Step 2: $q \rightarrow r$
$q' \rightarrow r'$

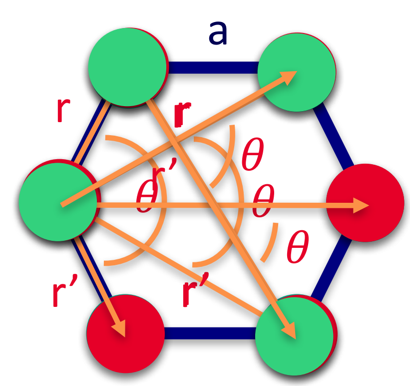
Step 3: $l \rightarrow \theta$

Output: $\Theta(r, r', \theta)$

Visualising 3-body correlations

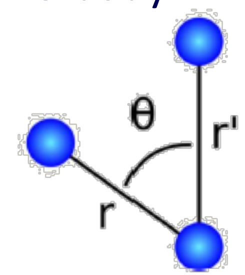
Peak positions in $\Theta(r, r', \theta)$



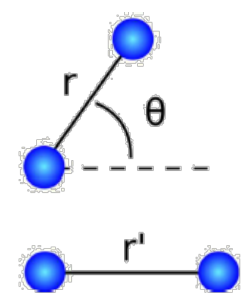


[Note : $\Theta(r, r', \theta)$ symmetry around 90 degrees]

3 body



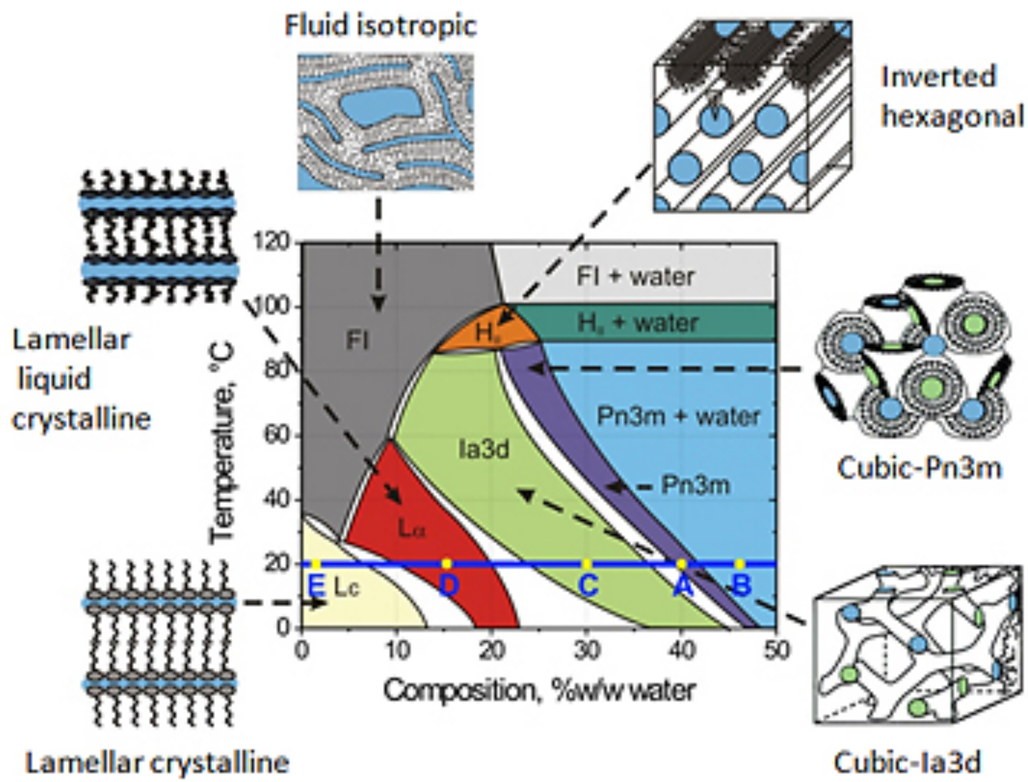
4 body



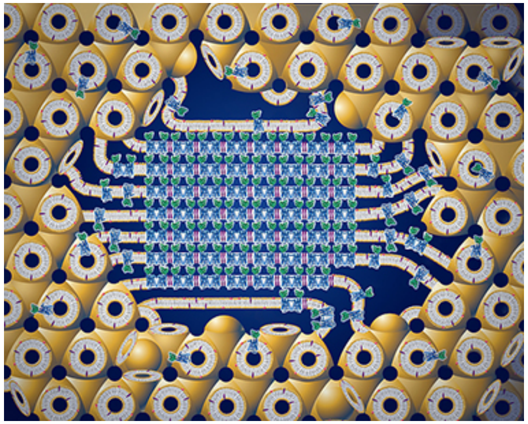
Self-assembled lipid materials

Applications: **drug-delivery, protein crystallization**

Monoolein:Water phase diagram



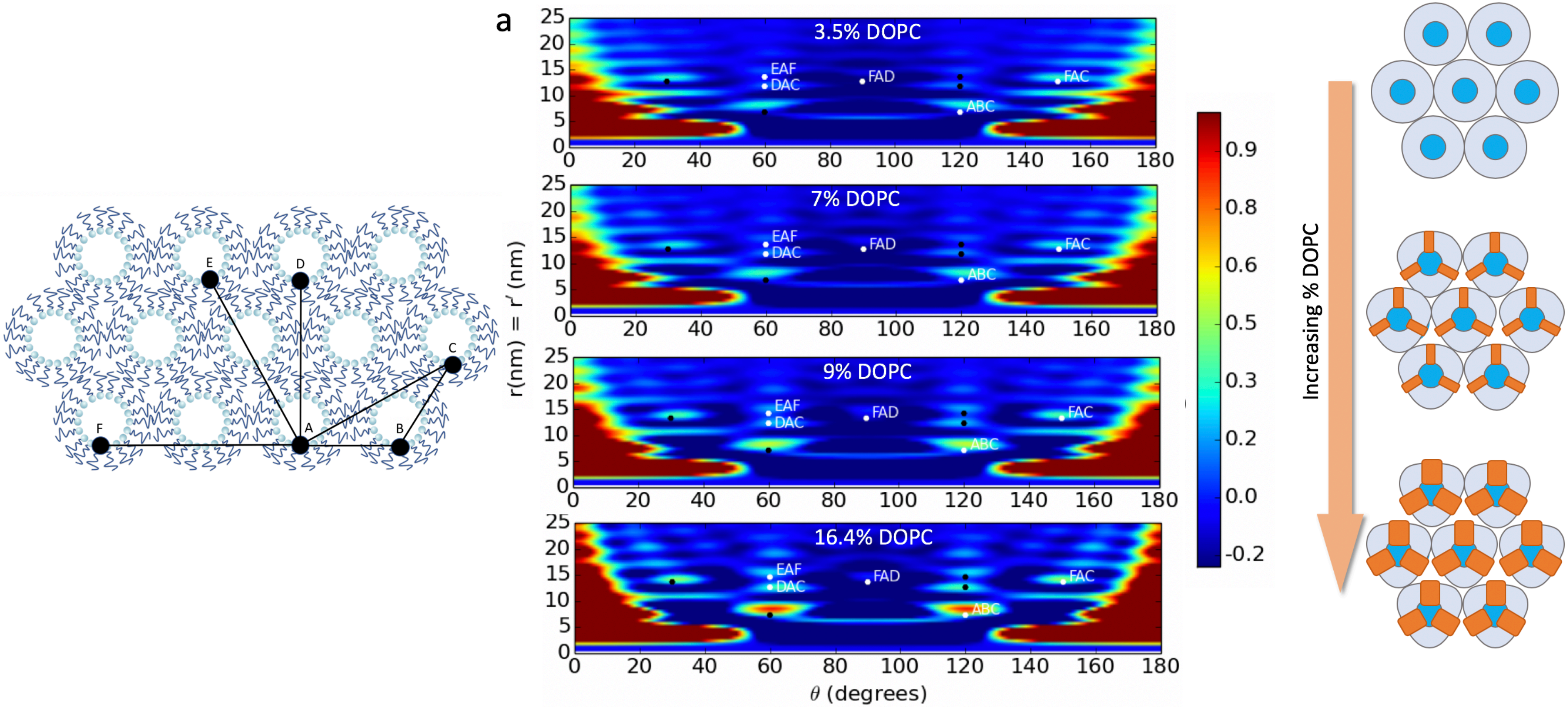
Membrane protein crystallization



http://cherezov.usc.edu/resources.htm

(Dis)order in self-assembled lipid structures

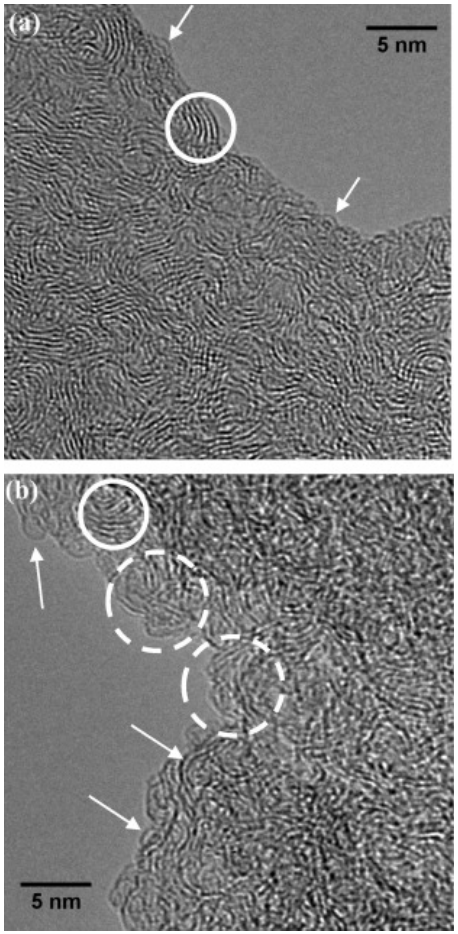
Monoolein:buffer hexagonal phase, doped with DOPC

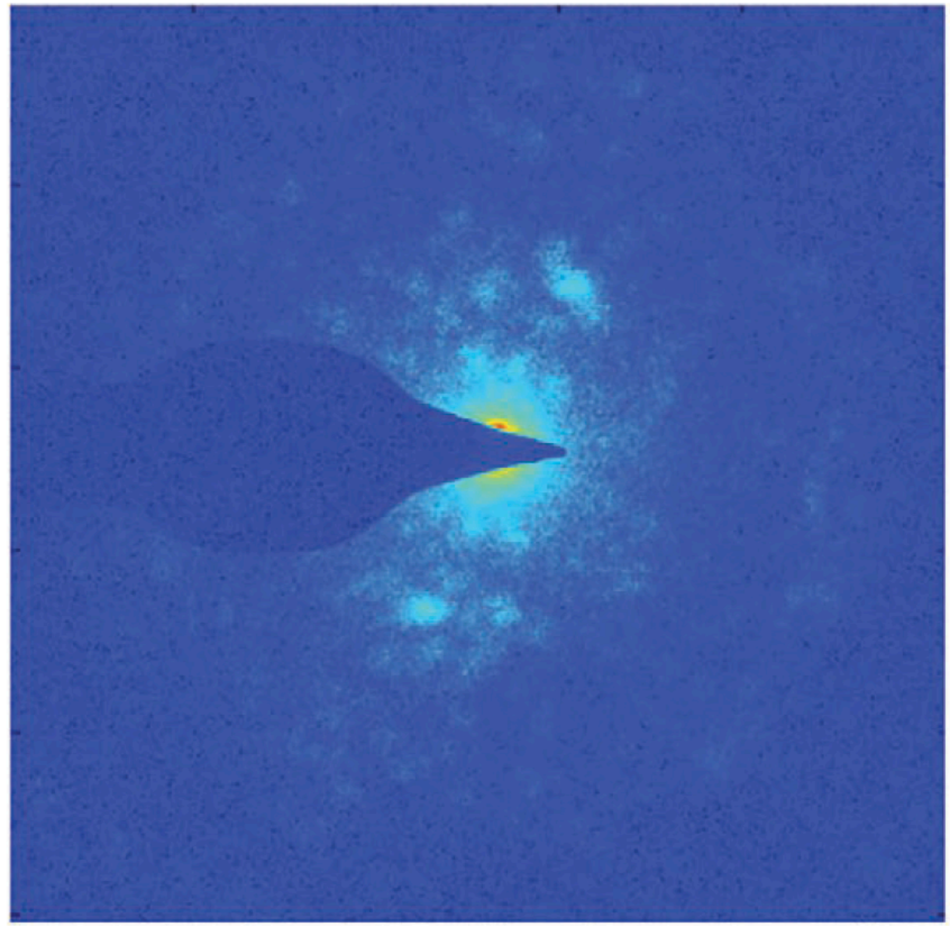


Beamline: SAXS beamline, Australian Synchrotron

Martin et al. *Commun. Materials* 2020, 1, 40.

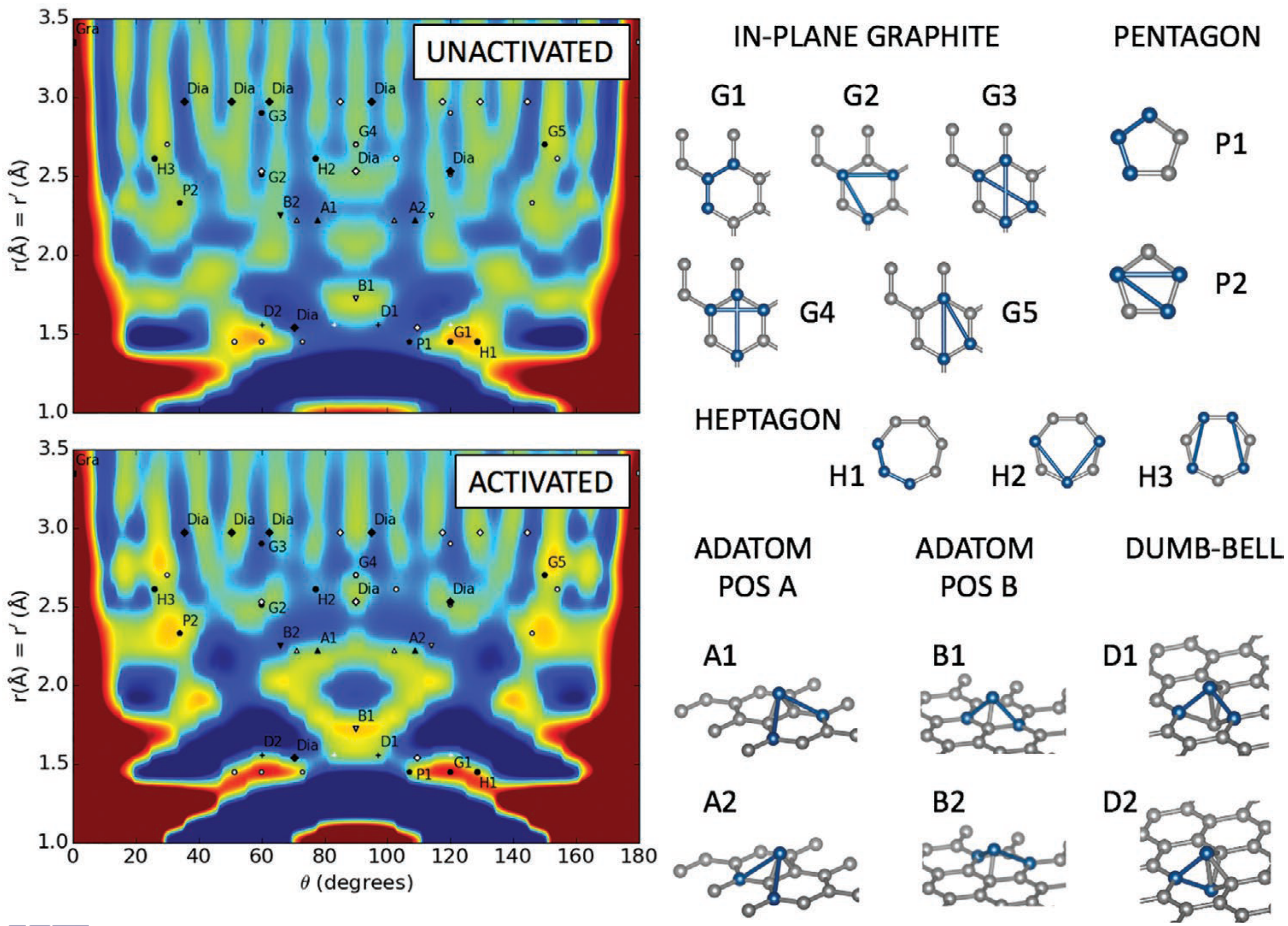
Electron diffraction – activated carbon





PADF of activated carbon

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

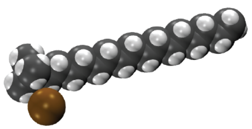


Can you have too many domains in the beam?

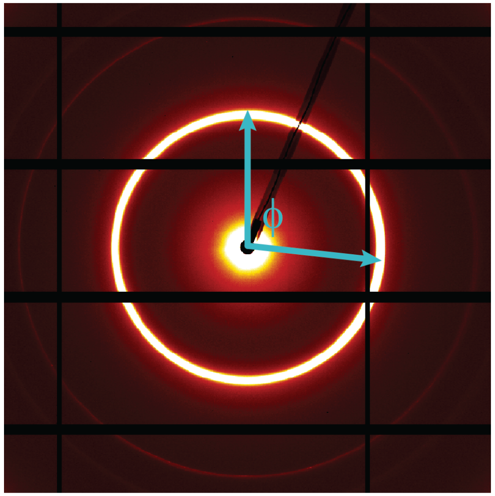
Binns et al. IUCrJ (2022). 9, 231–242

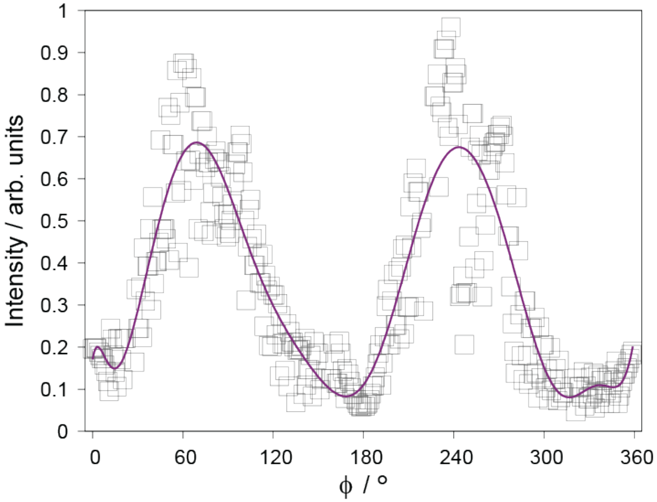
Jack Binns

Yes… the data becomes sensitive to preferred orientation → 'micro-texture analysis'



CTAB:Water
@SAXS beamline





$$R = N\frac{P_{orientation}}{P_{nano}}$$

R>>1 orientation dominates

R<<1 nanostructure dominates

P_x = angular power spectrum
N is the number of crystals per exposure

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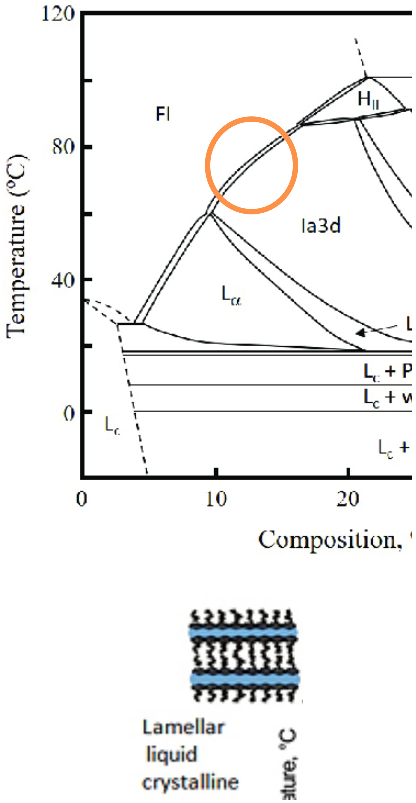
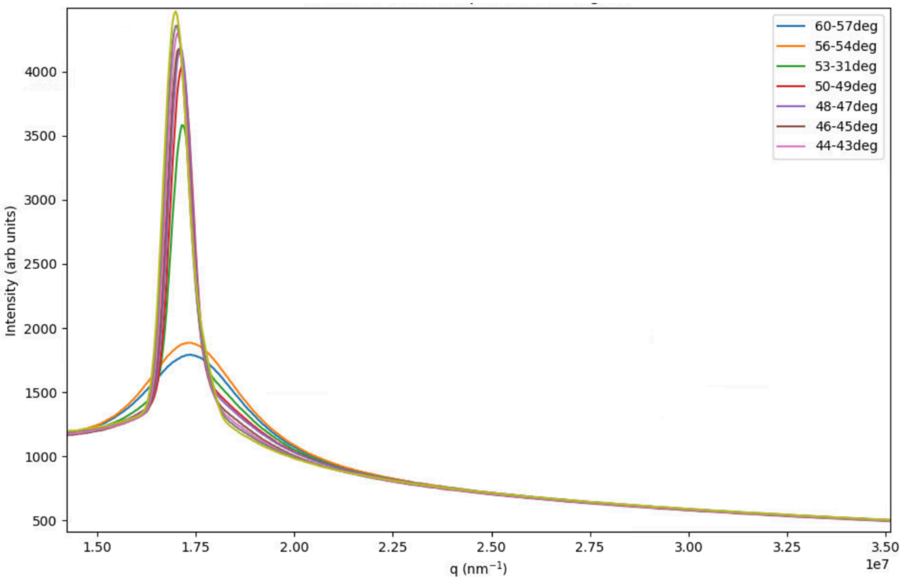
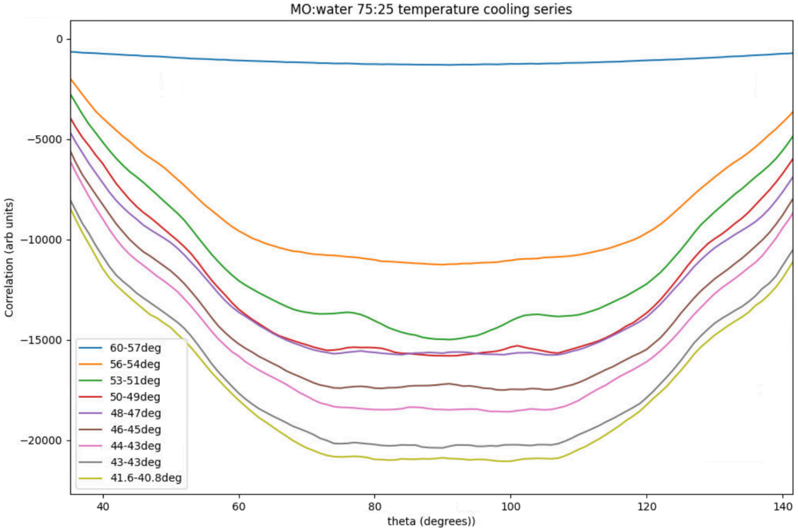
Looking for something that we haven't seen before

Monoolein:water

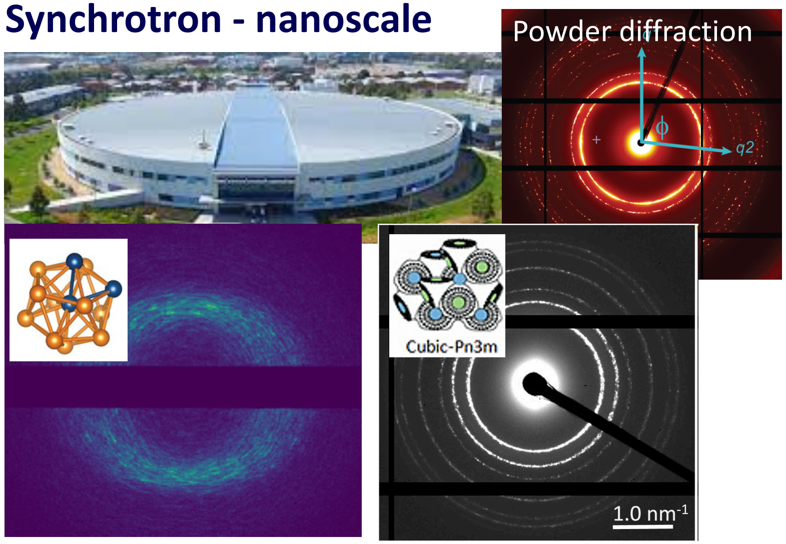






Potential applications

Synchrotron - nanoscale

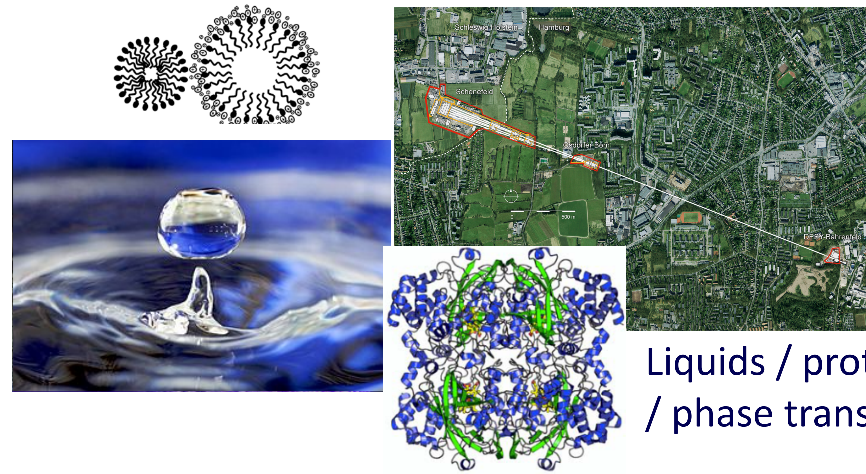


Colloids

Self-assembly

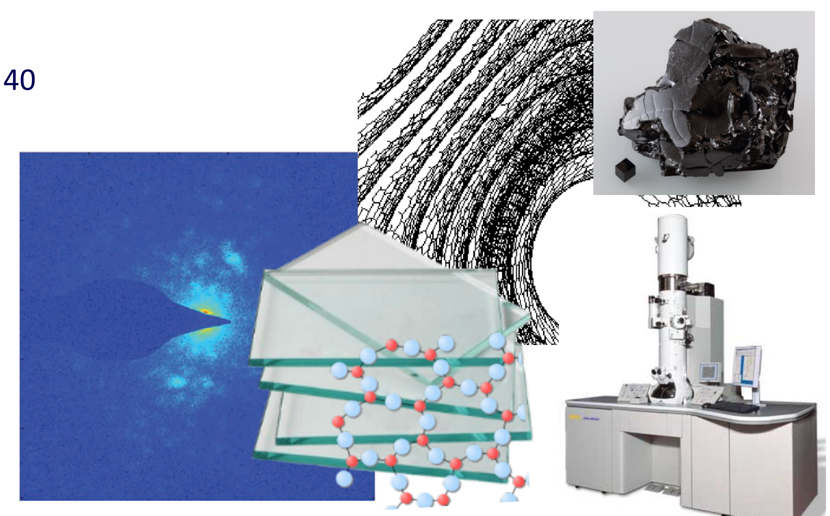
Binns et al. IUCrJ (2022). 9, 231–242
Martin et al. Commun. Mater. (2020) 1, 40

X-ray free-electron lasers



Liquids / proteins / phase transitions

Adams et al. *Crystals* 2020, 10, 724



Amorphous solids / glasses

Electron Microscopy - Atomic scale

Bojesen et al. *J. Phys. Mater.* 3 (2020) 044002

Thank you for listening!

Fourier analysis in spherical coordinates

Plane-wave expansion

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(kr) P_l(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{r}})$$

$P_l(x)$ is a Legendre polynomial : $\theta \rightarrow l$

Kam *Macromolecules* (1977) 10, 927

$j_l(x)$ is a spherical Bessel function : $q \rightarrow r$

Lanusse et al. A&A (2012), 540, A92.

Input:	$C(q, q', \theta)$
Step 1:	$\theta \rightarrow l$
Step 2:	$q \rightarrow r$ $q' \rightarrow r'$
Step 3:	$l \rightarrow \theta$
Output:	$\Theta(r, r', \theta)$

Why scattering?

Require wavelength smaller than the structure → X-rays, electrons, Neutrons

X-rays & Neutrons	**weakly interacting**	**single scattering**
Electrons	strongly interacting	multiple scattering

Often its not possible to form a direct 3D image of the structure at these length scales.

Instead, characterize structure with diffraction.