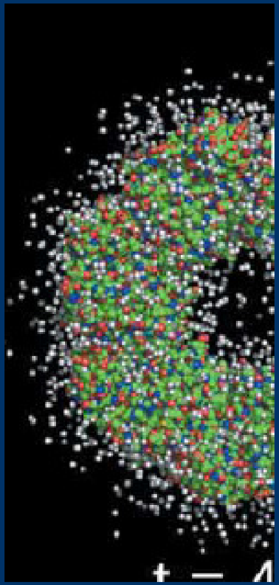
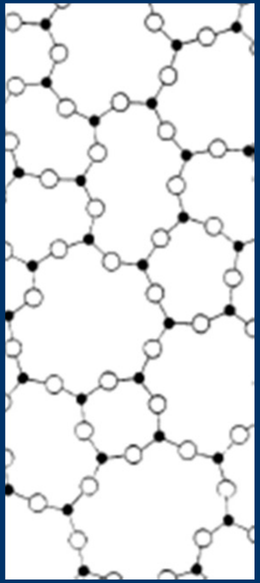




THE UNIVERSITY OF MELBOURNE

Real-space local 3D structure of disordered matter from fluctuation diffraction

CENTRE FOR ADVANCED MOLECULAR IMAGING
AN ARC CENTRE OF EXCELLENCE

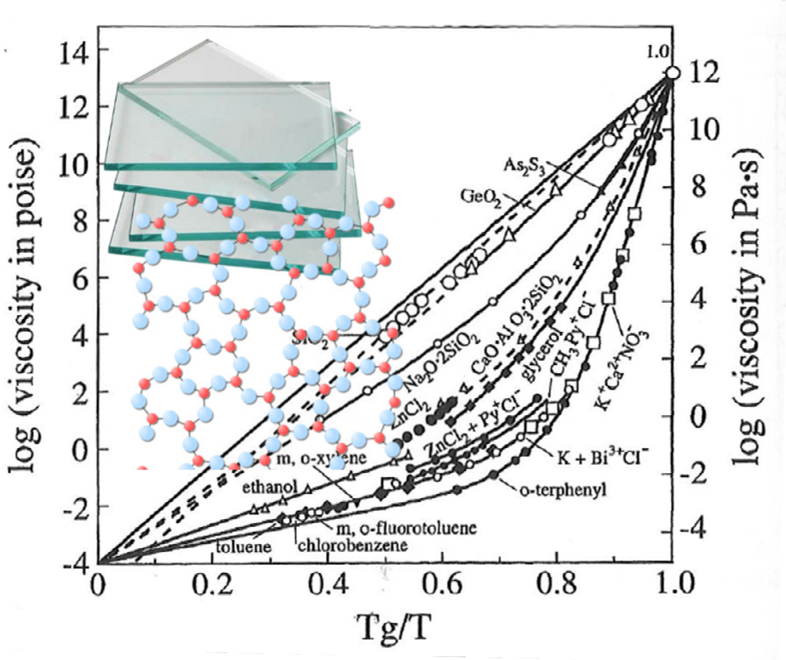
Dr. Andrew V. Martin

Outline

- Background: disordered matter and pair-distribution analysis
- Extracting real-space angular distributions from diffraction data of disordered matter
- Early experimental results

We live in a disordered world!

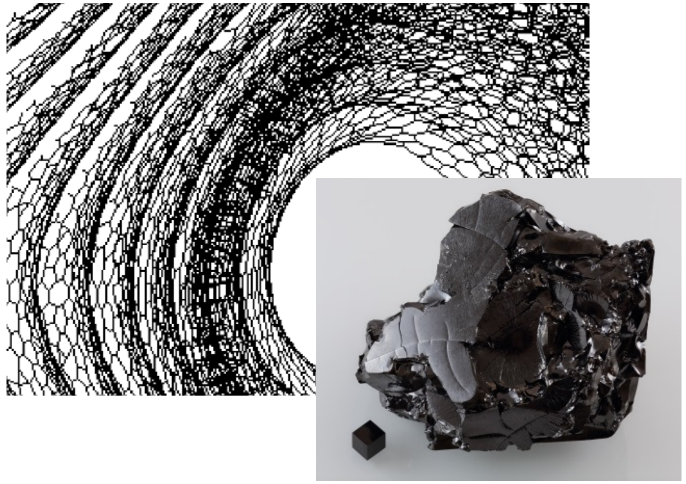
Mystery of the glass transition



Metallic glass

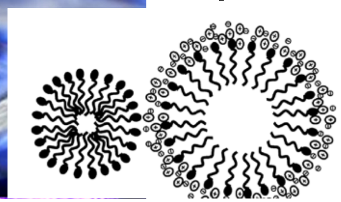
Amorphous Materials

Glassy carbon (High T crucibles; electrochemistry)



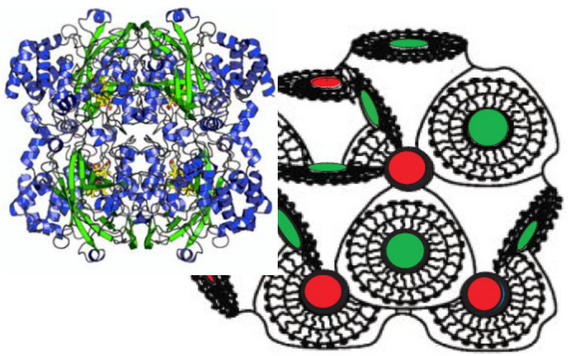
Liquids

Ionic Liquids

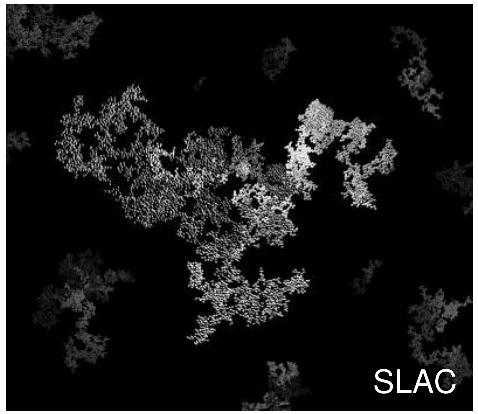


Lipidic membrane materials /Proteins

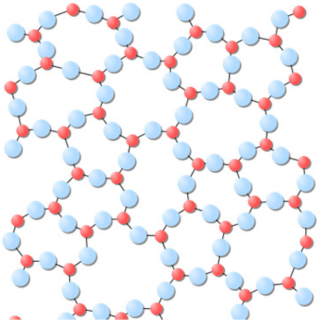
Cubic – Pn3m

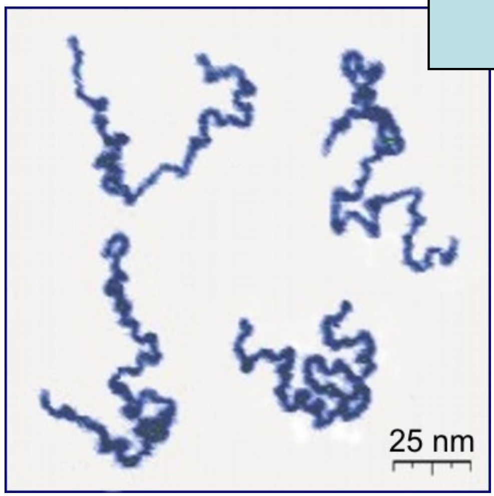


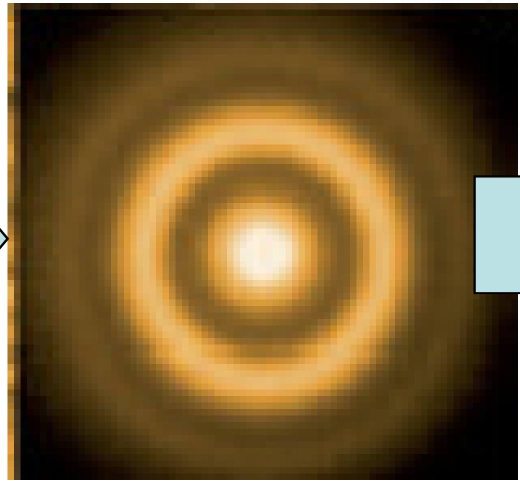
Airborne particles (soot)
(pollution/respiratory health)

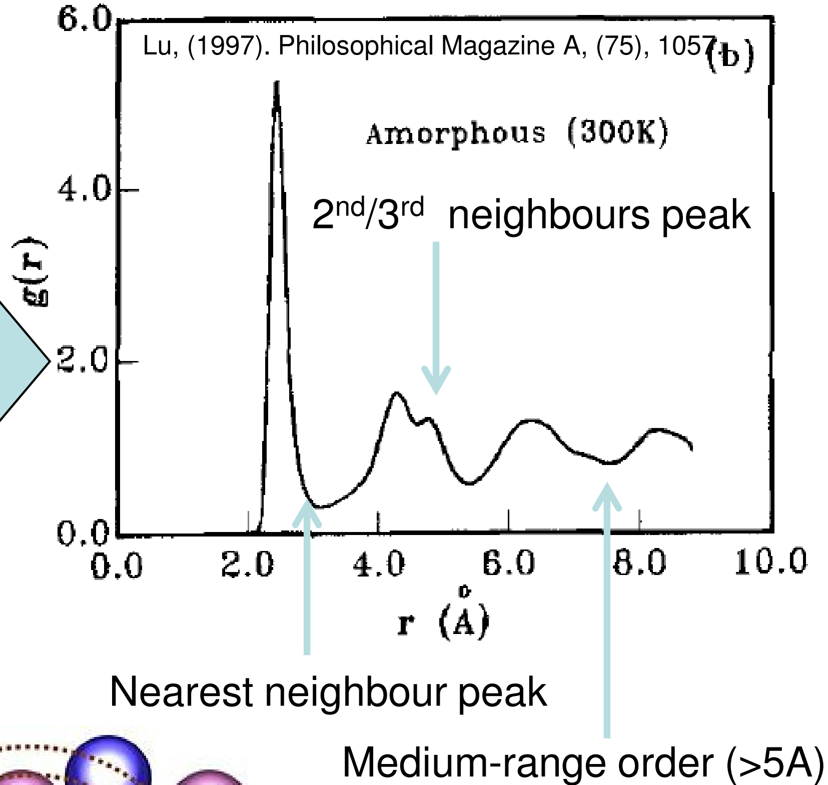


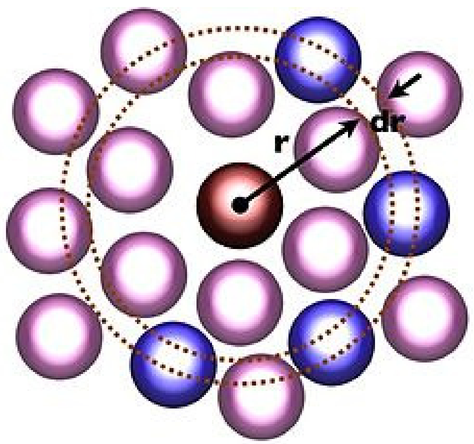
SAXS and the Pair-distribution function [g(r)]







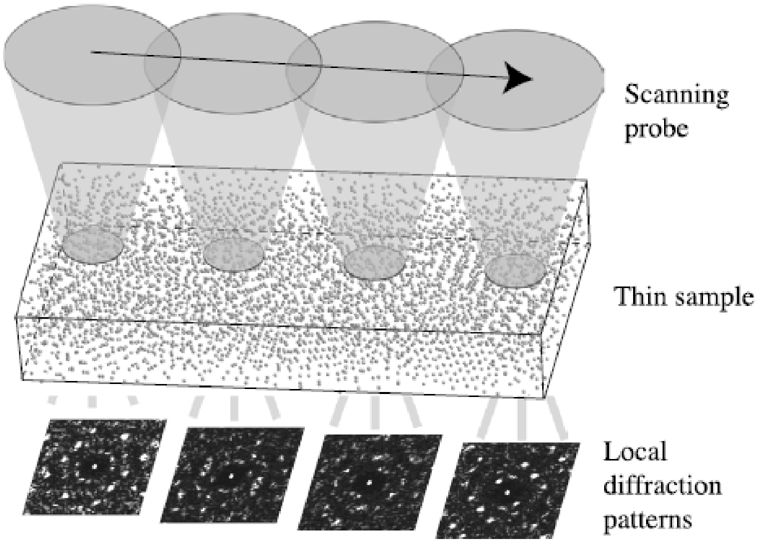




No information about local orientation!

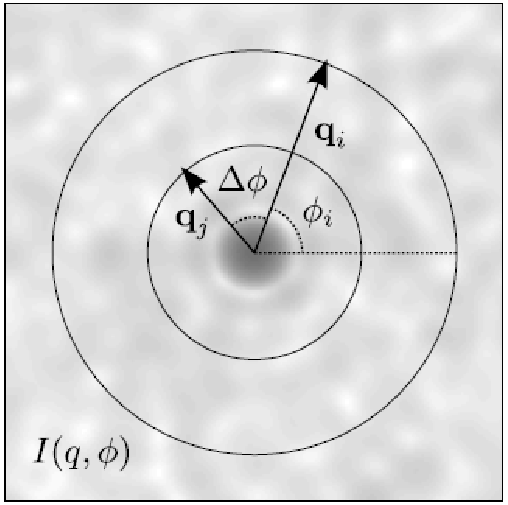
Fluctuation diffraction

Electrons

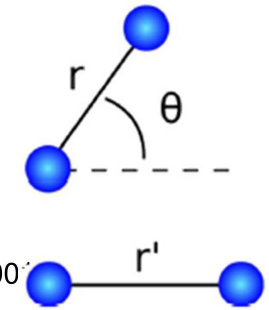


Treacy *Rep. Prog. Phys.* 68 (2005) 2899

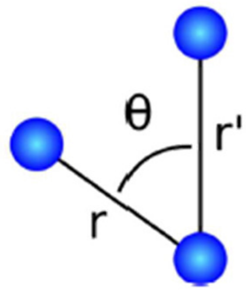
X-rays

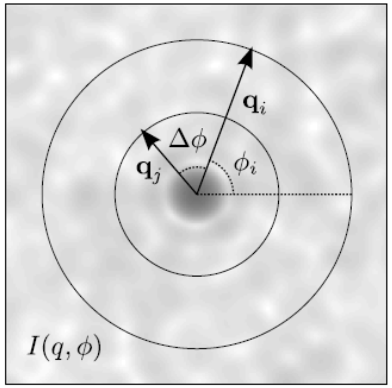


Kirian J. Phys. B: At. Mol. Opt. Phys. 45 (2012) 22300



- In principle, sensitive to third and fourth order correlations: $g^{(3)}$, $g^{(4)}$.
- In practice, theory has been missing to directly obtain these functions.





$$\langle I(\mathbf{q})I(\mathbf{q}')\rangle$$

Intensity correlation between two points

Spherical harmonic analysis

Kam, *Macromolecules*, 10, 927 (1977)
(more recently Saldin, Kirian, Kurta, Spence and more)

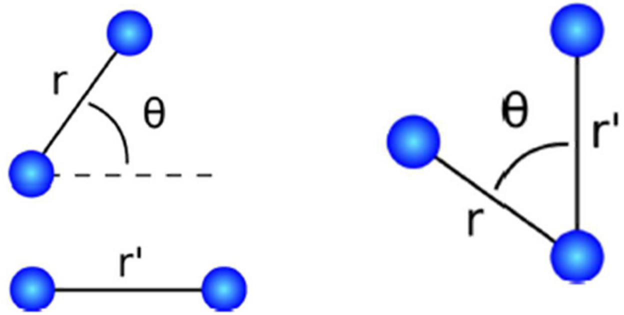
$$B_l(q_i,q_j)=\sum_{m=-l}^{l} I_{lm}(q_i)I^*_{lm}(q_j)$$

q-space density matrices
(Assume even sampling of local 3D orientation)

Mapping into real space
A.V.Martin, IUCrJ, 4, 24 (2017)

Real-space correlation functions

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



Three linear steps

Step 1 - obtain $B_l(q, q')$ by numerical inversion

$$\int d\theta \langle I(q,\theta) I(q', \theta + \Delta\theta) \rangle = \sum_l \frac{1}{4\pi} P_l \left(\frac{\boldsymbol{q} \cdot \boldsymbol{q}'}{|\boldsymbol{q}||\boldsymbol{q}'|} \right) B_l(q, q')$$

- P_l : Legendre polynomials

Step 2 – transform to real space with a spherical Bessel transform

$$S_{q'r'}\left[S_{qr}[B_l(q, q')]\right] = B_l(r, r')$$

$$\hat{S}_{qr}[f(q)] = 4\pi \int_0^{q_{\max}} f(q) j_l(2\pi q r) q^2 \mathrm{d}q$$

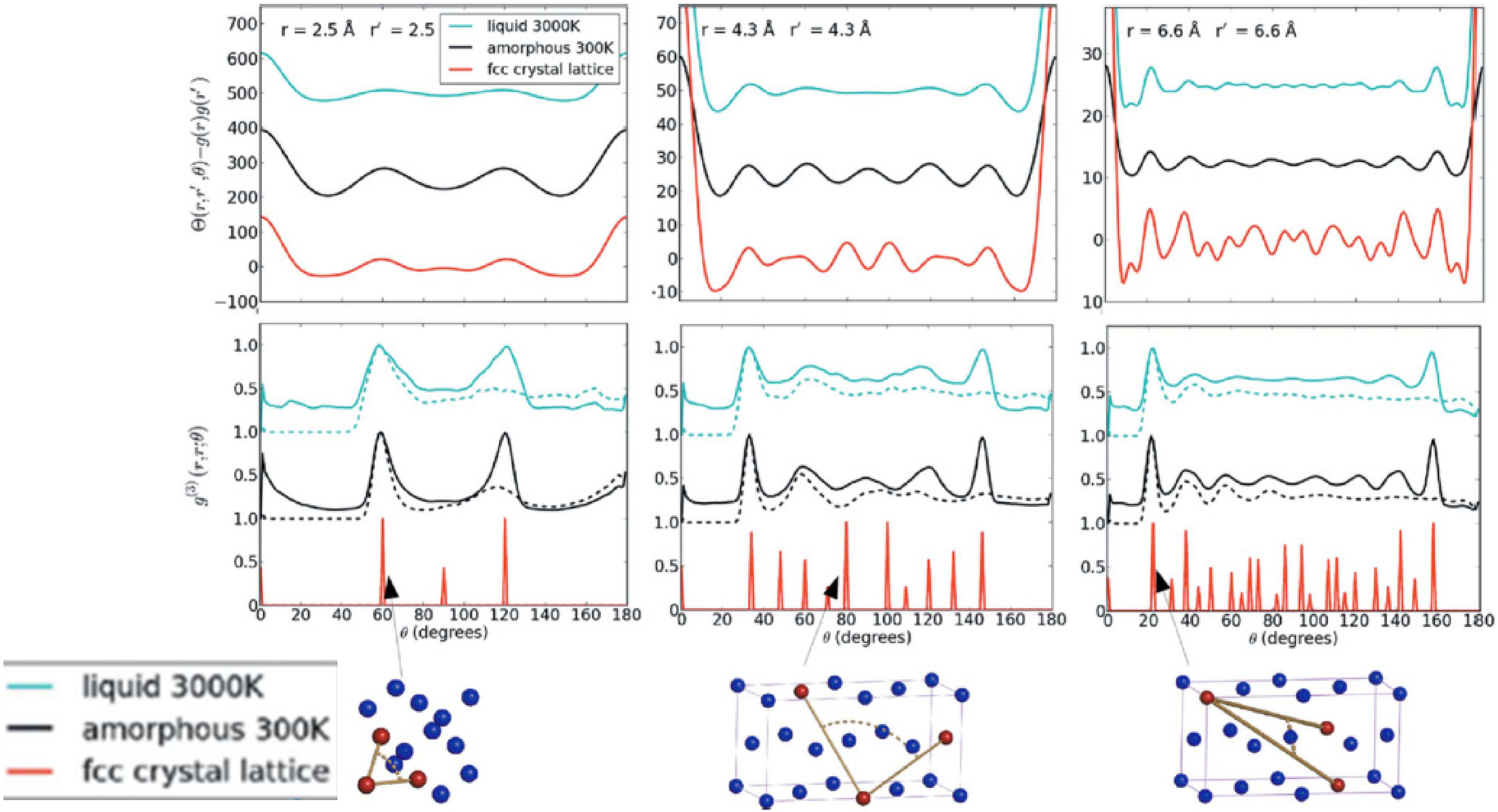
Step 3 – recover angular dependence

$$\Theta(r, r', \theta) \equiv 2\pi N_a \sum_l P_l(\cos\theta) \langle B_l^\alpha(r, r') \rangle_\alpha$$

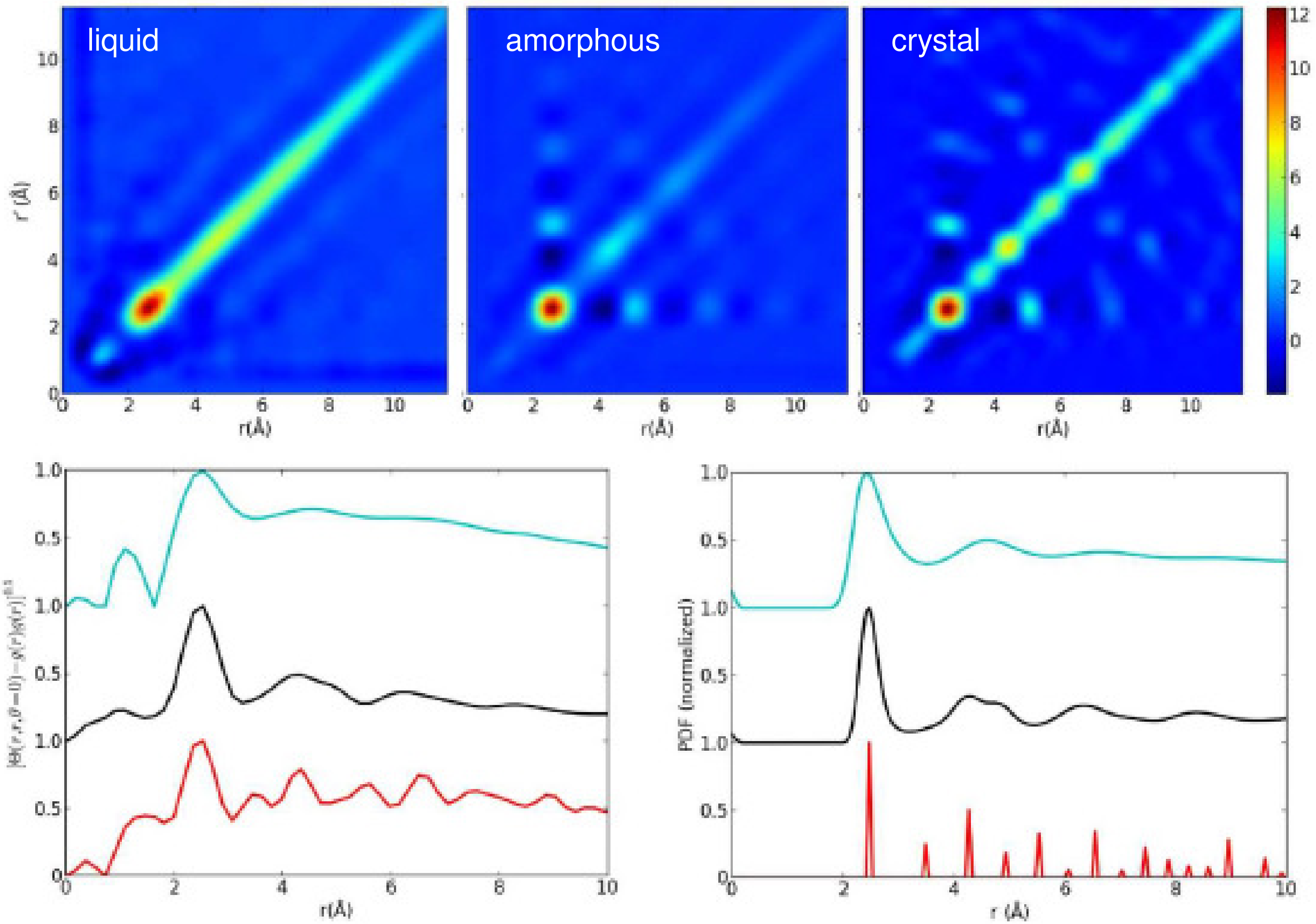
$$= \int \int N_a \langle g^\alpha(\mathbf{r}) g^\alpha(\mathbf{r}') \rangle_\alpha \delta\left(\cos\theta - \frac{\mathbf{r} \cdot \mathbf{r}'}{|\mathbf{r}||\mathbf{r}'|} \right) \mathrm{d}\Omega_r \mathrm{d}\Omega_{r'},$$

Molecular dynamics : Nickel

Nearest neighbour **Higher coordination shells**



Radial correlations

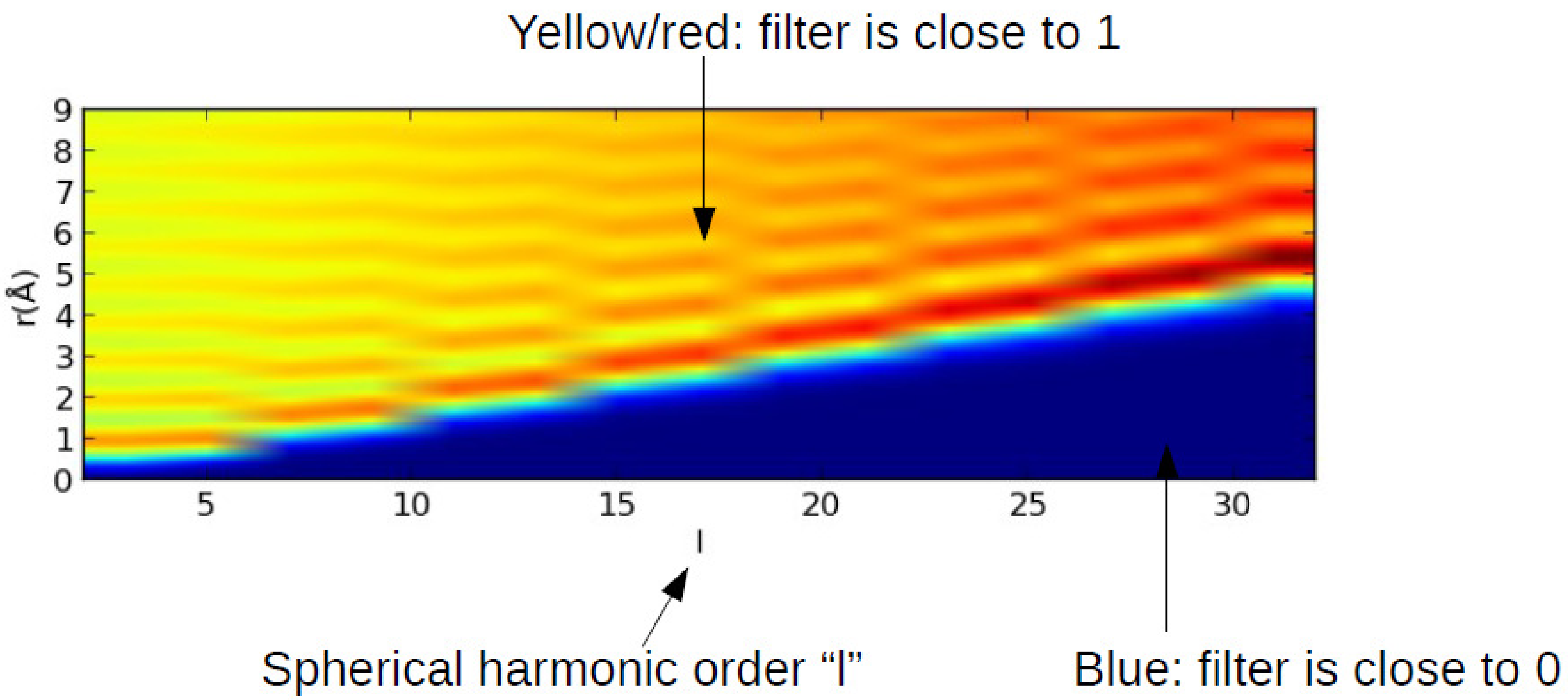


Two-body fluctuation term **Pair-distribution**

Angular and radial resolution are coupled

<u>Resolution filter</u>

At the highest radial resolution, angular resolution is poor.



Prediction of experimental noise

Sources of noise: shot-noise, diffraction from uncorrelated atoms, background scattering.

$$N_\alpha \propto A^2 N_{ph}^{-2} \bar{f}^{-4}$$

# of patterns required

Beam Area

# of incident photons (electrons)

Mean atomic scattering factor

X-ray free-electron lasers

XFEL pulses are generated by positive feedback between an electron beam and spontaneously emitted undulator radiation.

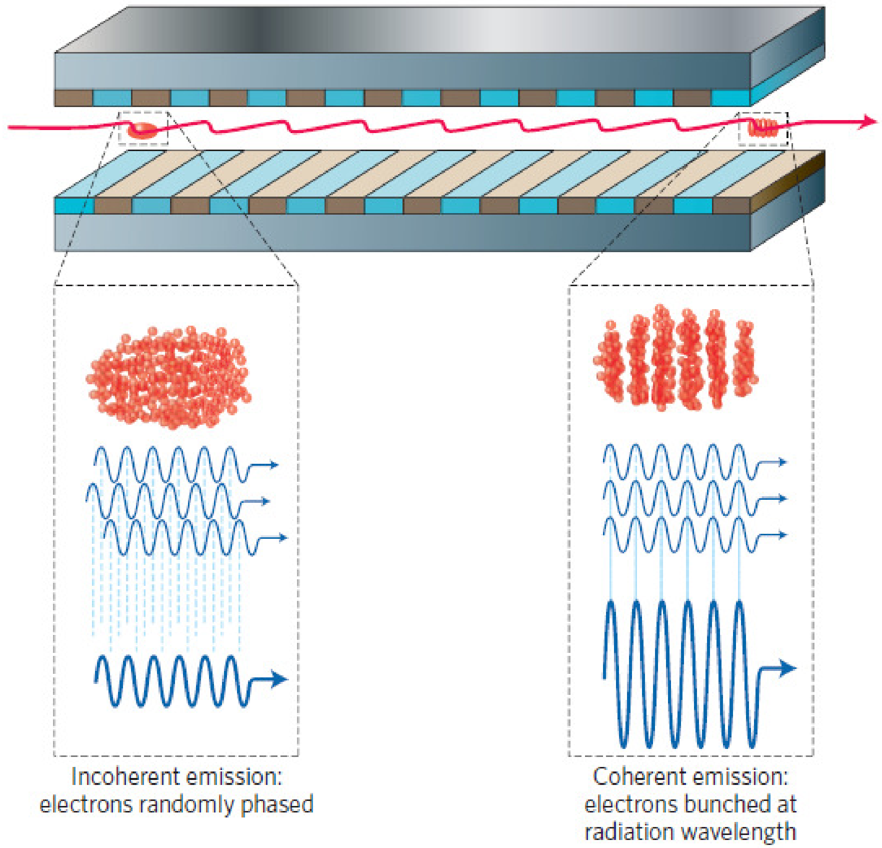
Highly intense: up to **10^{20} W cm^{-2}**

Ultrafast: **5 – 100 fs** pulse duration

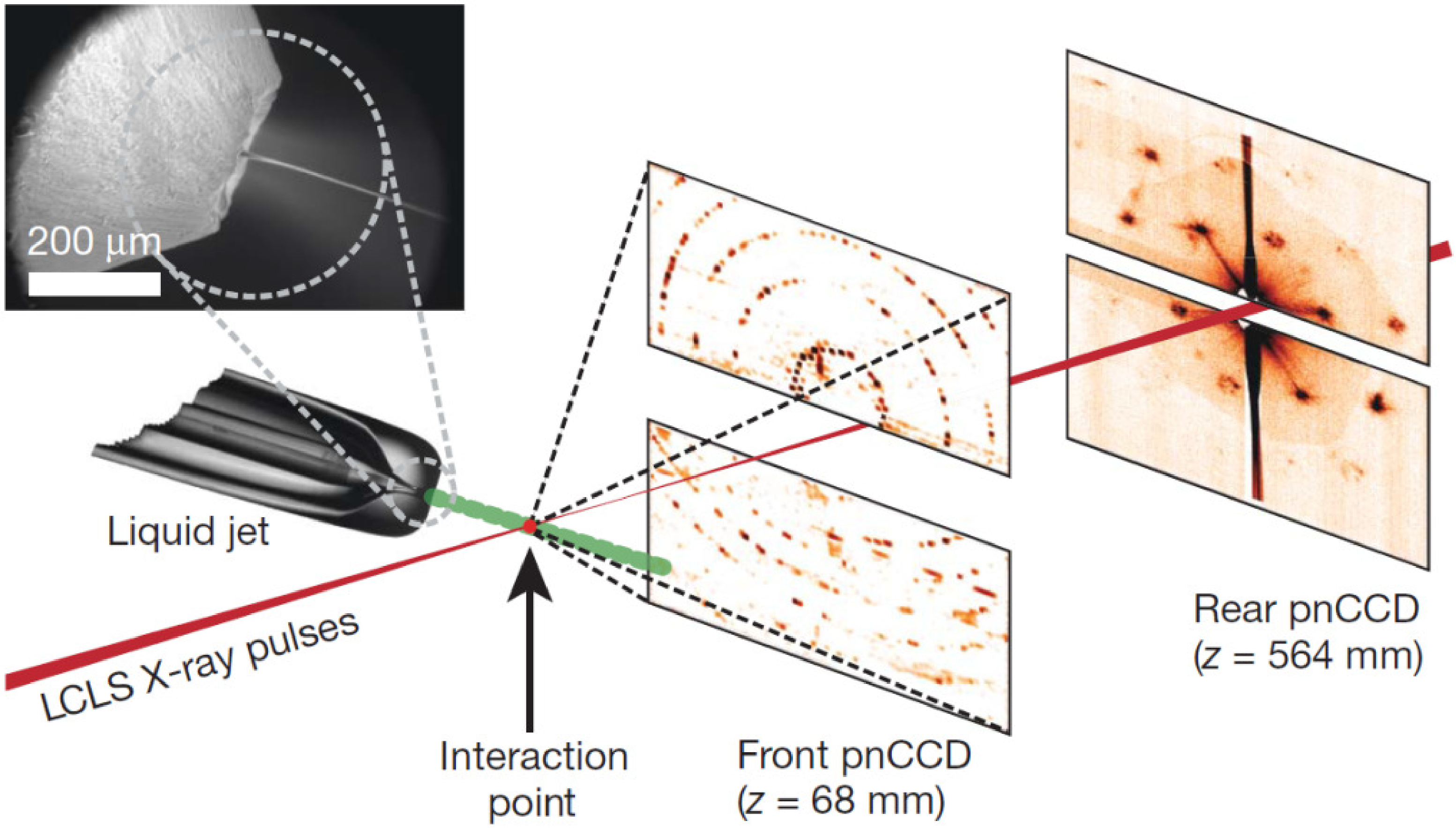
High resolution: **0.1 nm – 40 nm** wavelength

Highly coherent

High repetition rates: up to **100 Hz - 27000Hz**



Serial XFEL data collection



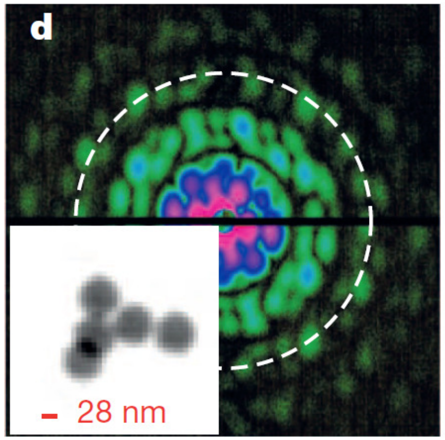
Sample is destroyed

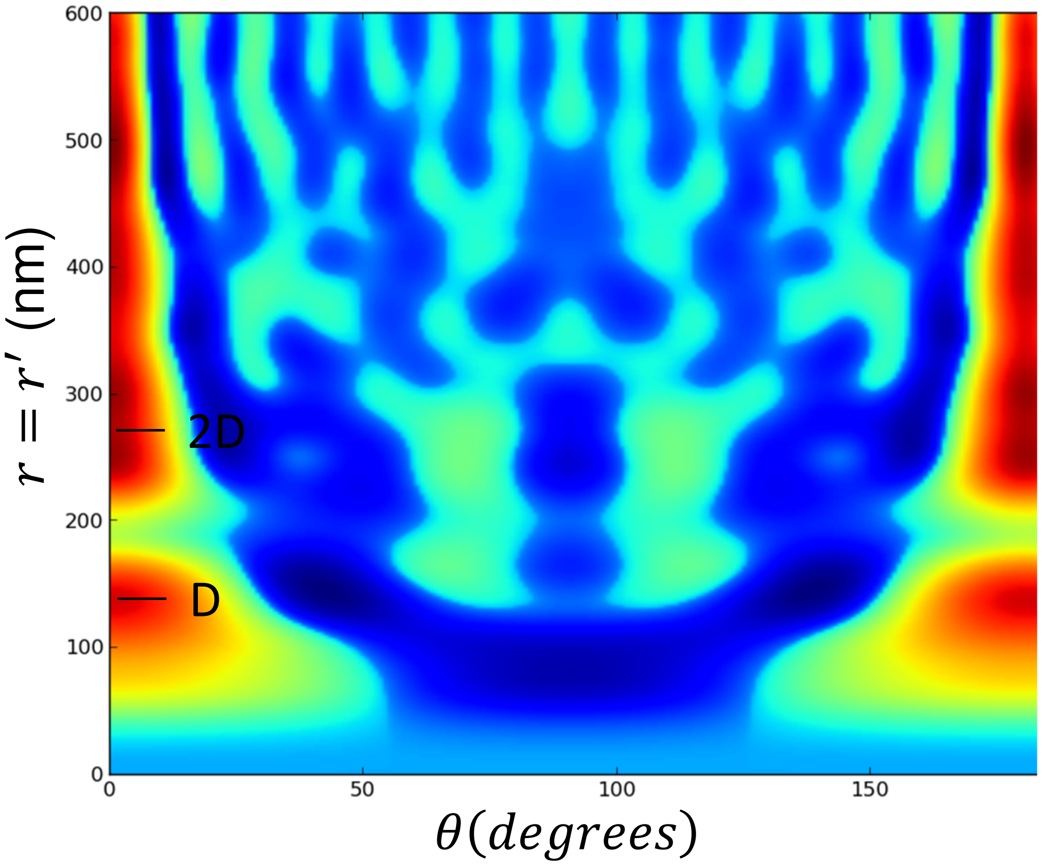
Serial injection of particles (>10^6)

Sample orientation unknown

Chapman, et al. *Nature* **470**, 73 (2011)

Nano sphere clusters measured at LCLS





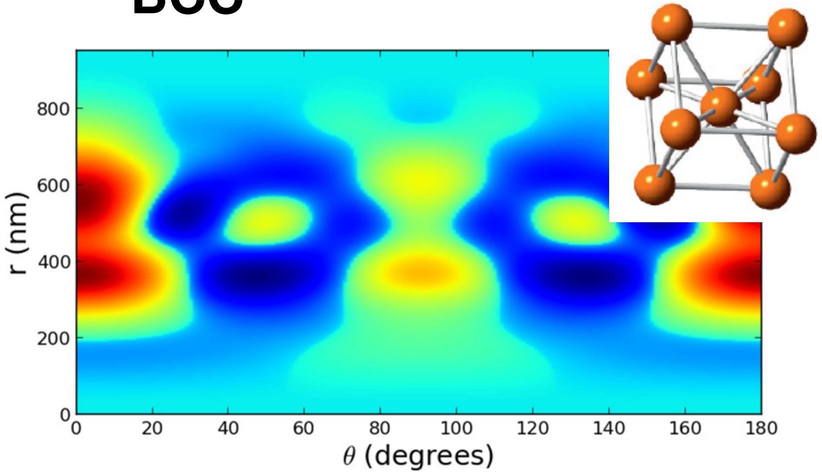
Striping indicates insufficient angular bandwidth or noise

Data from Loh et al. Nature (2012) 486, 513.

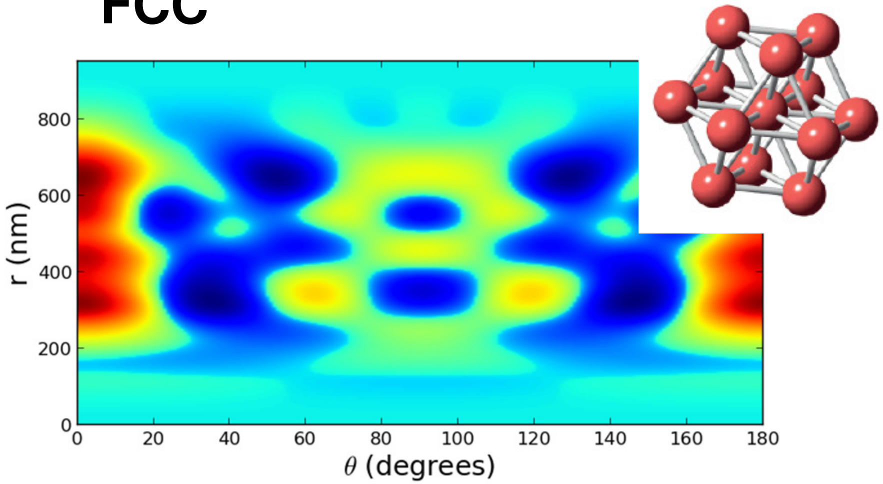
(D = diameter)

Simulated sphere clusters

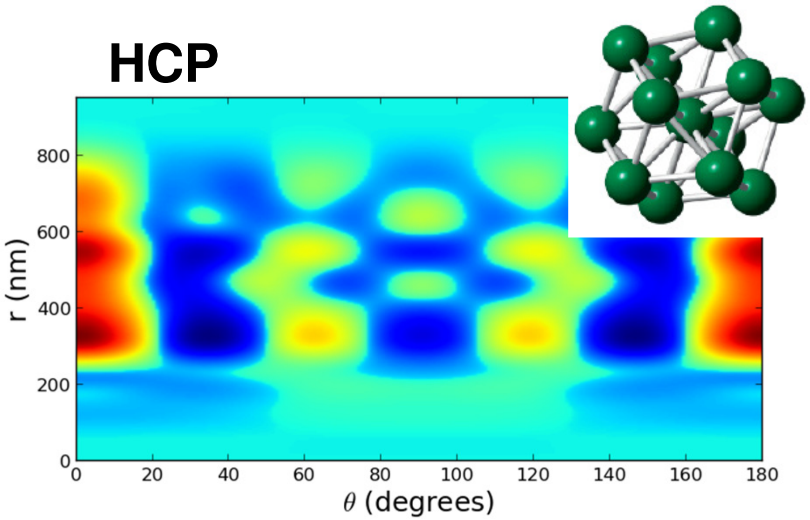
BCC



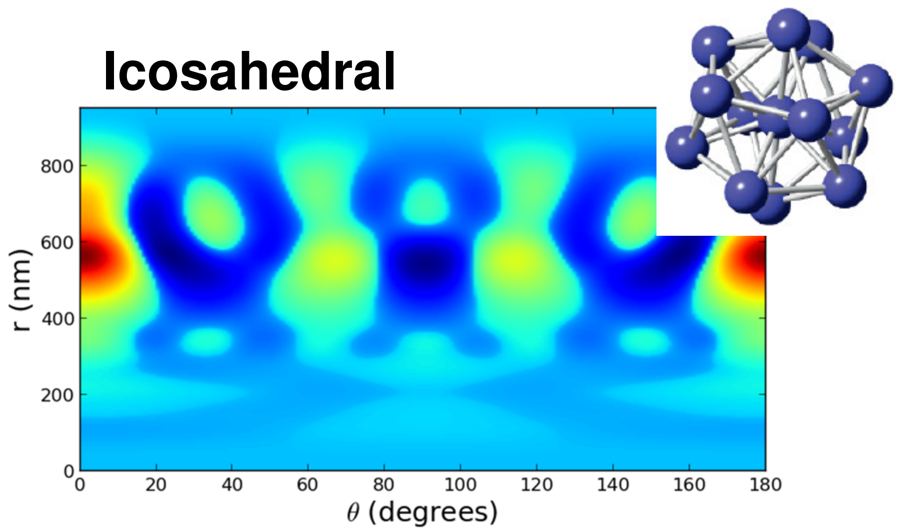
FCC



HCP

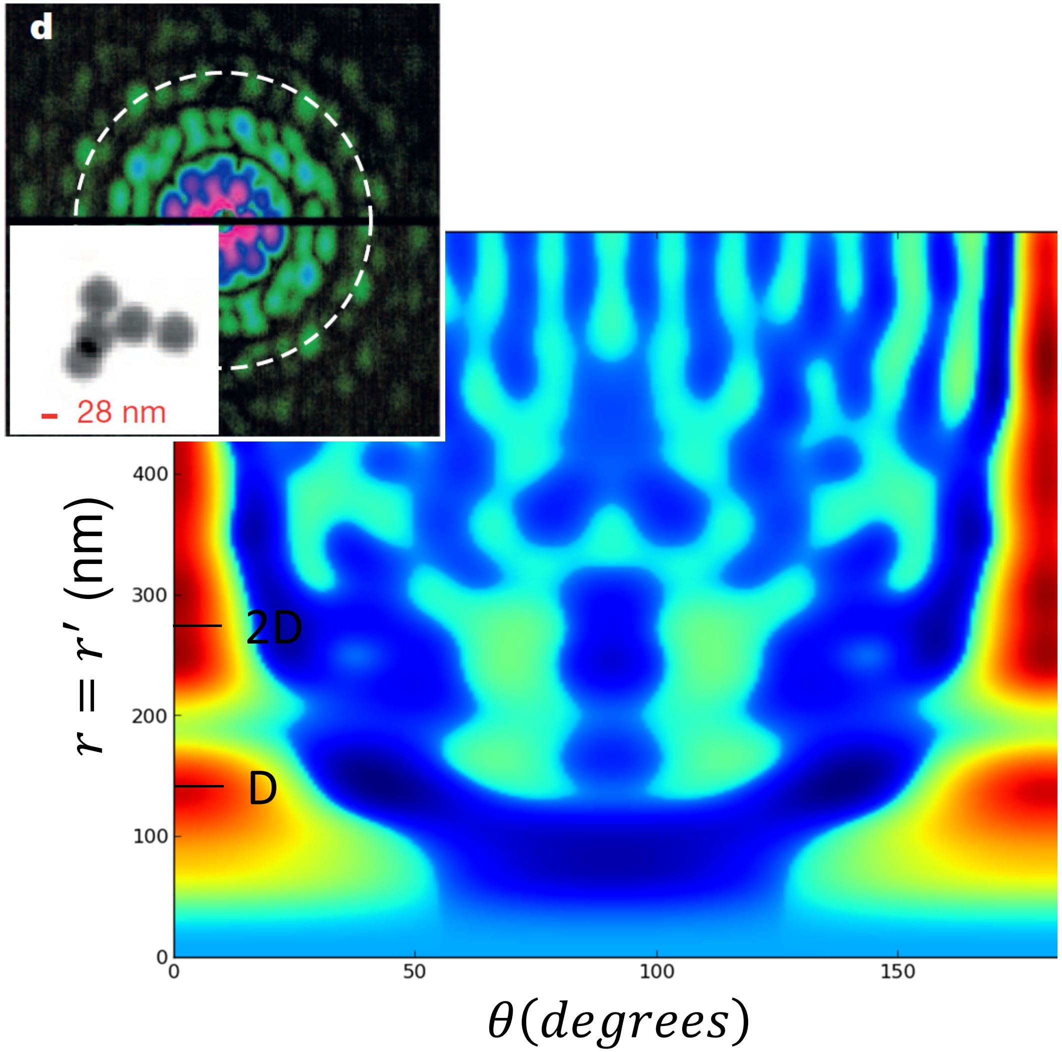


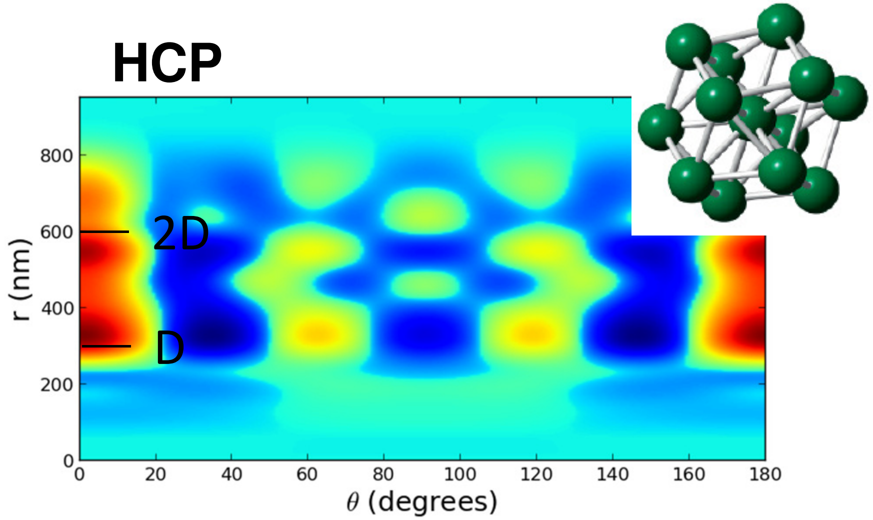
Icosahedral

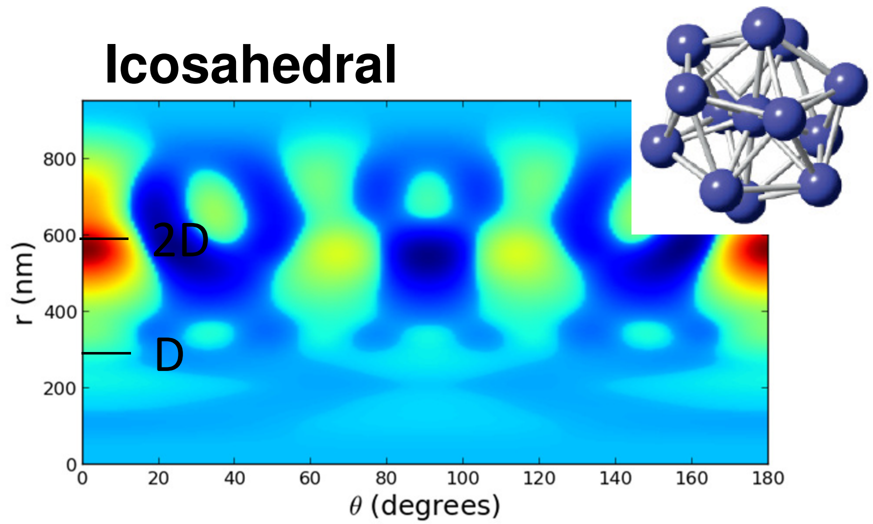


Nano sphere clusters measured at LCLS

Data from Loh et al. Nature (2012) 486, 513.

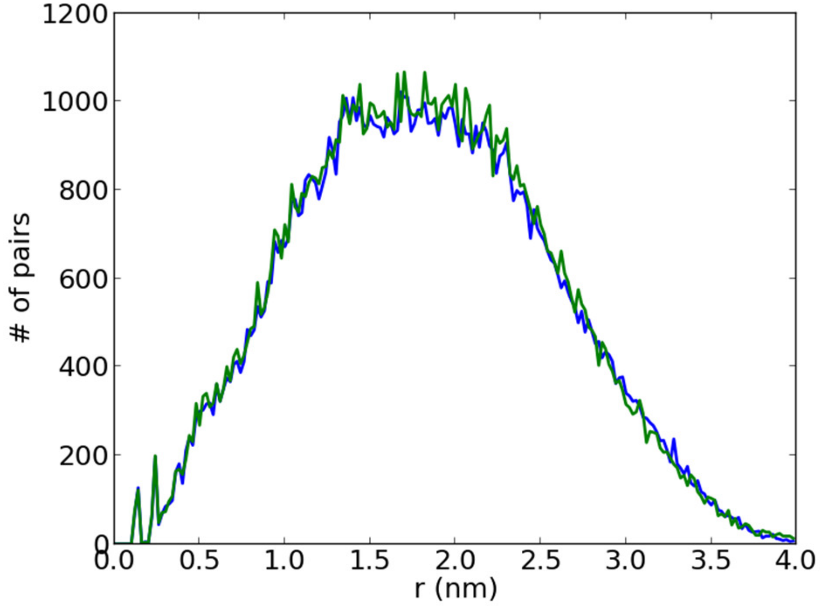




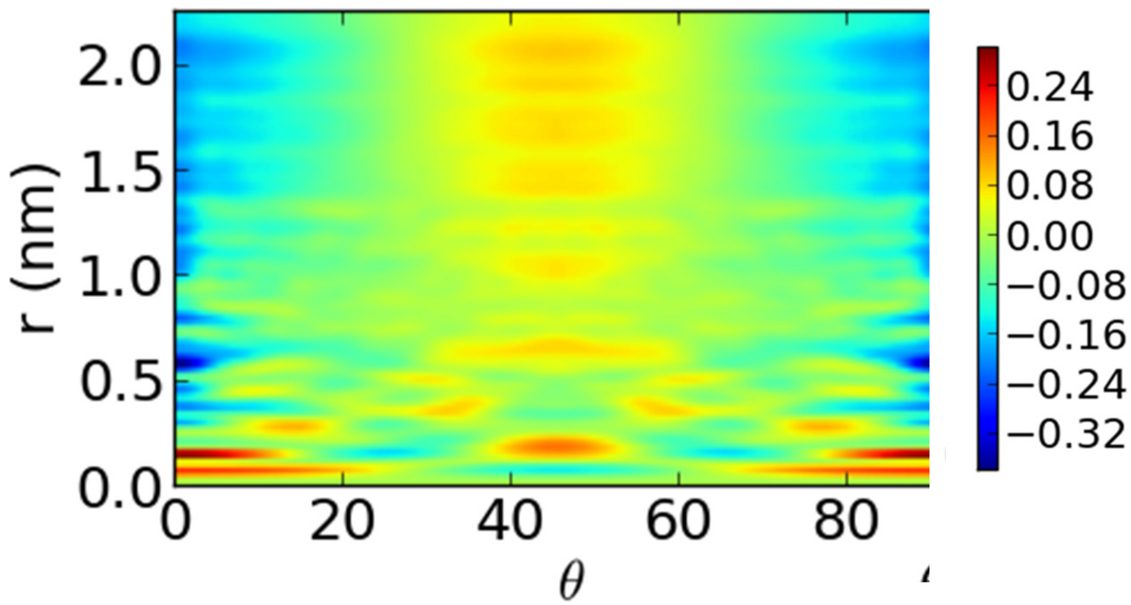


Angular Small/Wide angle x-ray scattering of proteins

Pair distribution



Angular difference plot



Turkey (1LJN) vs Hen (1vds) Lysozyme differ by a few residues

Angular SAXS of proteins

Full protein structure : >10^{13} photons @ LCLS; 10:1 water:protein (Kirian et al.)
Not currently feasible (?)

Angular SAXS: >10^{10} photons

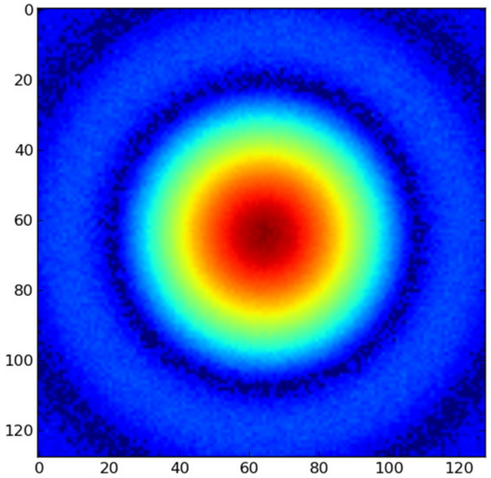
Currently feasible with an XFEL

10:1 H_2O:GroEL

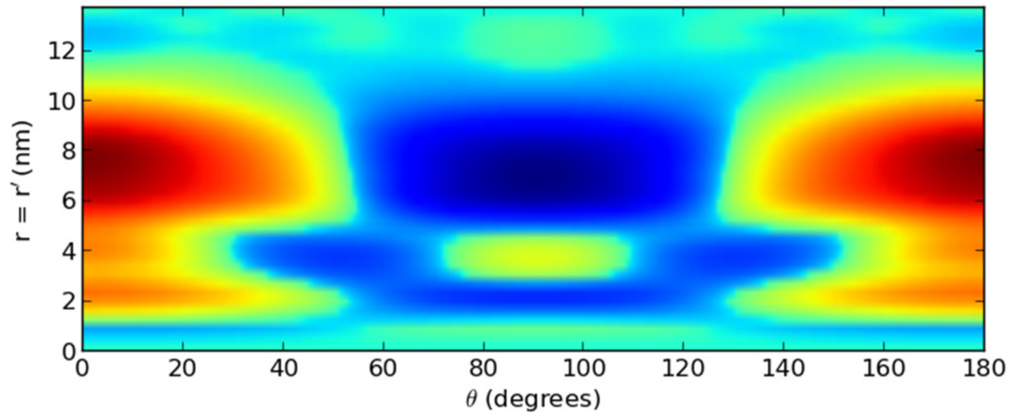
10k protein molecules

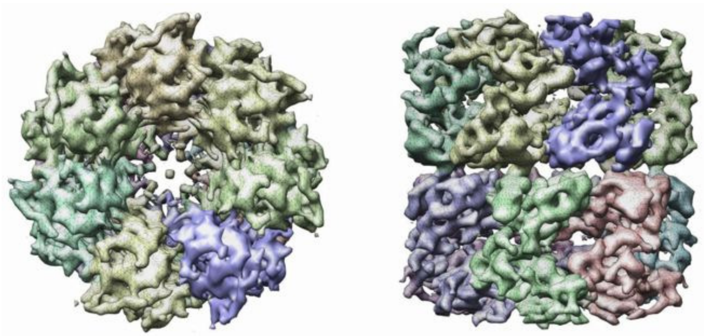
10^{10} photons

Beam width: 100 nm



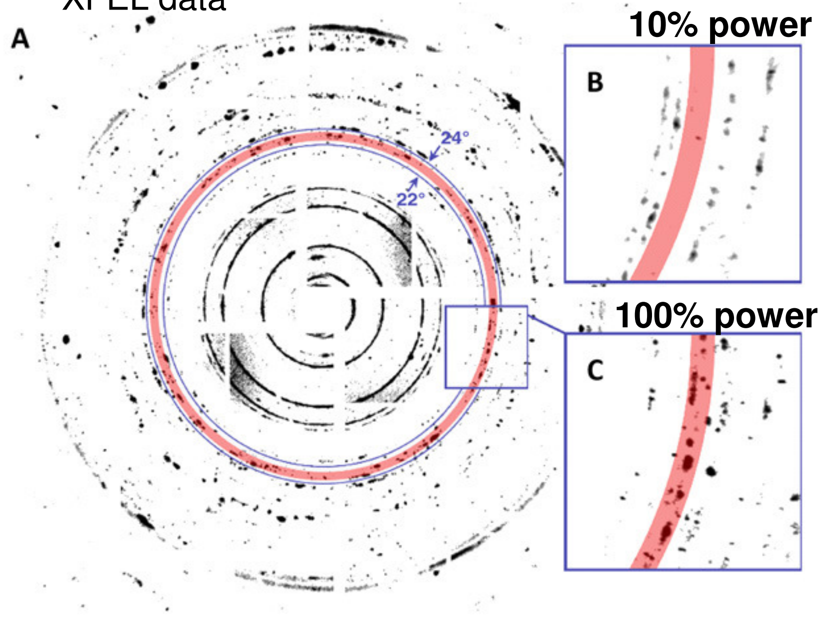
$l_{max} = 12$

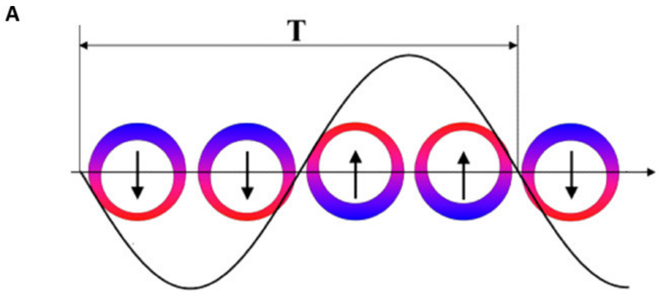


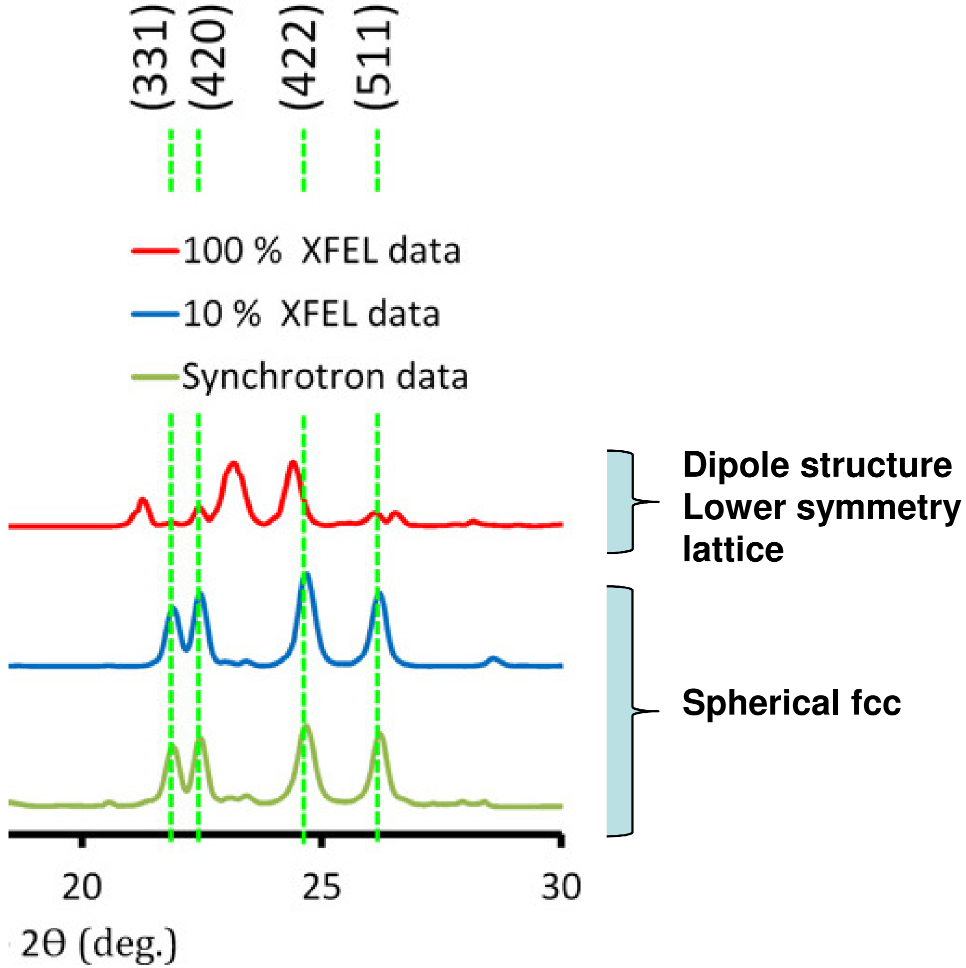


Transient electronic structure in C_{60} crystals

XFEL data



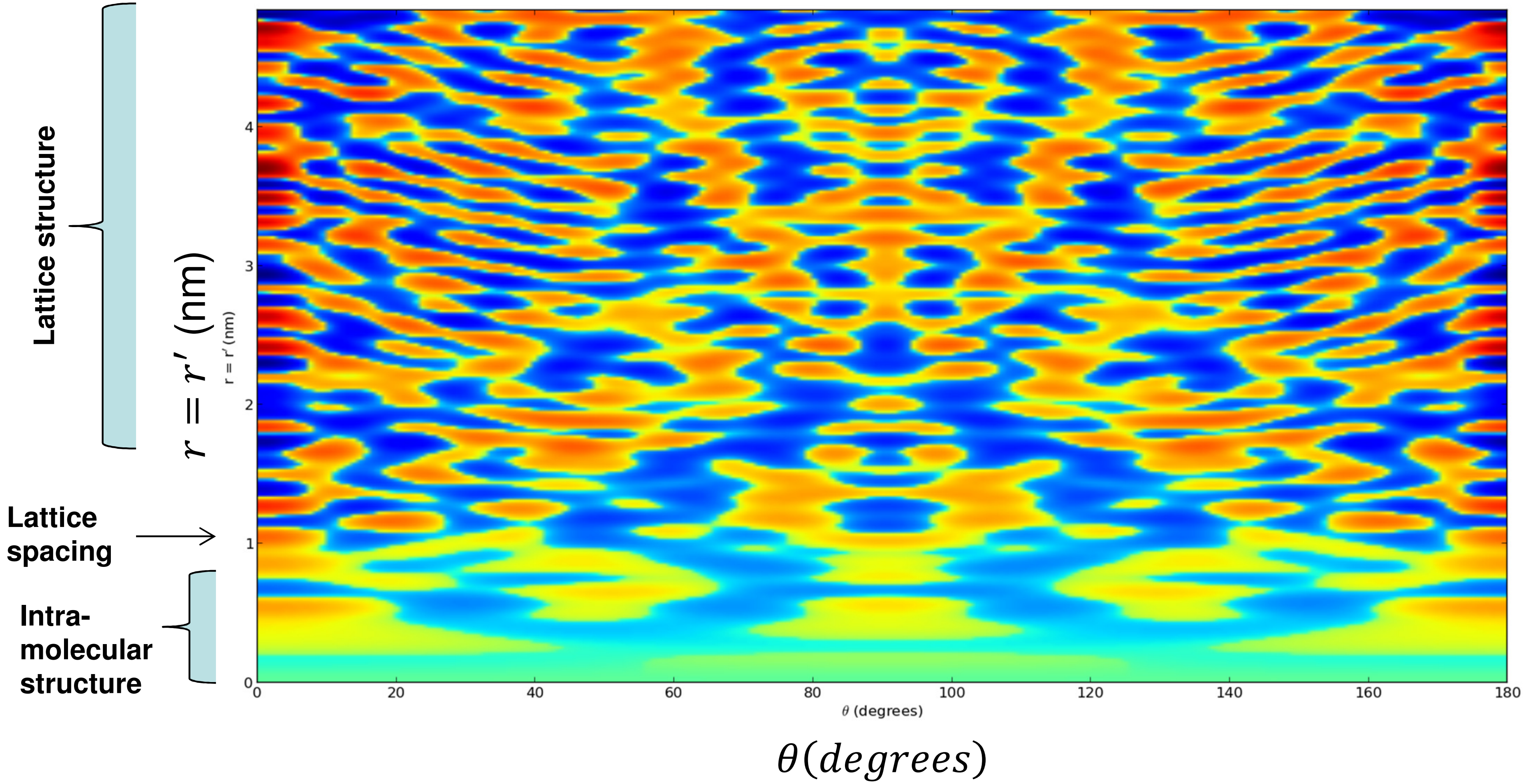




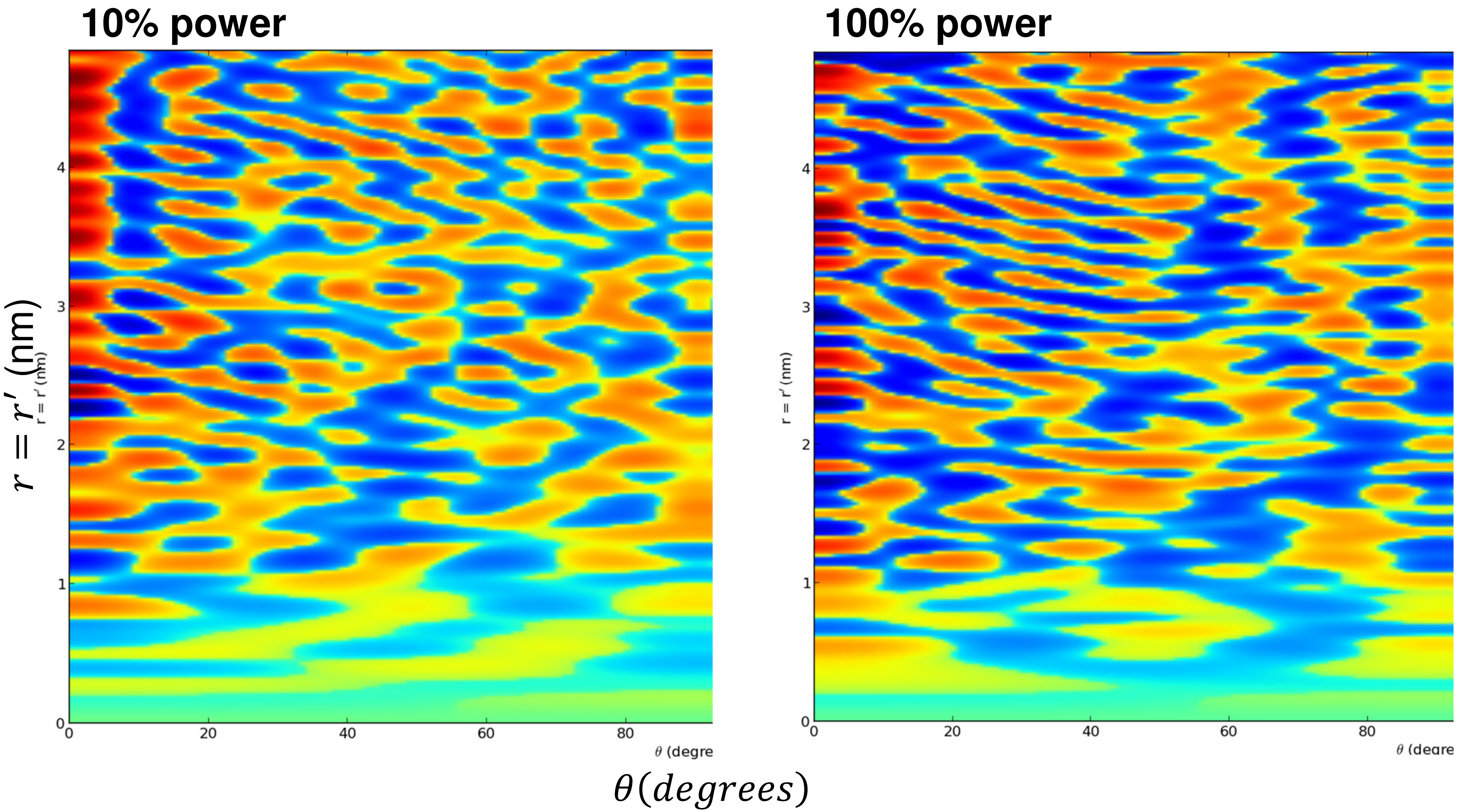
Abbey et al. Sci. Adv. 2016; 2 : e1601186

C_{60} 100% XFEL data

"Fluctuation powder diffraction"

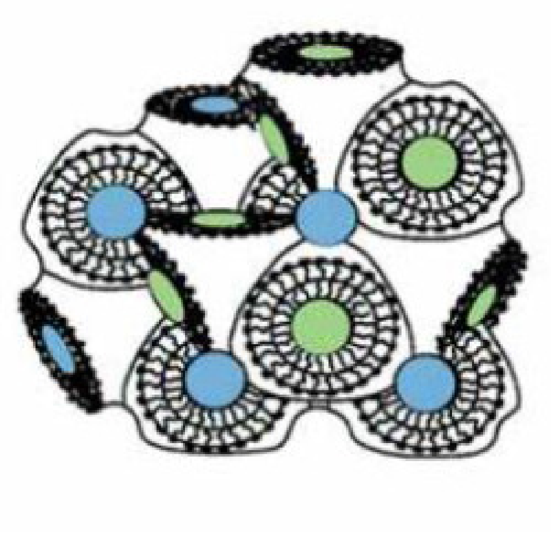


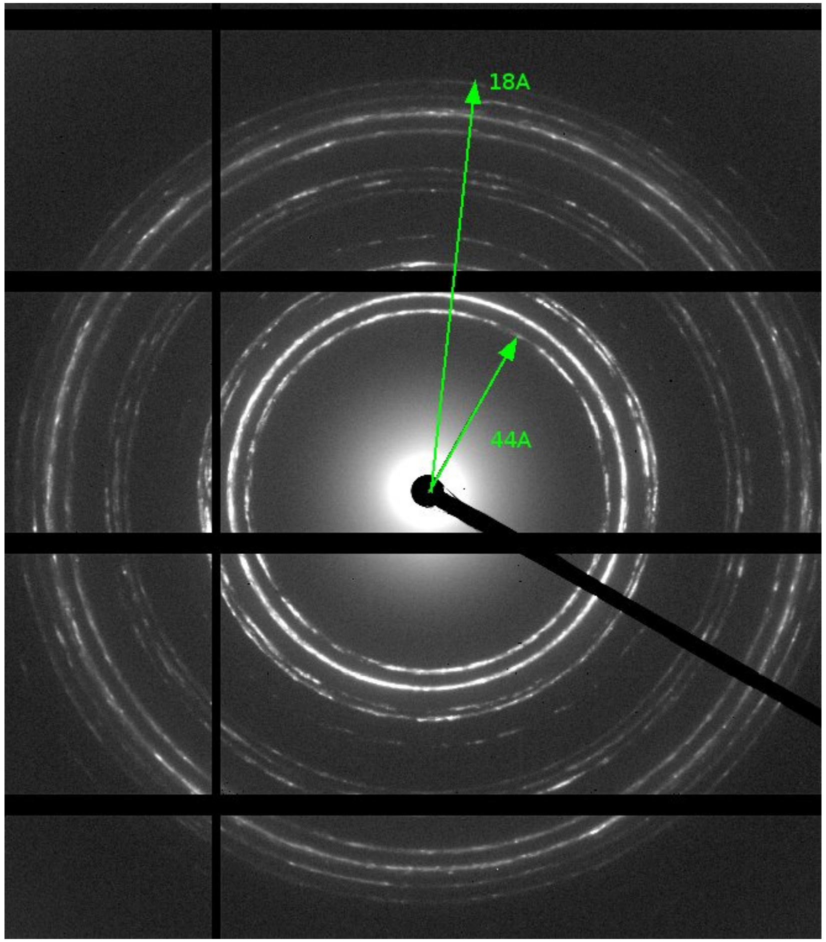
10% vs 100% XFEL power



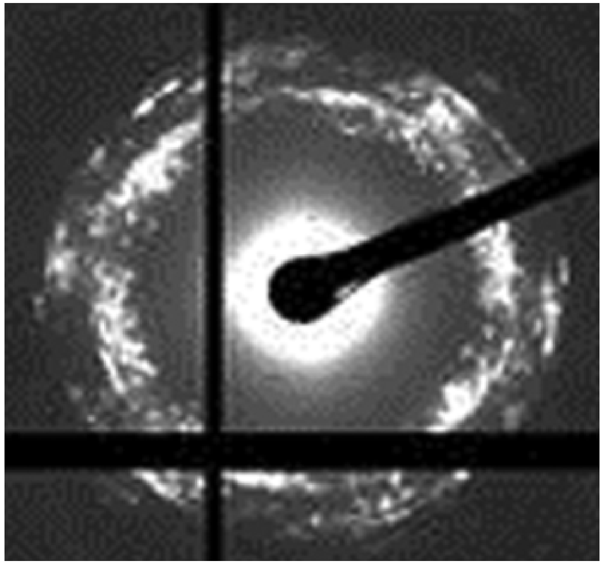
Future application: Lipidic cubic phase

With Peter, Berntsen, Connie Darmanin (La Trobe), Charlotte Conn, Tamar Greaves (RMIT)





Doped LCP Buffer
SAXS Australian Synchrotron
Note: angular structure!



+ Dopamine 2 receptor (D2L)
Note: lattice is disrupted

Acknowledgements

University of Melbourne (Physics)
Les Allen
Harry Quiney
Alex Kozlov
Saumitra Saha
Tim Gureyev
Justine Corso
Sophie Williams

La Trobe University
Keith Nugent
Brian Abbey
Connie Darmanian
Leonie Flueckiger
Peter Berntsen

Monash University
Amelia Liu
Tim Petersen
Espen Bojesen

Uppsala University
Carl Caleman
Nic Timneanu
Christofer Ostlin

Singapore National University
Duane Loh

Possible applications

Electrons:	amorphous solids
Synchrotrons:	nano-scale disorder, soft matter
X-ray free-electron lasers:	Liquids, proteins