X-ray Cross Correlation Analysis

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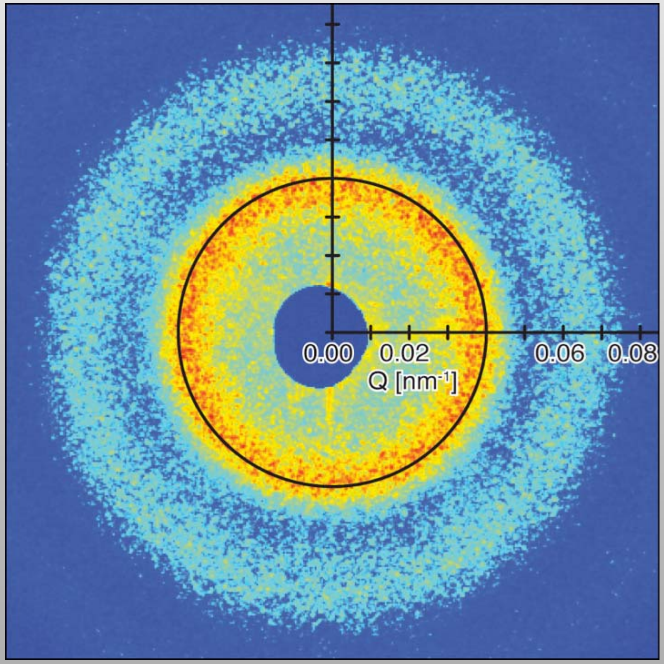


International Workshop on the Materials Imaging and Dynamics
Instrument at the European XFEL, Grenoble, October 28/29, 2009

Outline

Peter Wochner

- Motivation
- Higher Order Correlation Functions and XCCA
- Proof of Principle Experiment
- Results
- Conclusions and Outlook

- Liquids and amorphous systems still among the oldest and least understood problems in cond. mat. physics

- Structure:
- only pair-correlations
- **no directional information**

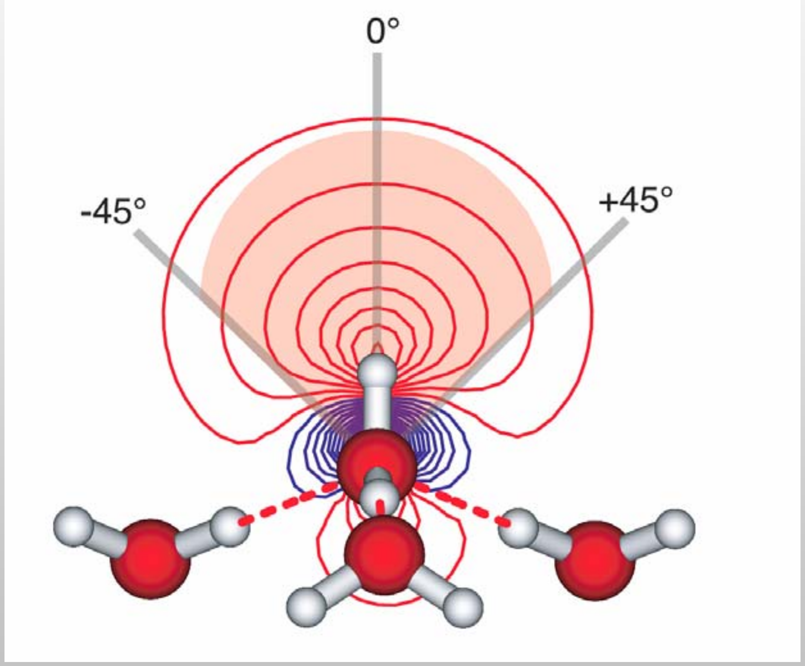
- Dynamics:
- **no directional information**
- time-averaged, long wavelength collective behaviour
- ultra-fast, local structural changes of interatomic distances

- Similar situation: solutions, nano-powders

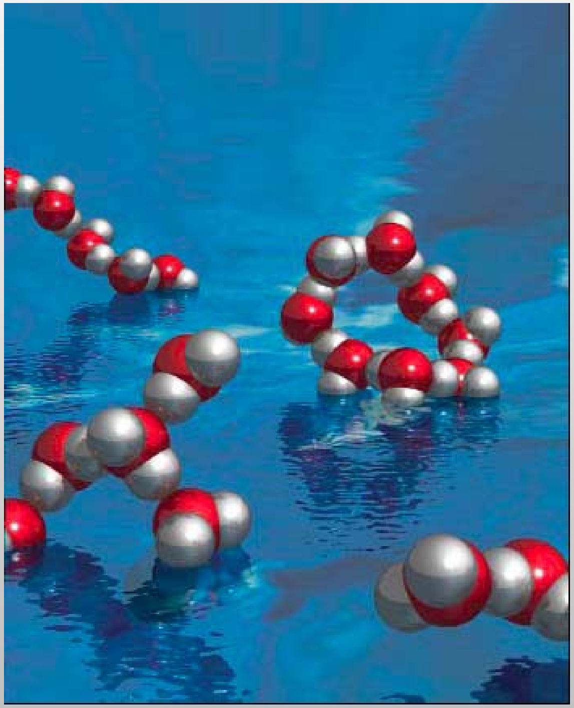
- Theoretically:
- Glass transition: freezing of density fluctuations $g_2(r)$
- dynamical heterogeneities and correlation length treated as fluctuation of $g_2(r)$: $g_4(r)$ (Parisi, Franz, Donati, Glotzer)

Motivation

- Most mysterious substance worldwide: H_2O
- Local order: Tetrahedral vs. rings and chains



Ph. Wernet et al., Science **304**. 995 (2004)



Y. Zubavicus, M. Grunze, Science **304**. 974 (2004)

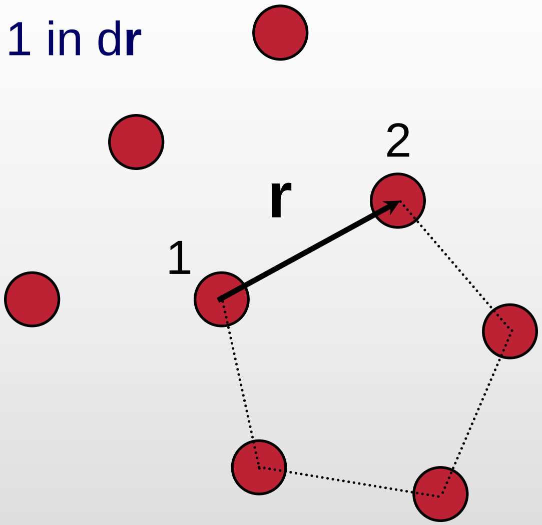
C. Huang et al.; "The Inhomogeneous Structure of Water at AmbientConditions", PNAS (2009)

N-Point Correlation Function

Peter Wochner

$n_0 g_2(\mathbf{r}) d\mathbf{r}$ probability to find particle 2 at distance **r** from 1 in d**r**

$$g_2(\mathbf{r}_1, \mathbf{r}_2) = n_0^{-2} \left\langle \sum_i^N \sum_{j \neq i}^{N-1} \delta(\mathbf{r}_1 - \mathbf{R}_i)\delta(\mathbf{r}_2 - \mathbf{R}_j) \right\rangle$$



- $g_2(\mathbf{r})$ independent of bond angles

N-Point Correlation Function

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MPI-MF

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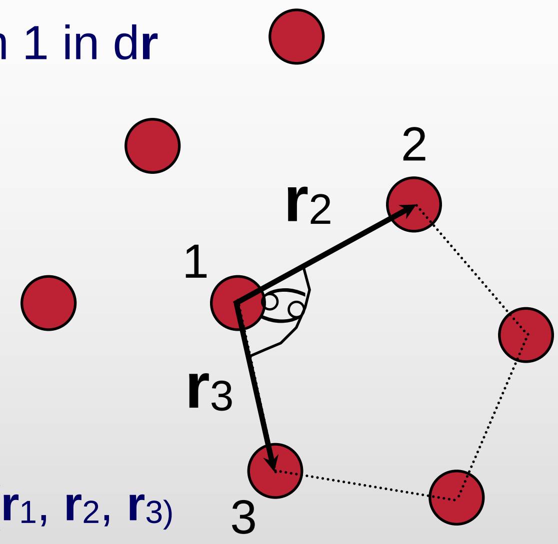
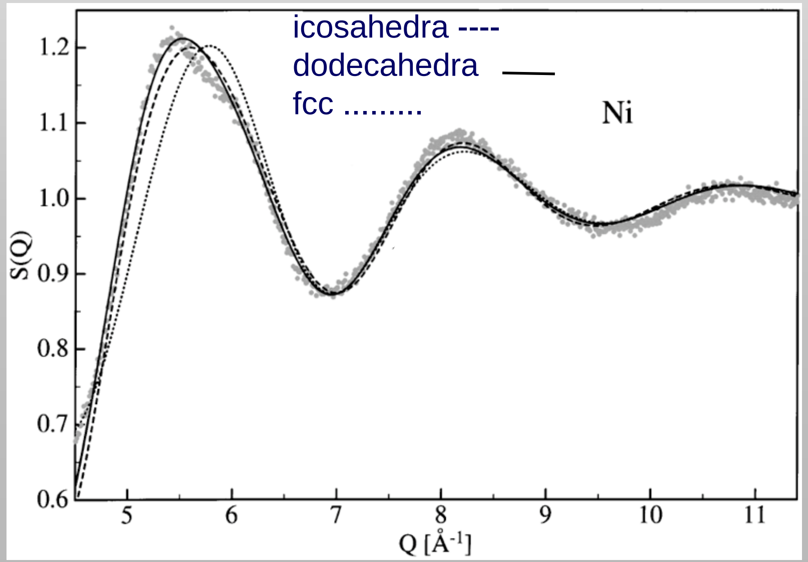


- $g_2(\mathbf{r})$ independent of bond angles

- analogous: 3-point and n-point distribution function $g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$
- but **depend on angles**

$$n_0 \int g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\, d\mathbf{r}_3 = (N-2) g_2(\mathbf{r}_1,\mathbf{r}_2)$$

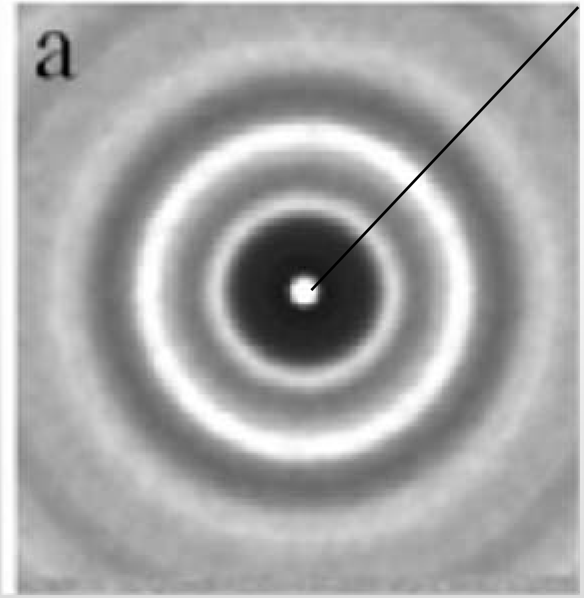
- N-2 different arrangements with same $g_2(\mathbf{r})$

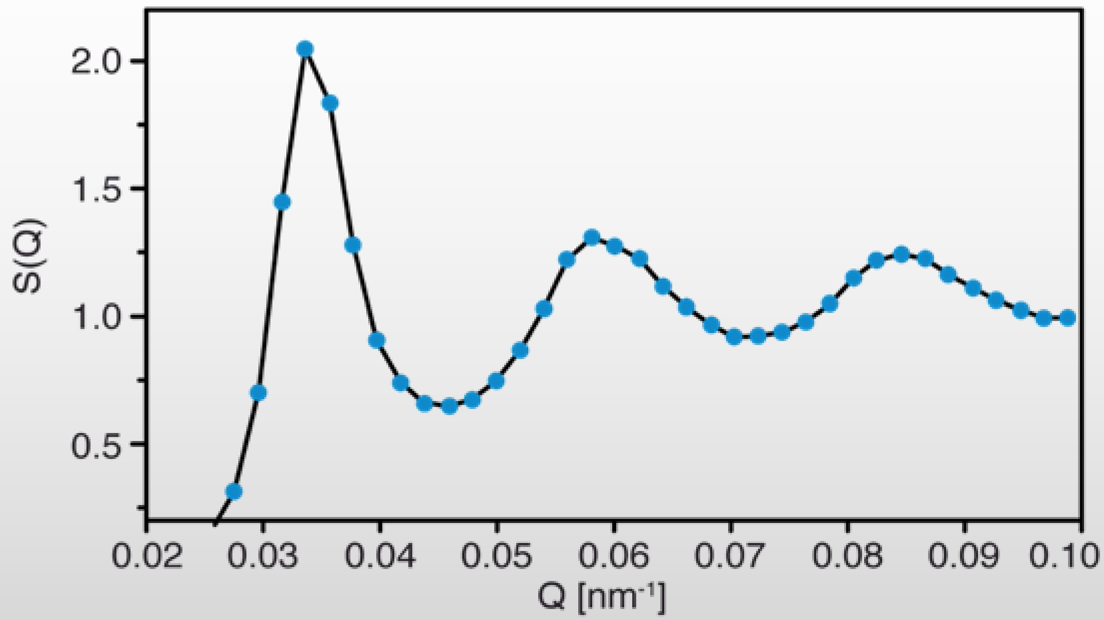


Schenk et al., PRL 89, 075507 (02)

Structure Determination of Disordered Systems

Peter Wochner





Traditional approach:

$$S(\mathbf{Q}) = \left\langle \left| \int \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r} \right|^2 \right\rangle$$

- **Ensemble or configuration (and time) average <...>**

- **g_2(r) 2-point (pair) distribution function**

$$g_2(\mathbf{r},\mathbf{r}') = n_0^{-2} \left(\left\langle \rho(\mathbf{r})\rho(\mathbf{r}') \right\rangle - \delta(\mathbf{r}) \right)$$

$$S(\mathbf{Q}) = 1 + \int (g_2(\mathbf{r}) - 1) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}$$

- Major breakthrough: beyond 2-point correlation functions

Higher Order Correlation functions

Peter Wochner

- **Eliminate intrinsic spatial and temporal averaging**

Coherence **Snap shot**

- **Construct new correlation function "by hand"**

- Speckle intensity $$I(\mathbf{Q},t) = \int\int e^{-i\mathbf{Q}\cdot(\mathbf{r}-\mathbf{s})} \rho(\mathbf{r},t)\rho(\mathbf{s},t)d\mathbf{r}d\mathbf{s}$$

- Speckle width $\Delta Q \approx \lambda / D_b$ (D_b beam size)

- **Intensity-Intensity correlation function (appropriate average)**

$$C(\mathbf{Q},\mathbf{Q}',t,t') = \langle I(\mathbf{Q},t)I(\mathbf{Q}',t')\rangle$$

$$= \int\int\int\int e^{-i\mathbf{Q}\cdot(\mathbf{r}-\mathbf{s})-i\mathbf{Q}'\cdot(\mathbf{r}'-\mathbf{s}')} \rho_4(\mathbf{r},\mathbf{s},t,\mathbf{r}',\mathbf{s}',t')\, d\mathbf{r}d\mathbf{s}d\mathbf{r}'d\mathbf{s}'$$

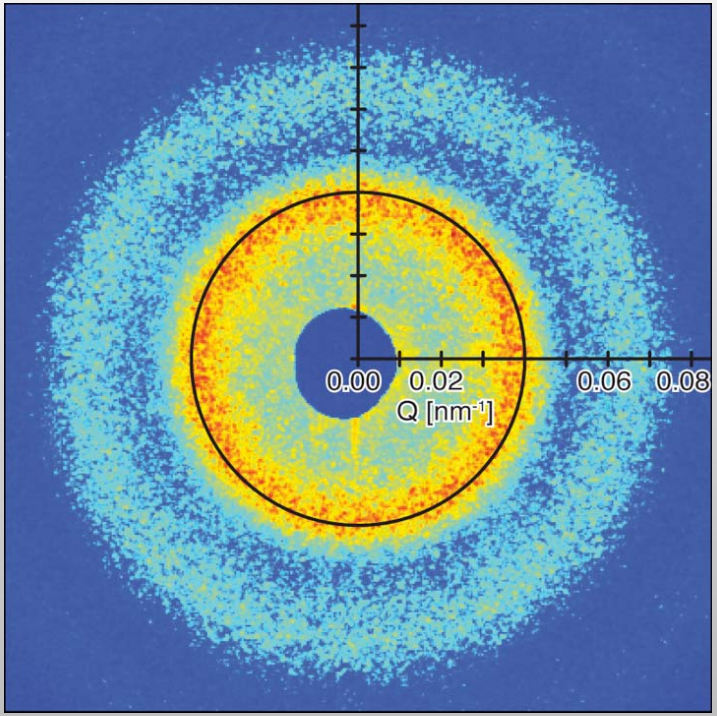
- **❒$_4$(r) 4-point correlation function**

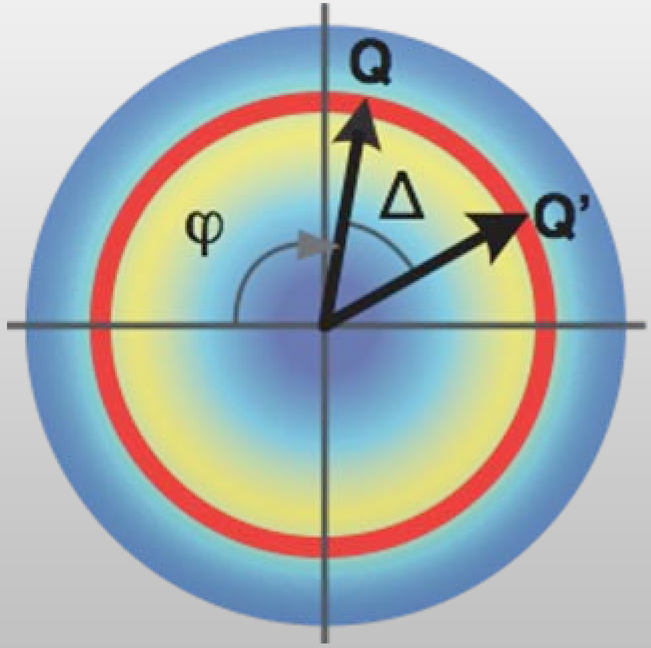
$$\rho_4(\mathbf{r},\mathbf{s},t,\mathbf{r}',\mathbf{s}',t') = \langle \rho(\mathbf{r},t)\rho(\mathbf{s},t)\rho(\mathbf{r}',t')\rho(\mathbf{s}',t')\rangle = f(g_2,g_3,g_4)$$

$\langle .... \rangle$ to be defined

- $\langle .... \rangle$ **for local orientational correlations (instantaneous *t* = *t'*):**

$$C_Q(\Delta) = \frac{< I(Q,\varphi) I(Q,\varphi+\Delta) >_\varphi - < I(Q,\varphi) >_\varphi^2}{< I(Q,\varphi) >_\varphi^2}$$





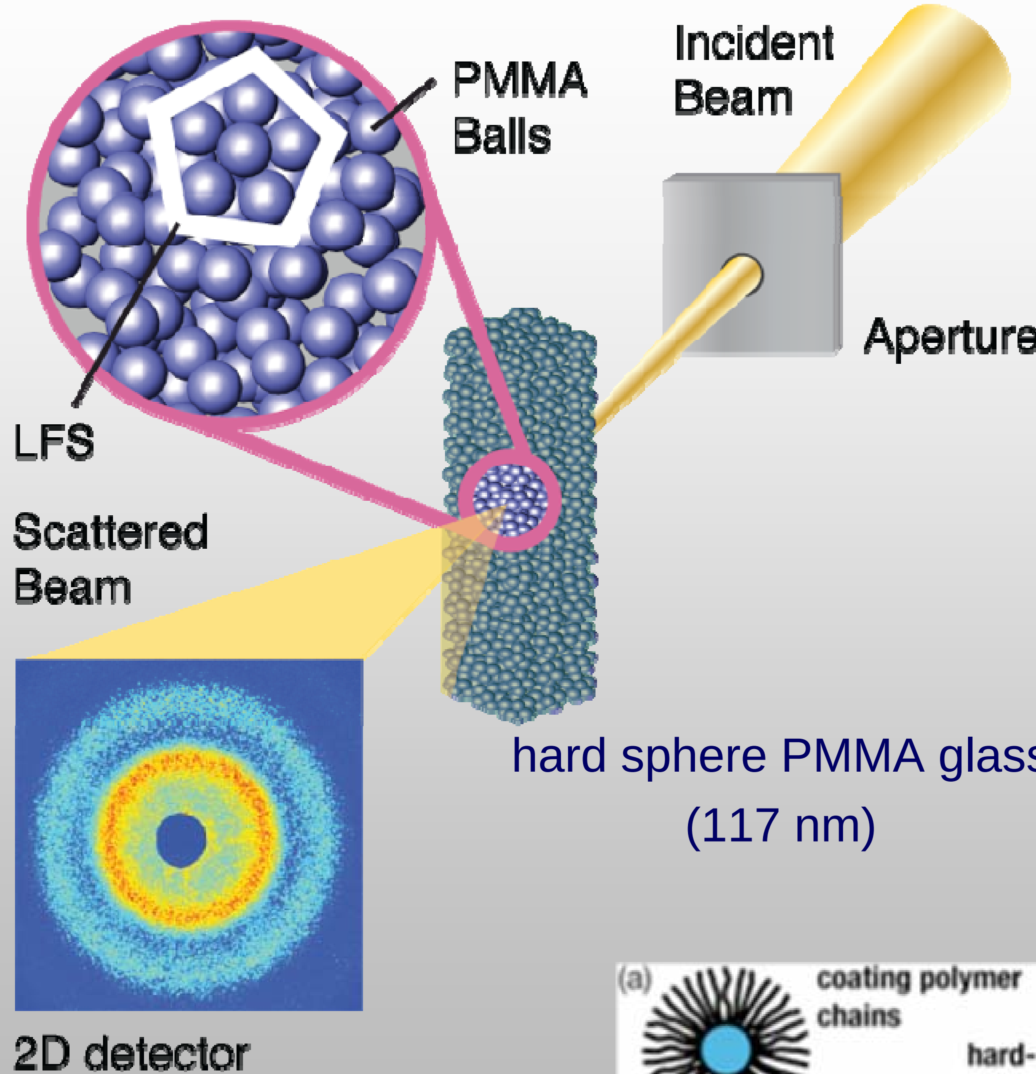
- **for medium range orientational correlations:** $|Q| \neq |Q'|$
- **time dependent:** $t \neq t'$

P. Wochner et al., PNAS **106**, 11511 (2009)

Proof of Principle: Colloidal Glass

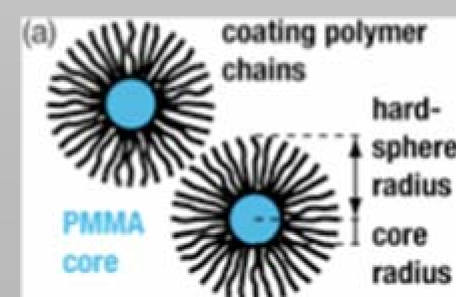
Peter Wochner

- Beamline ID10A, ESRF
- Energy 8.03 keV
- Vertical focusing by CRL
- Aperture: 10 ❍m
- Flux : 3.6e9 ph/s at 56 mA
- Coherent fraction ~ 30%
- CCD camera, 22 ❍m pixel size



Speckle “noise”

hard sphere PMMA glass (117 nm)

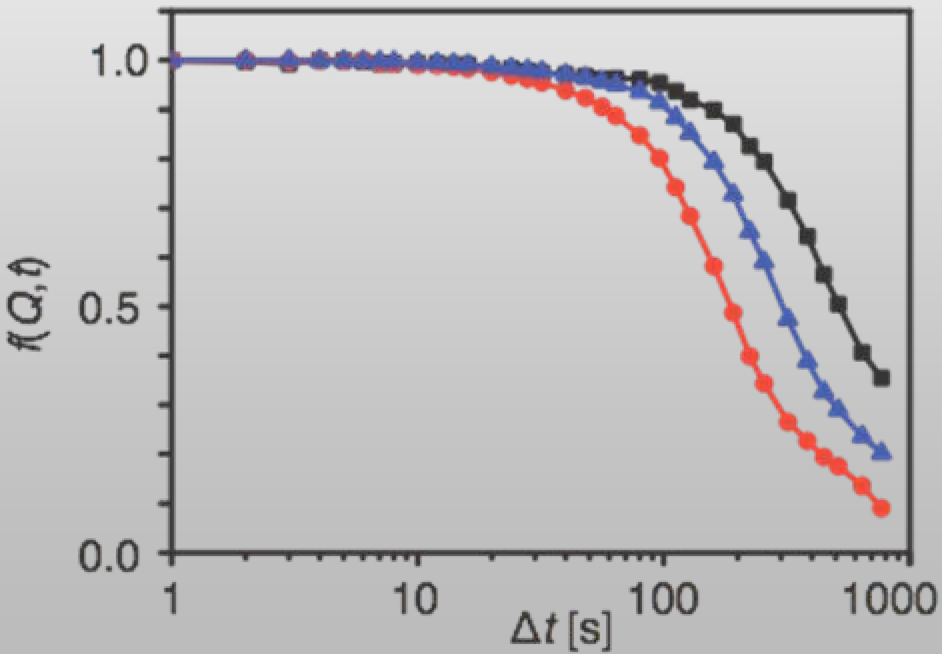


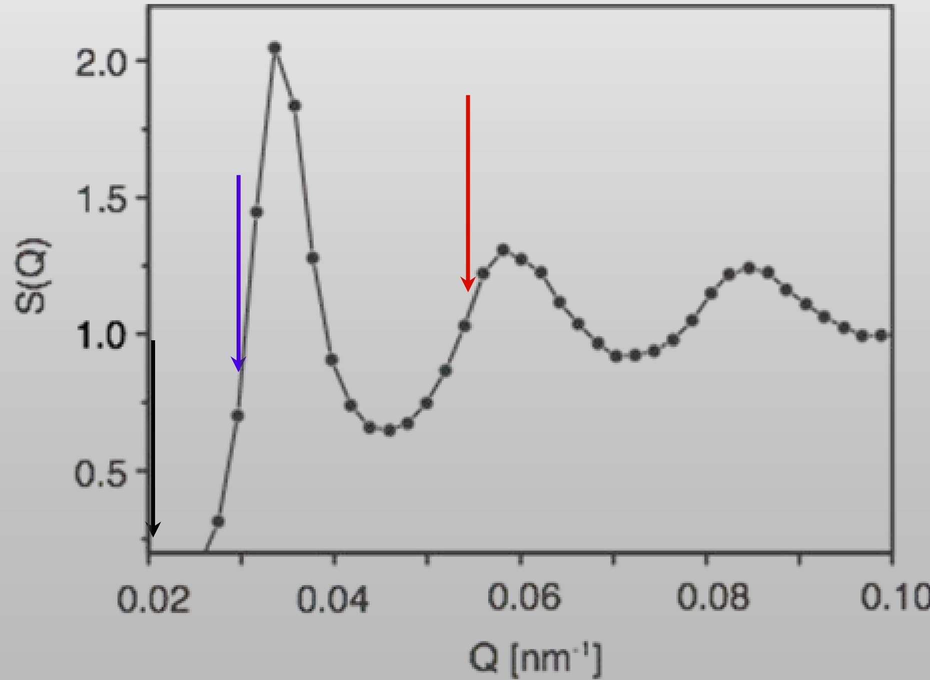
- **“Fast” hard sphere PMMA system (117 nm)**

Temporal auto-correlation function

$$f(Q,\Delta t) = \frac{< I(Q,t) I(Q,t+\Delta t) >_t}{< I(Q) >_t^2}$$

Structure factor $\langle S(Q) \rangle_{eT}$





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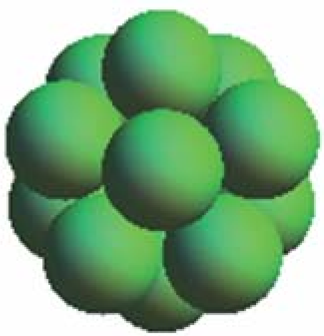
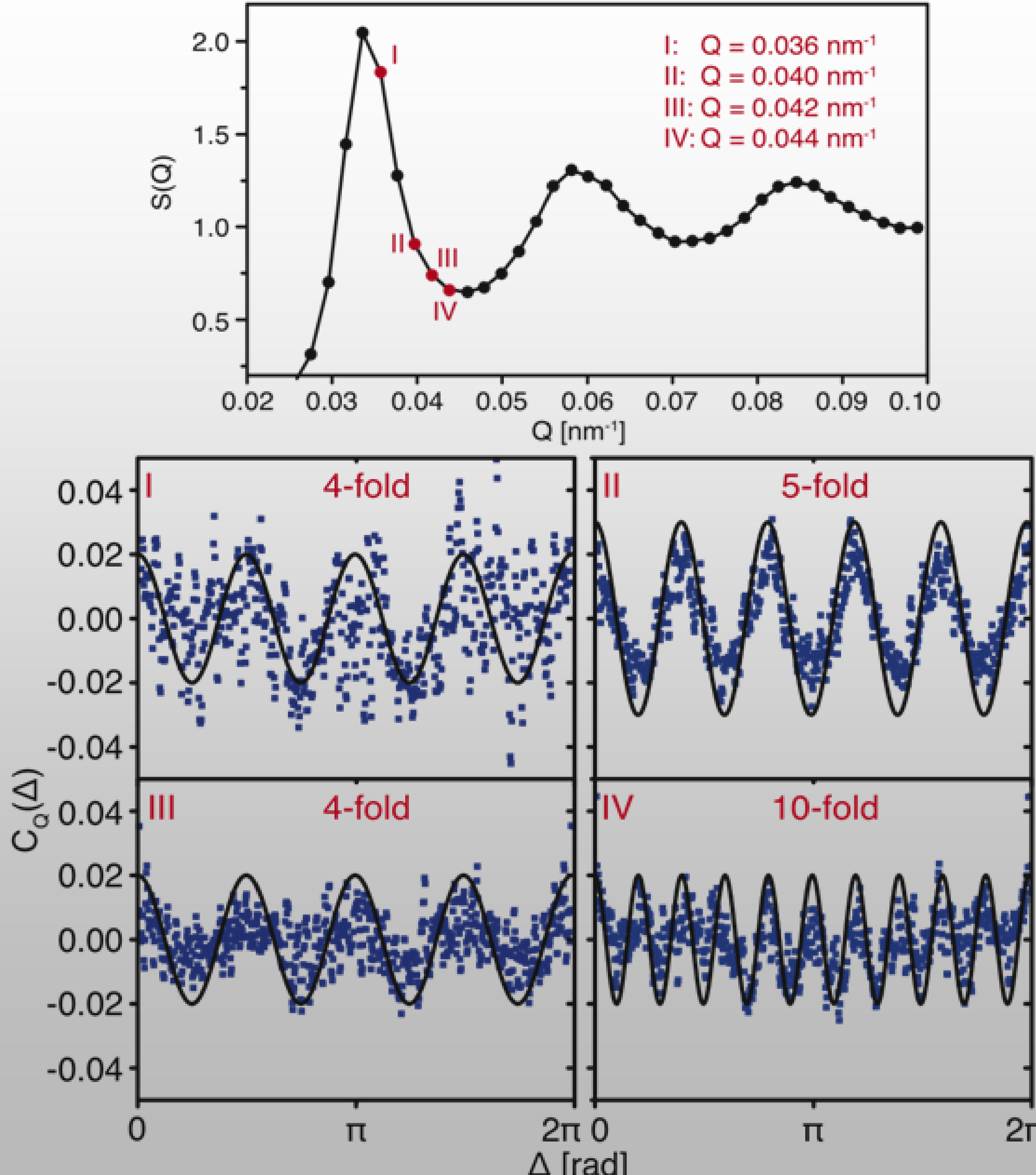
Typical angular dependence of C_Q(👎)

- **“Fast” hard sphere PMMA system (117 nm)**

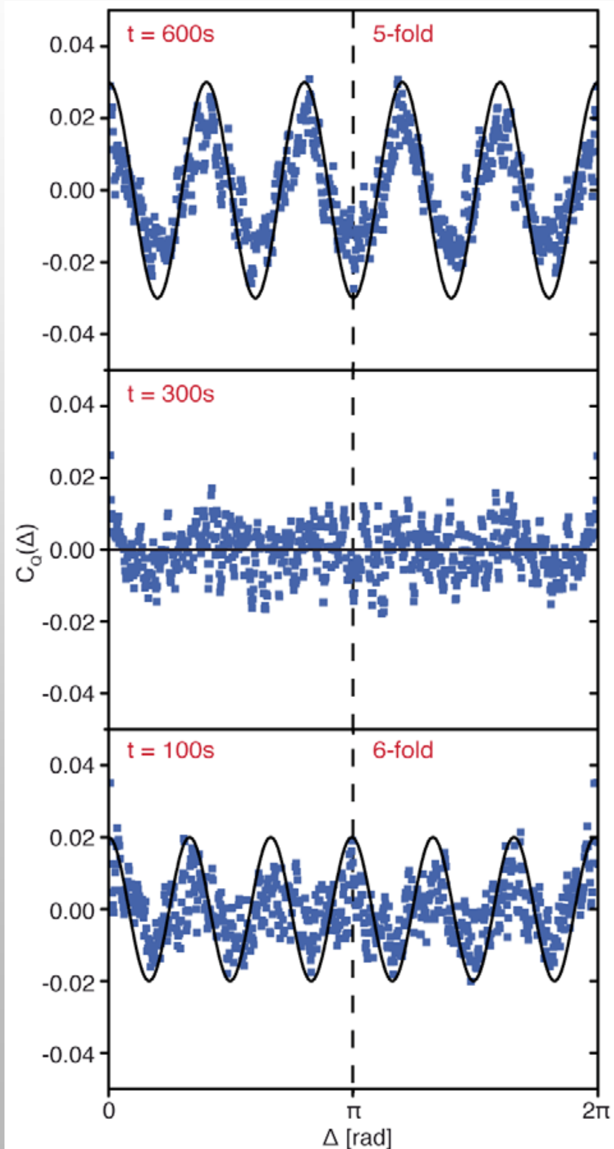
Icosahedral

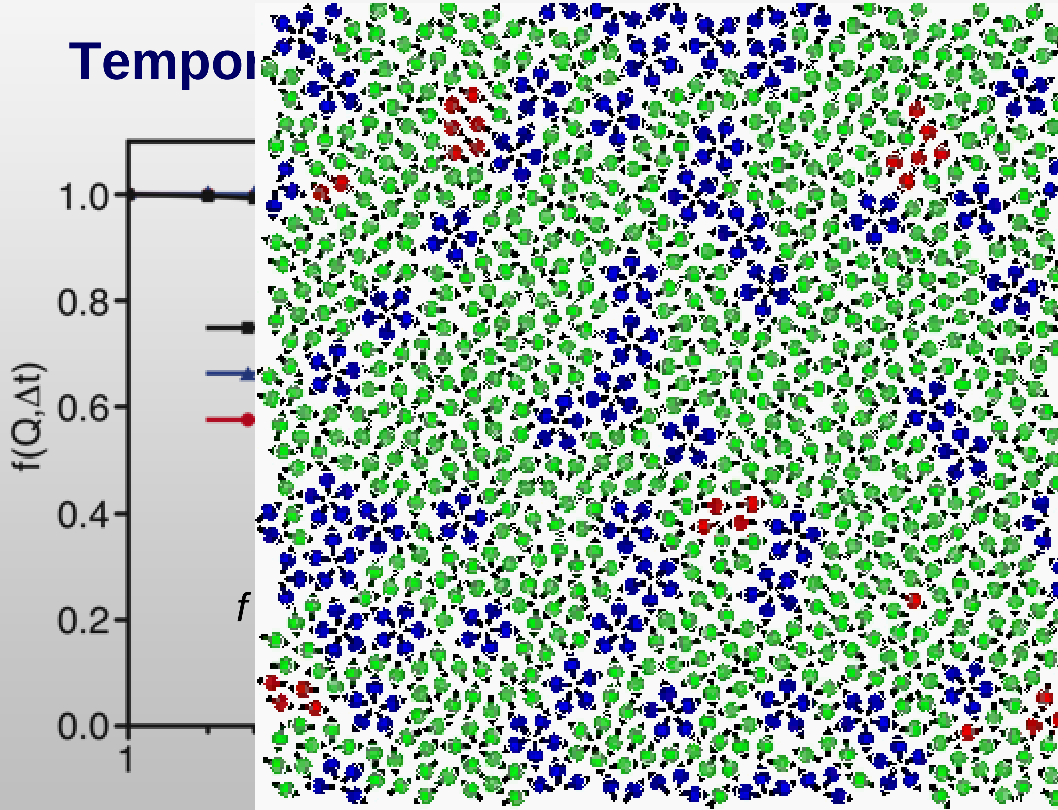


Cluster



- **“Fast” hard sphere PMMA system (117 nm): dynamical heterogeneity**





H.Shintani, H. Tanaka, Nature Physics **2**, 200 (2006)

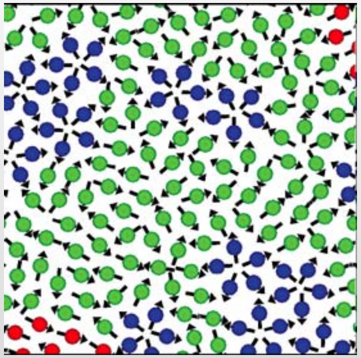
X-ray Cross-correlation Analysis XCCA

Peter Wochner

MPI-MF

$$< I(\varphi)I(\varphi+\Delta) >_{\varphi} = < \rho_Q(\varphi)\rho_Q^*(\varphi)\rho_Q(\varphi+\Delta)\rho_Q^*(\varphi+\Delta) >_{\varphi}$$

- **Hypothesis:**



- **Sample = Ensemble of random clusters (LFS)**
- $\rho_Q^i(\varphi)$ **structure factor of cluster i**

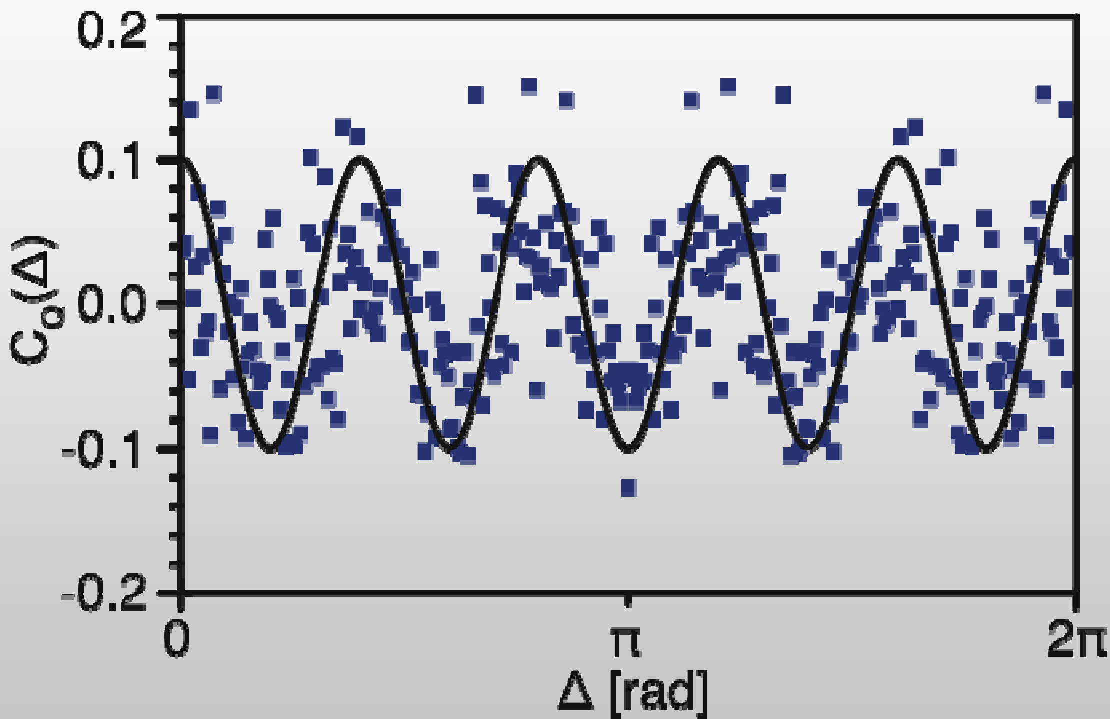
$$C_Q(\Delta) \sim \sum_{i=clusters}^{N} \left| < \rho_Q^i(\varphi)\rho_Q^{i*}(\varphi+\Delta) >_{\varphi} \right|^2$$

- **Angular auto-correlation function of individual cluster**

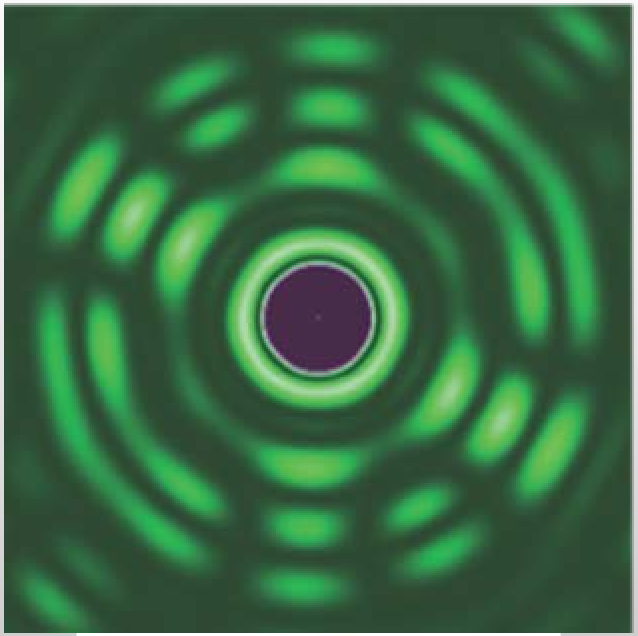
- **In general**: correlation of pair-correlations = Medium-range correlations

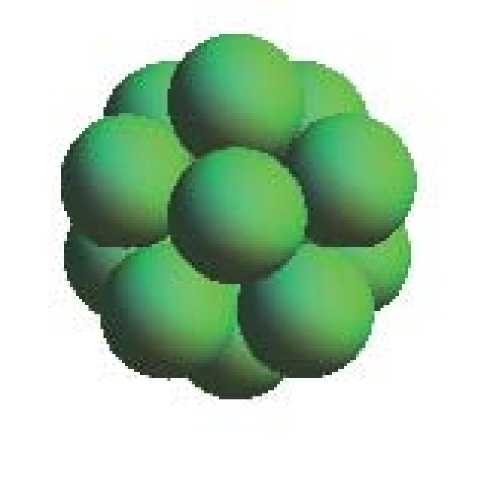
Numerical Simulation

- **8000 random icosahedral cluster on a lattice**



- **Single icosahedral cluster**





$$C_Q(\Delta) \sim \langle I(Q,\varphi) I(Q,\varphi+\Delta) \rangle_\varphi - \langle I(Q,\varphi) \rangle_\varphi^2$$

Summary and Outlook

Peter Wochner

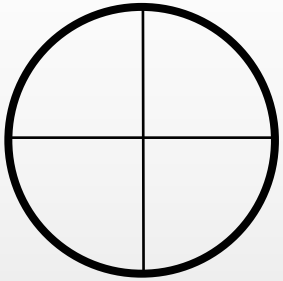
- **XCCA with XFEL will revolutionize studies of liquids (H_2O):**
  - **XCCA with single lasershots (100 fs)**

- **XCCA opens a new world for structural analysis of disordered systems**
  - **Glasses**
  - **transient complex molecular solutions and reactions in solutions**
  - **nano-powders**

- **Sophisticated Cross-correlators $C_{Q,Q'}(\Delta,t)$:**
  - **time-dependent mid-range orientational correlations**

- **Q-space Formalism (mode-coupling): Interaction potentials**

- **NEED: 2◻ - Pixel detector with low dynamic range + fast readout**
  - **@ 2✈=20º & distance 2m: U=4.3m**
  - **160 Princeton CCD (27mm) or 52 PILATUS (83mm)**
  - **(beam focus 2❍m)**
  - BETTER: New design with fast readout!



- **Limited data set (angular range)**
  - Can certain symmetries still be extracted?

$$C_Q(\Delta) \square \sum_{\varphi \in \{0,\varphi_{\max}\}} I(Q,\varphi) I(Q,\varphi+\Delta)\ with\ \varphi_{\max} > 360/n \qquad for\ n-fold$$

  - analogous to crystallography: maximum spatial resolution determined by Q-range limit.

Experimental (and theoretical) Challenges for XFEL/LCLS

Peter Wochner

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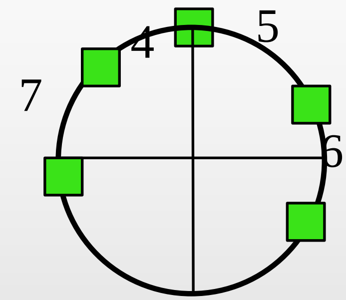

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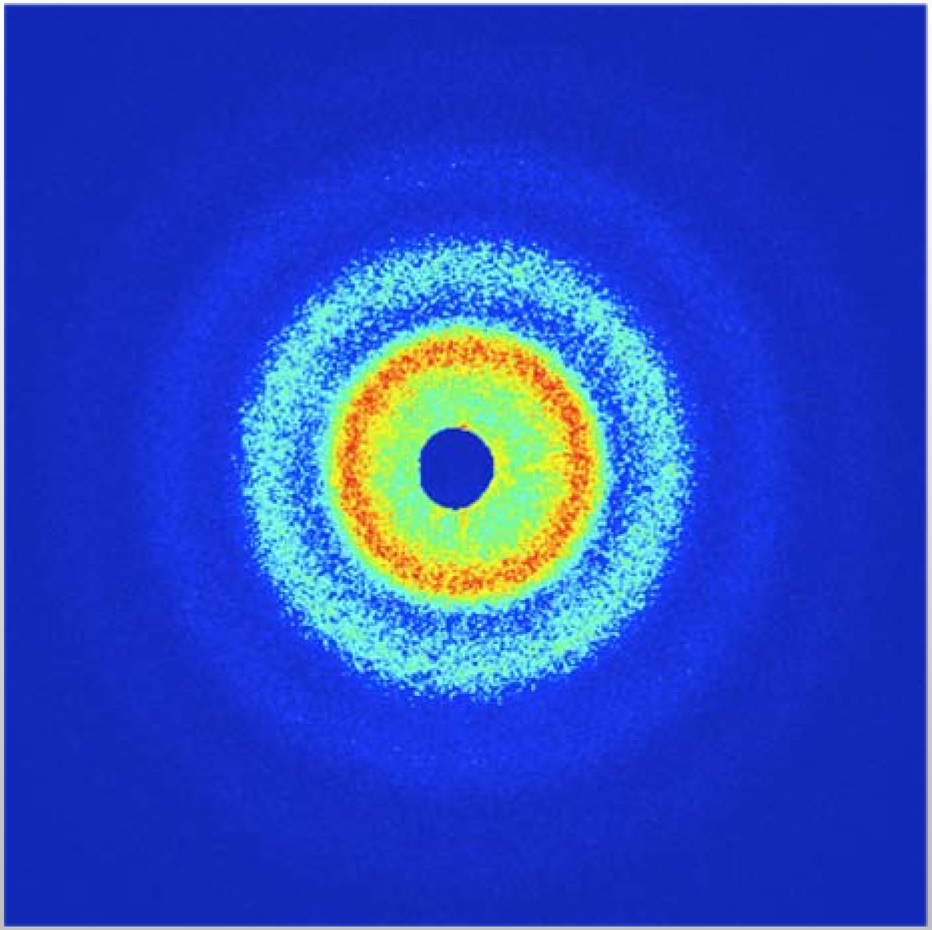
- **Limited number of detectors (wide-angle range)**

Experimental (and theoretical) Challenges for XFEL/LCLS

- **Limited statistics (intensity range): LCLS, XFEL**
  - single shot measurement: each snapshot different configuration
  - due to dynamics or radiation damage
- **Solution:**
  - correlate each shot (XCCA)
  - extract angular correlations from thermodynamic ensemble
- **Frequent shots with complete readout or storage on chip**

END

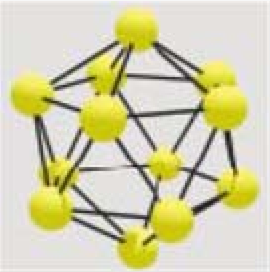
- Thanks to ESRF
- to A. Schofield for samples
- Thank you for your attention



Origin of Symmetries

Peter Wochner

- **Hypothesis: Icosahedral clusters (LFS)**
- **form factor expansion**: in icosahedral harmonics and orthogonal rotator functions
  – e.g. icosahedron: l=0, **l=6, l=10, l=12** ...



$$\rho_i(\mathbf{Q}) = 4\pi f_{sphere}(\mathbf{Q})\sum_{l,\tau} i^l g_l j_l(QR) \sum_{\gamma} S_l^{\gamma}(\Omega_Q) U_l^{\gamma,\tau}(\omega_i)$$

- **Conclusion:**
  - **form factor g_l can select dominant Q-ranges.**
  - **medium-range correlation length will also influence the Q-dependence**