Hidden Symmetry in Disordered Matter

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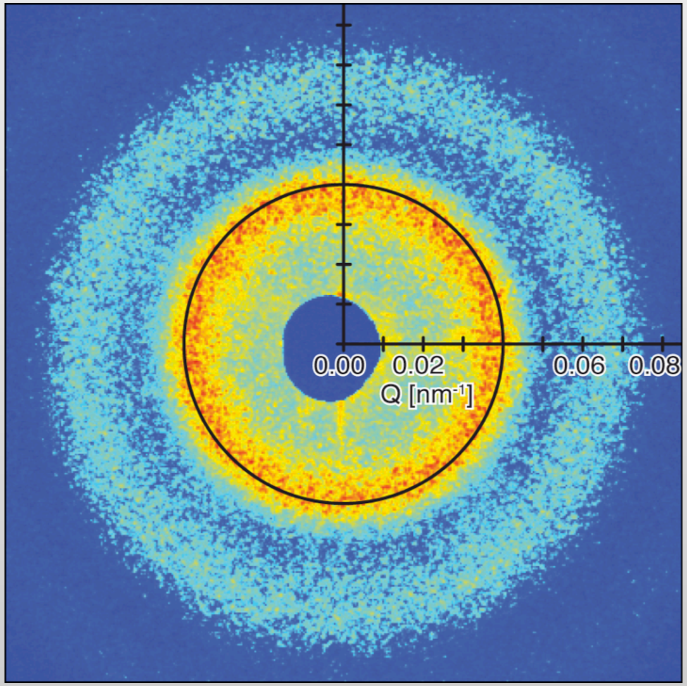


4th European XFEL User Meeting, DESY Hamburg, January 27, 2010

Outline

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

Motivation

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

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

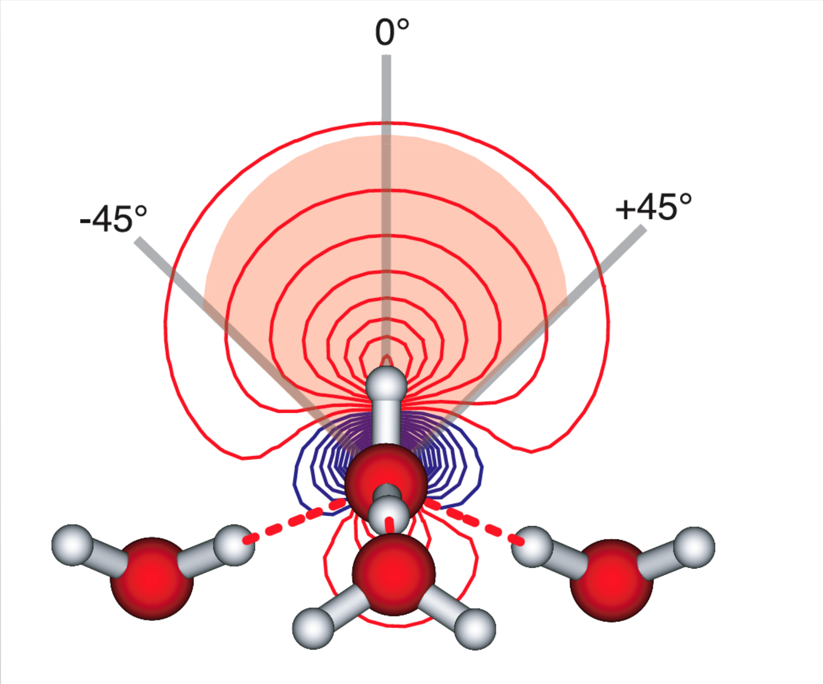
- Dynamics:
- **no directional information**
- time-averaged, long wavelength collective behaviour
- ultra-fast, local structural changes of interatomic distances

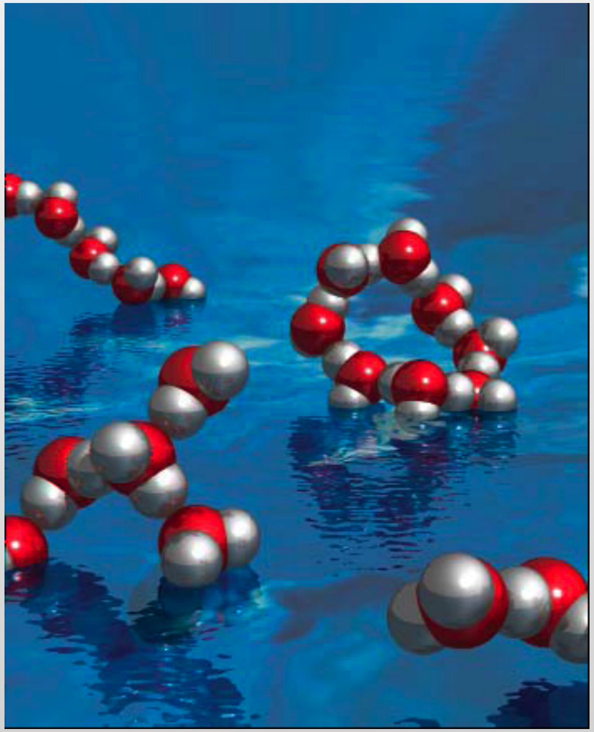
- Similar situation: solutions, nano-powders

- 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)

- 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)

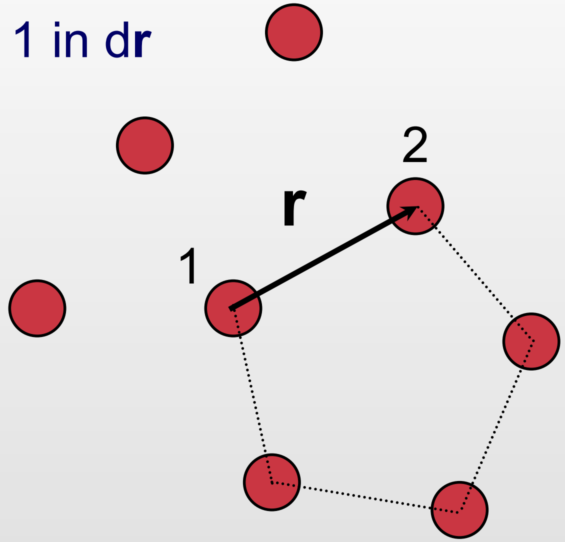
T. Head-Gordon, M.E. Johnson: “Tetrahedral structure or chains for liquid water”, PNAS (2006)
C. Huang et al.; "The Inhomogeneous Structure of Water at AmbientConditions", PNAS (2009)

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

Peter Wochner

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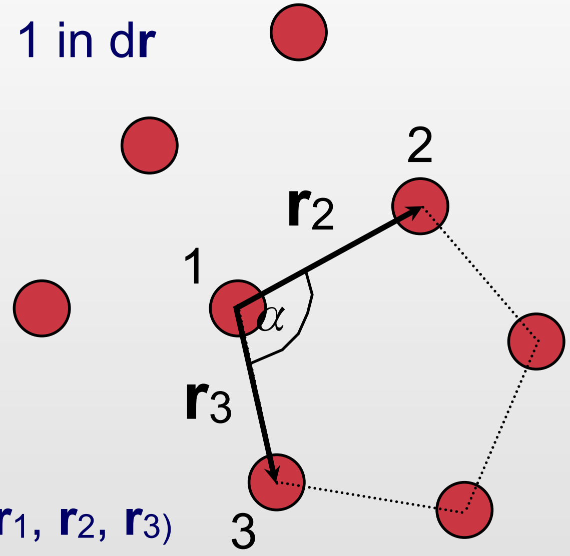
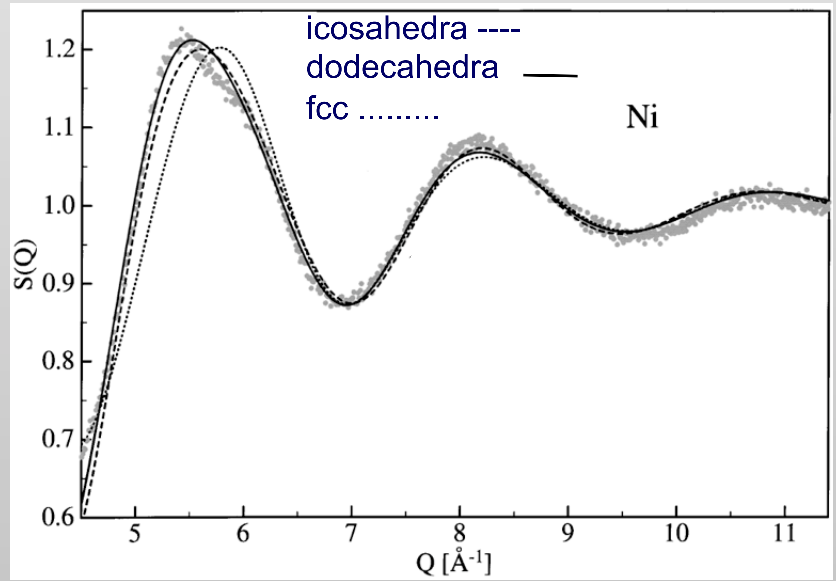


- $g_2(\mathbf{r})$ independent of bond angles

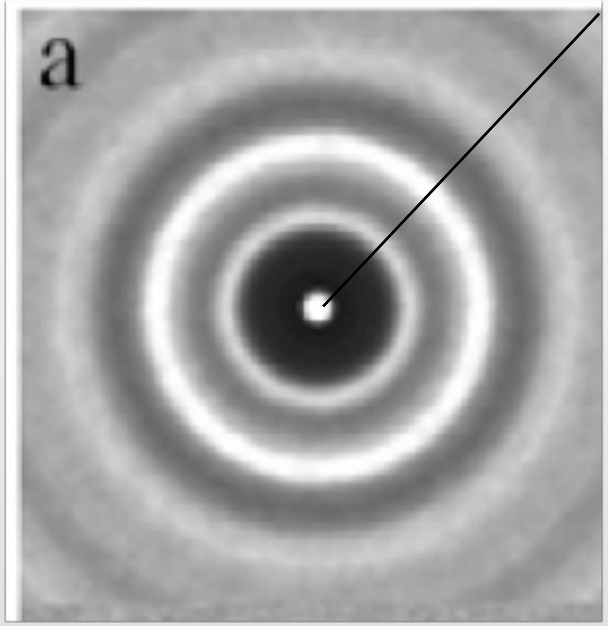
- analogous: 3-point and n-point distribution function $g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$
- but **depend on angles**

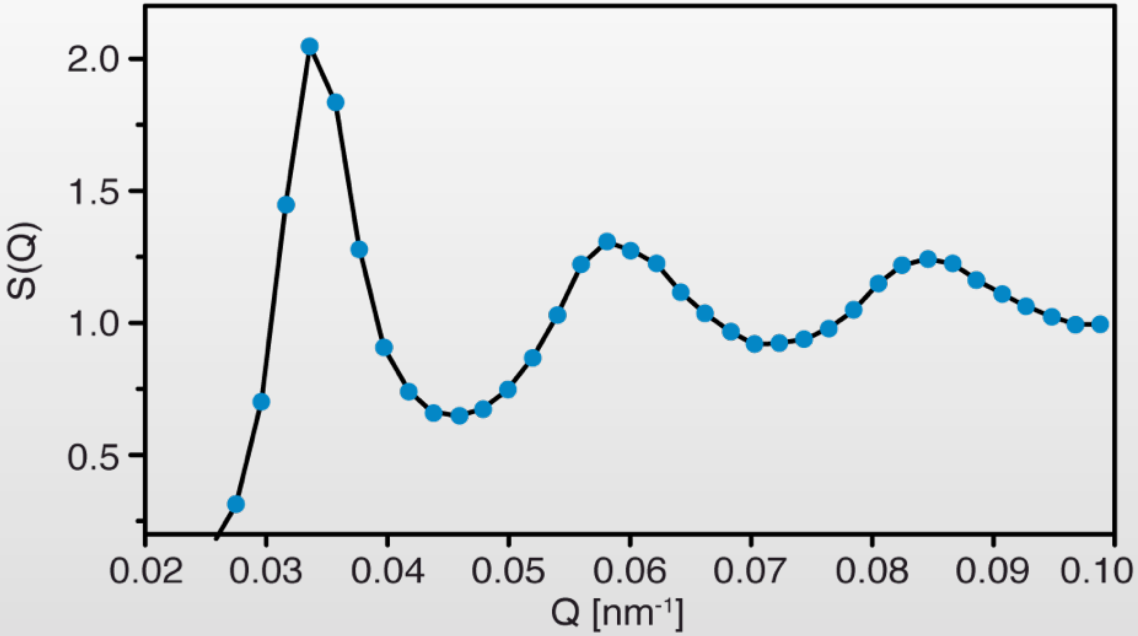
$$n_0\int g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\,d\mathbf{r}_3 = (N-2)g_2(\mathbf{r}_1,\mathbf{r}_2)$$

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



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





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

- **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)**

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

- **ρ_4(r) 4-point correlation function**

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

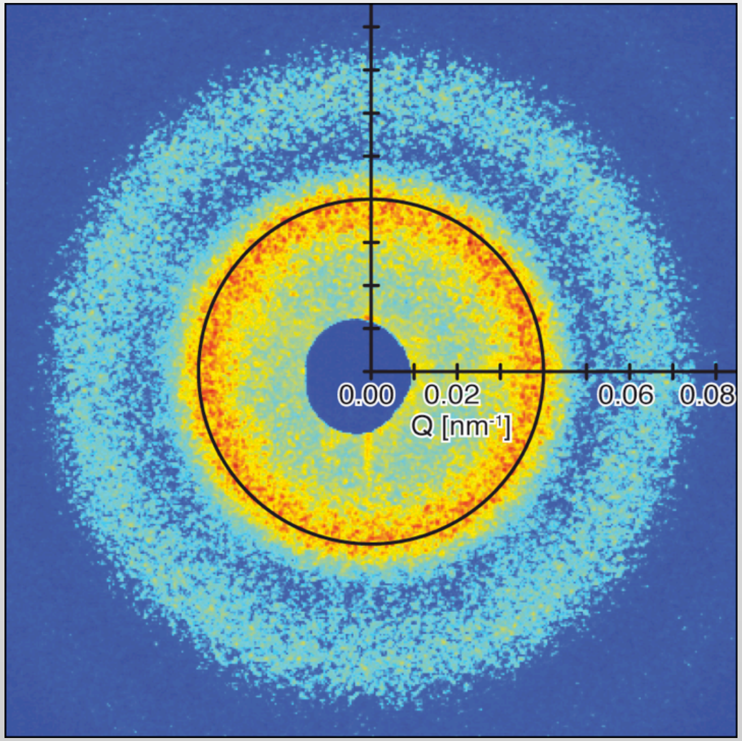
$\langle....\rangle$ to be defined

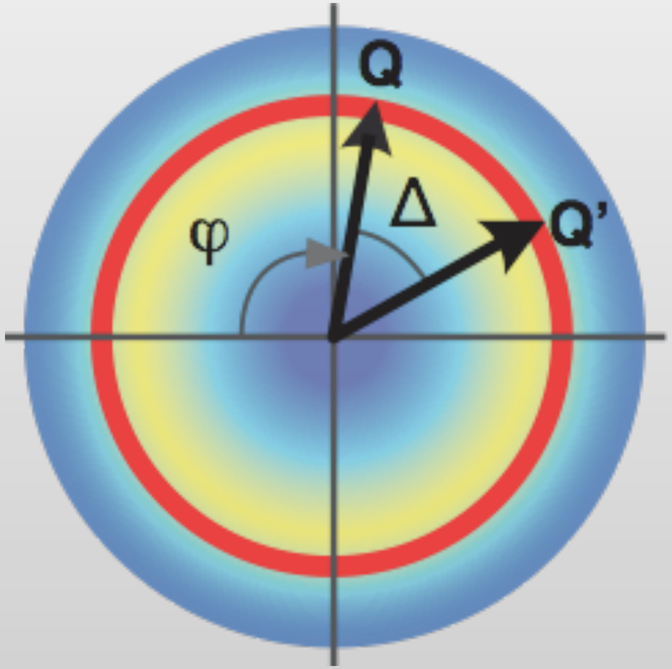
X-ray Cross-Correlation Analysis XCCA

Peter Wochner

- $\langle .... \rangle$ **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: $t \neq t'$**

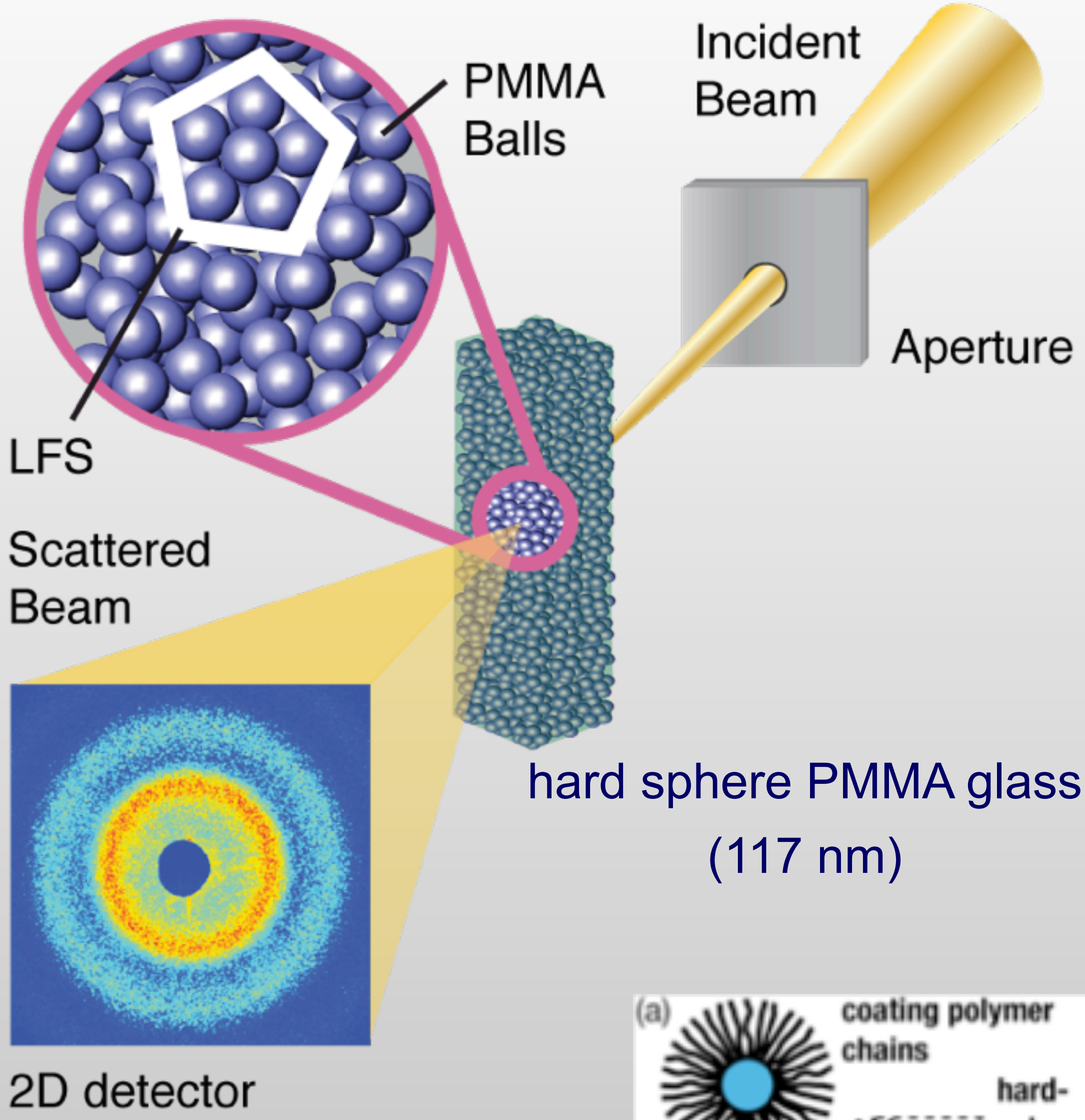
P. Wochner et al., PNAS **106**, 11511 (2009)

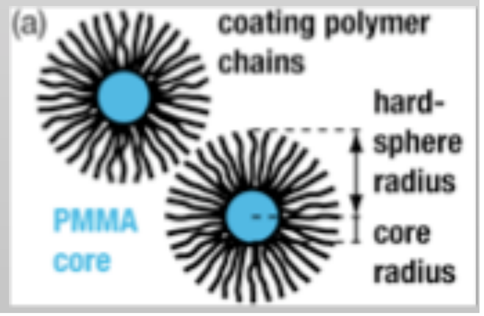
Proof of Principle: Colloidal Glass

Peter Wochner

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

Speckle “noise”



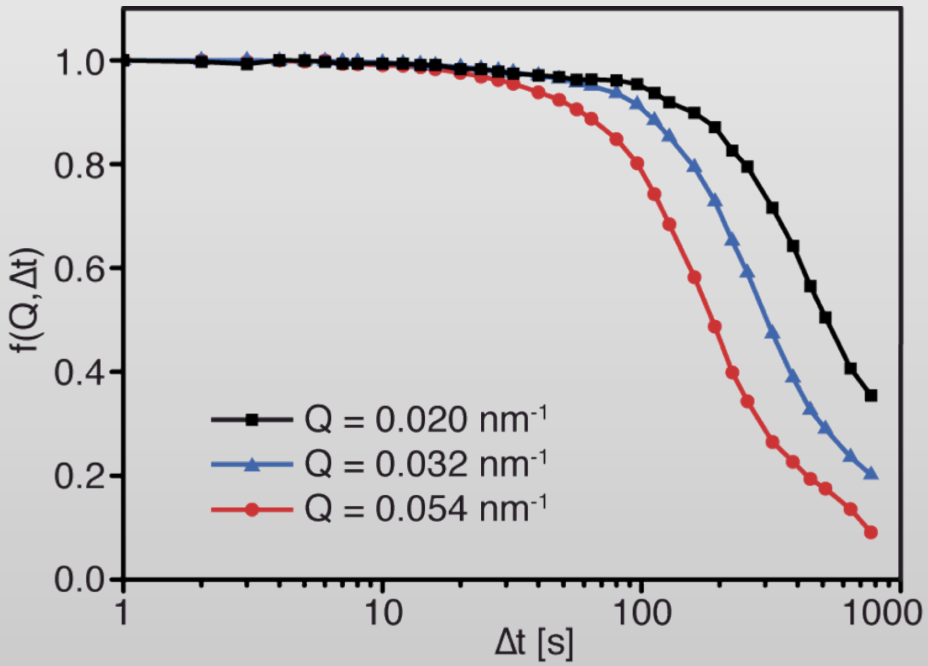


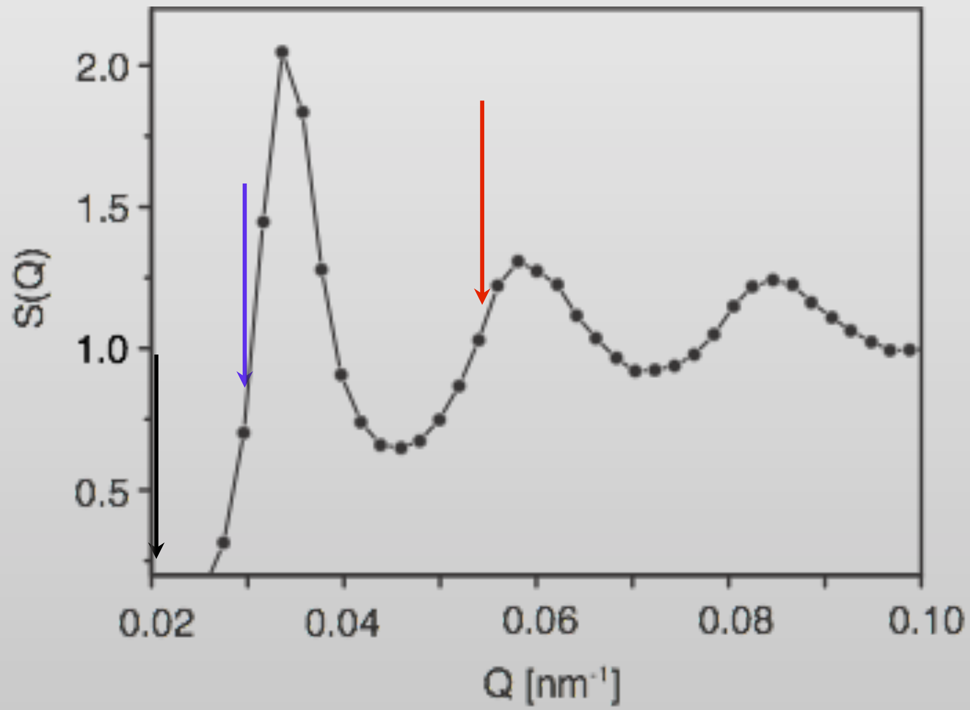
- **“Fast” hard sphere PMMA system (117 nm)**

Temporal auto-correlation function

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

Structure factor <*S*(*Q*)>$_\varphi$

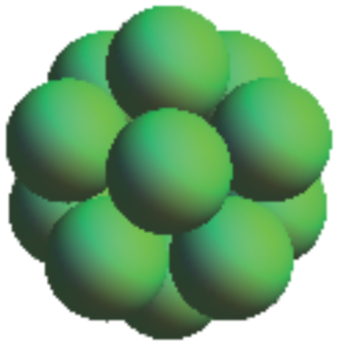




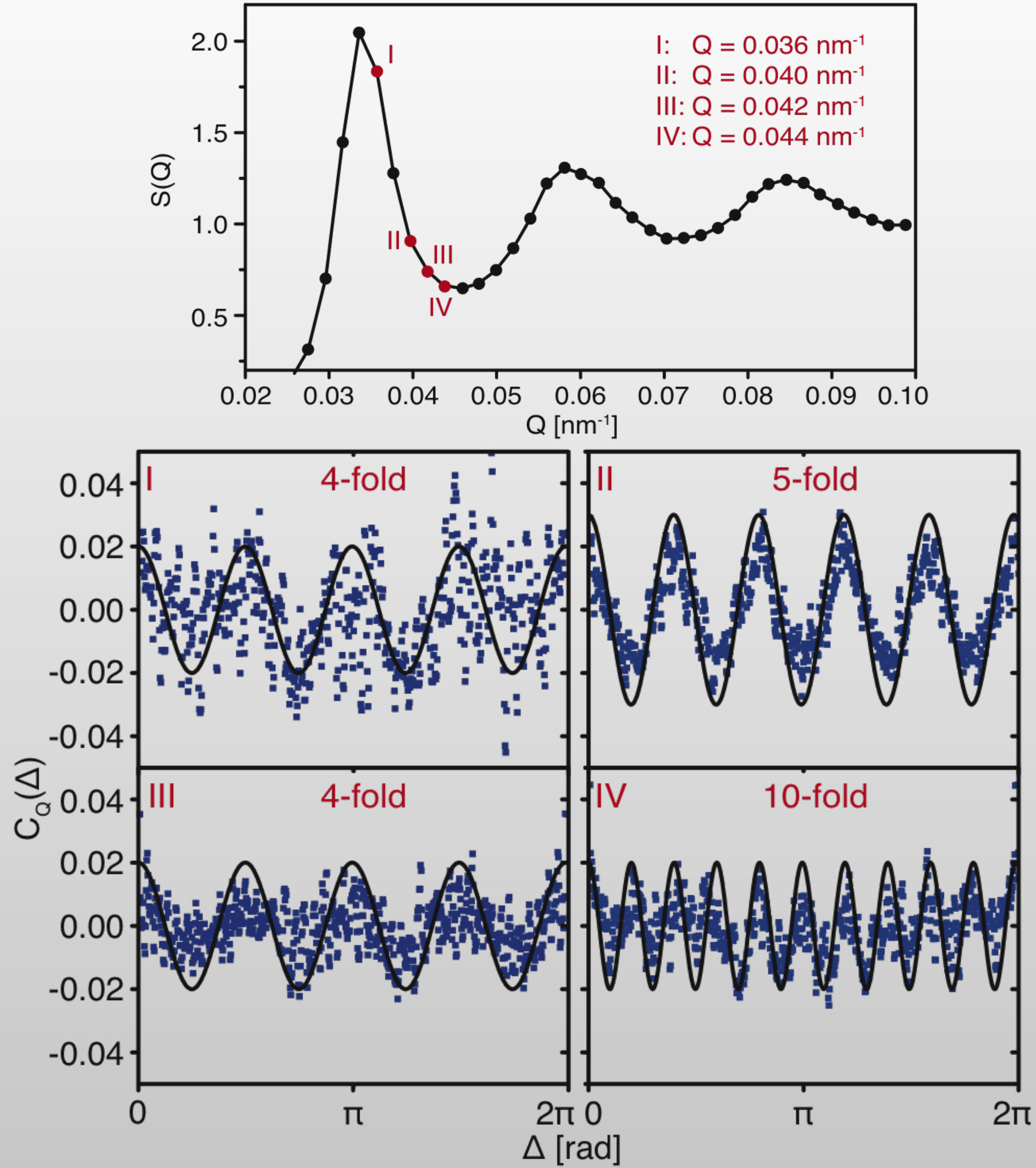
Typical angular dependence of $C_Q(\Delta)$

- **"Fast" hard sphere PMMA system (117 nm)**

Icosahedral



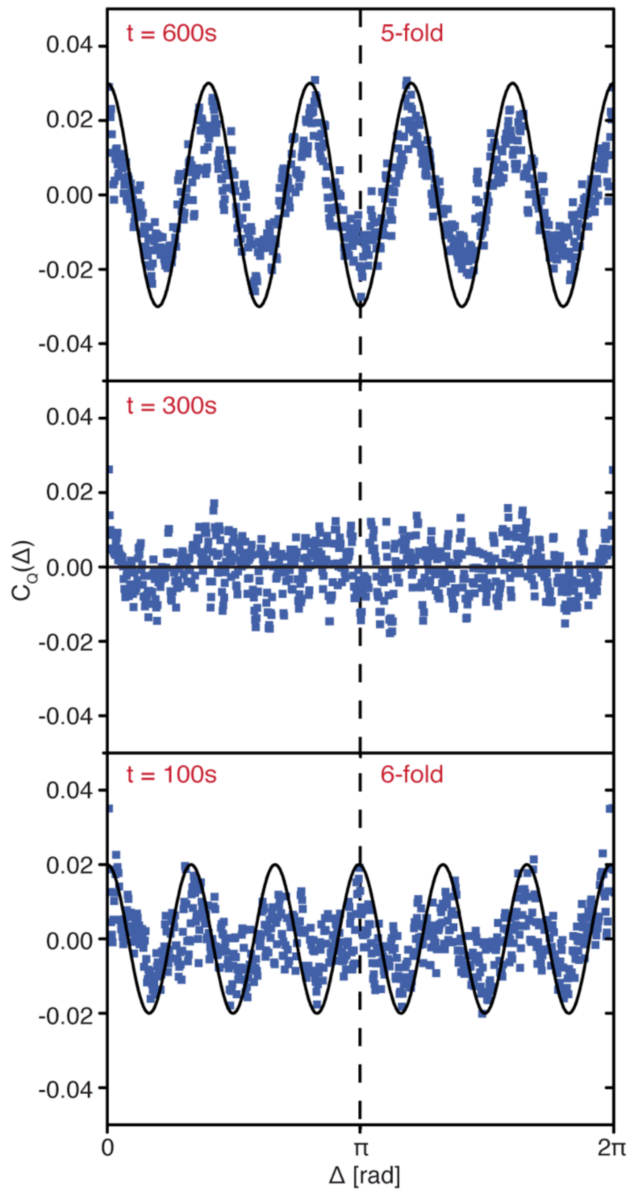
Cluster



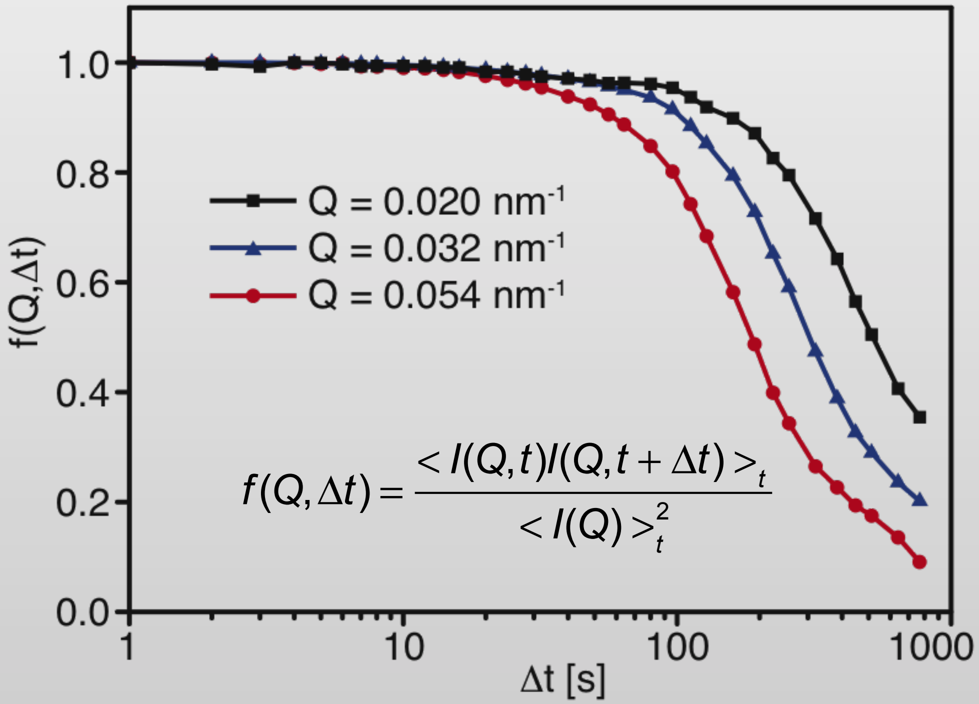
Time dependence of $C_Q(\Delta)$ in "fast" systems

Peter Wochner

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



Temporal auto-correlation function



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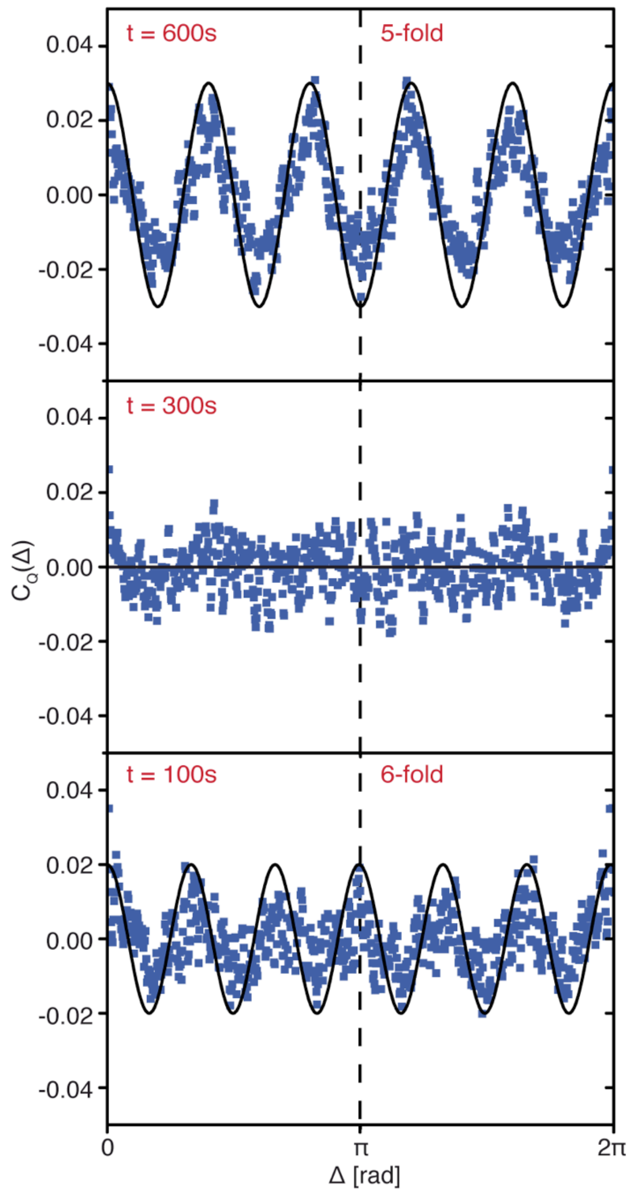
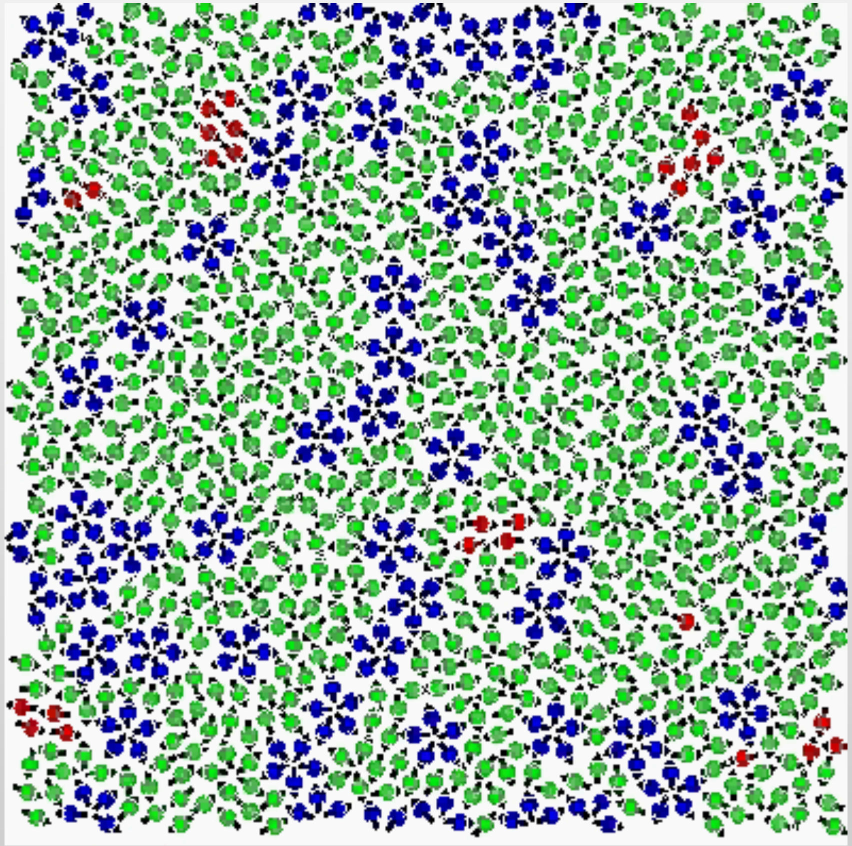
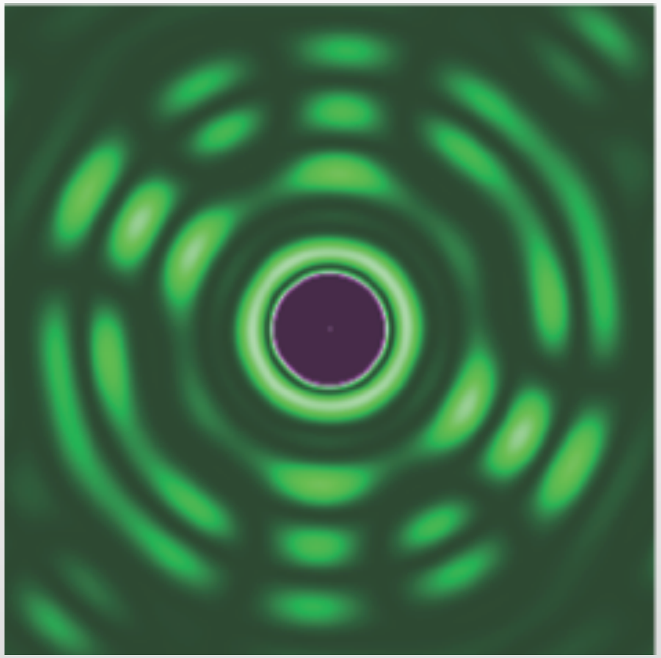


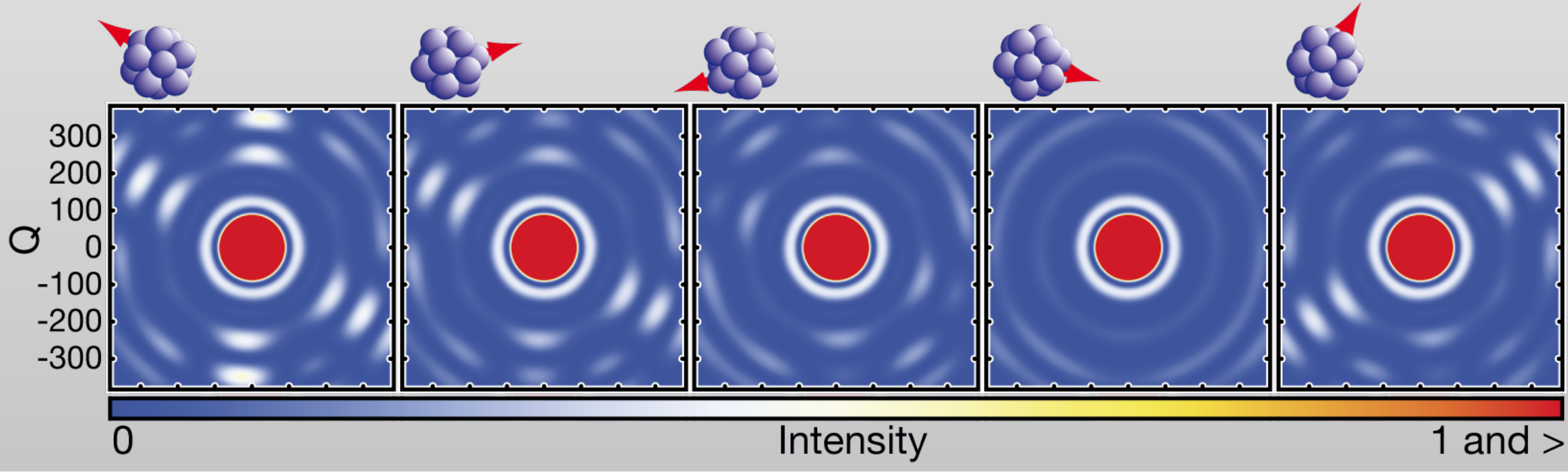


H.Shintani, H. Tanaka, Nature Physics **2**, 200 (2006)

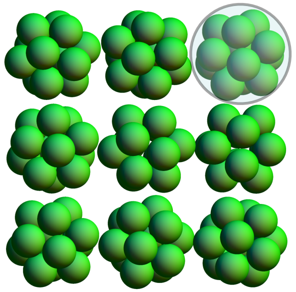
- **Single icosahedral cluster**
  - **Intensity in Q_x-Q_y plane**

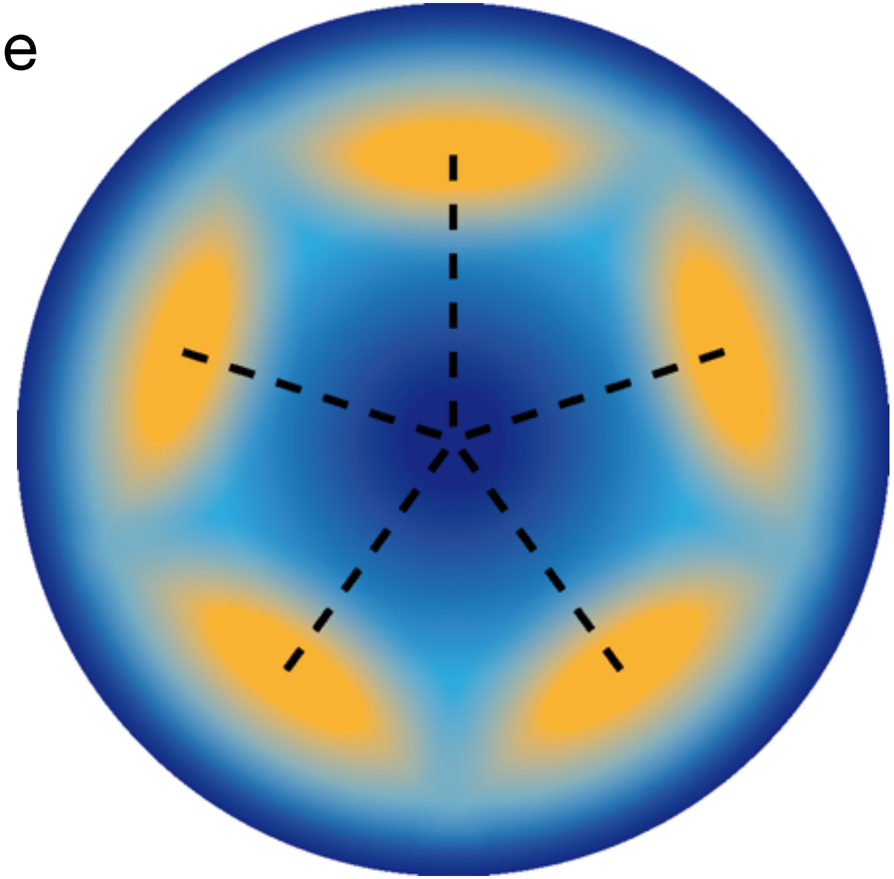


- **Wanted:** $< I(\varphi) I(\varphi + \Delta) >_{\varphi}$

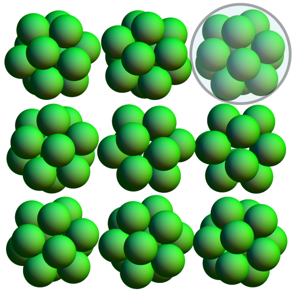


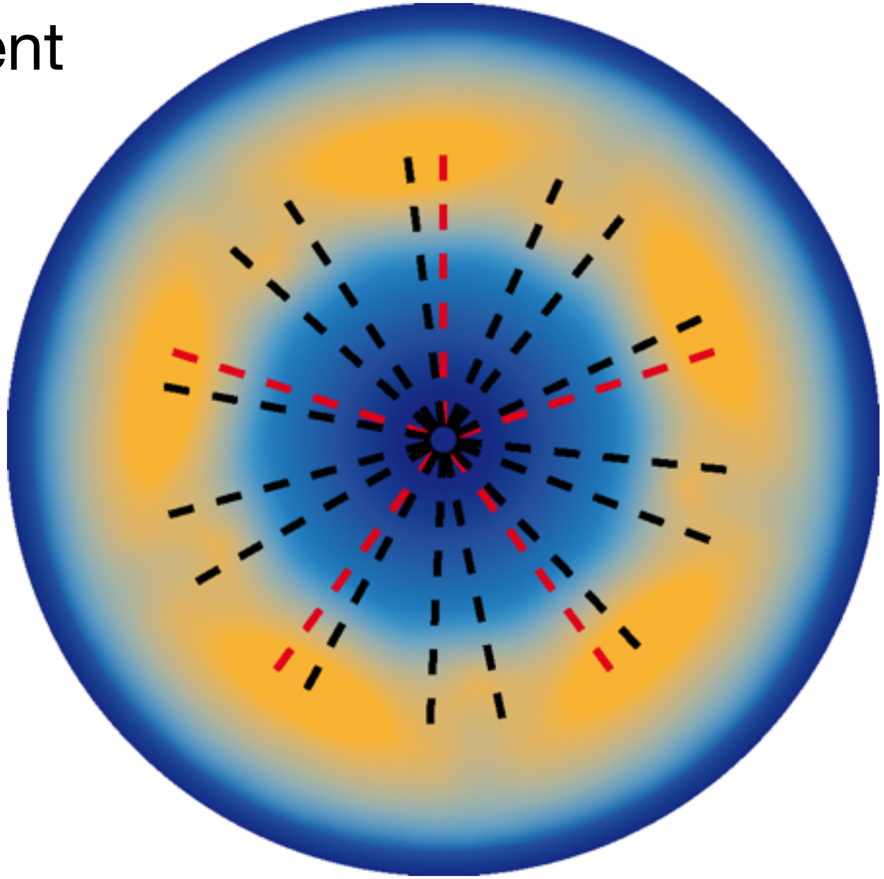
Single-molecule
diffraction



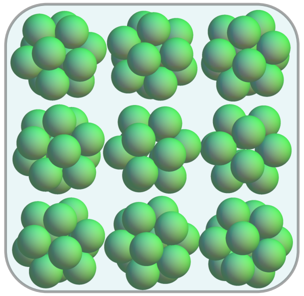


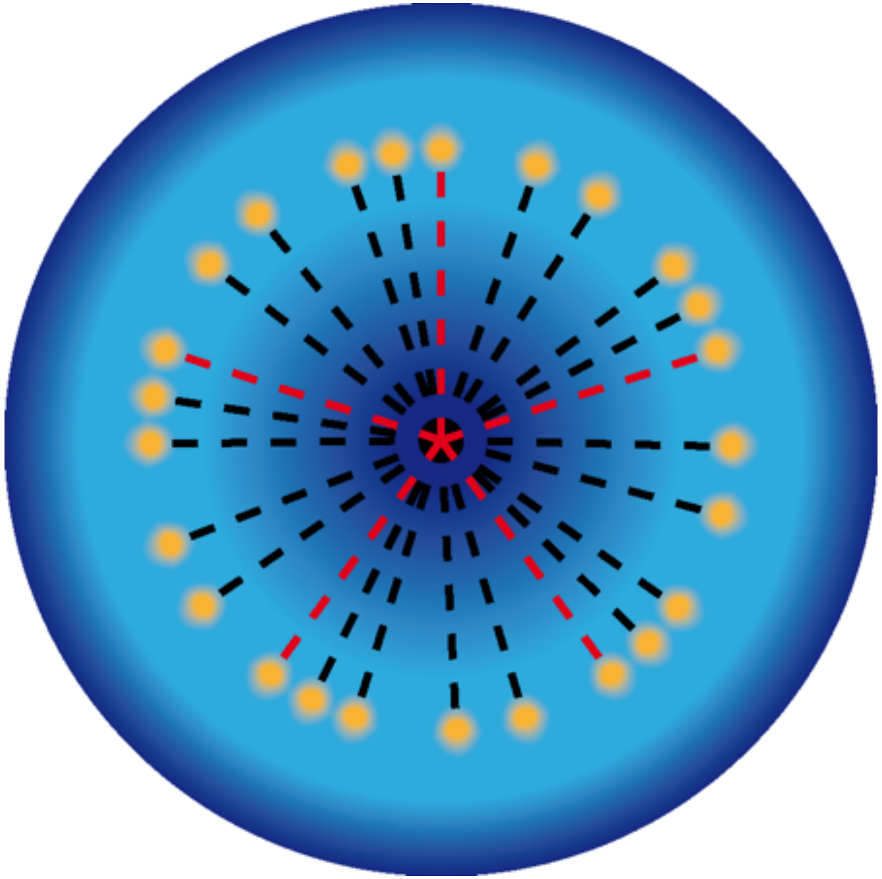
Partially coherent diffraction





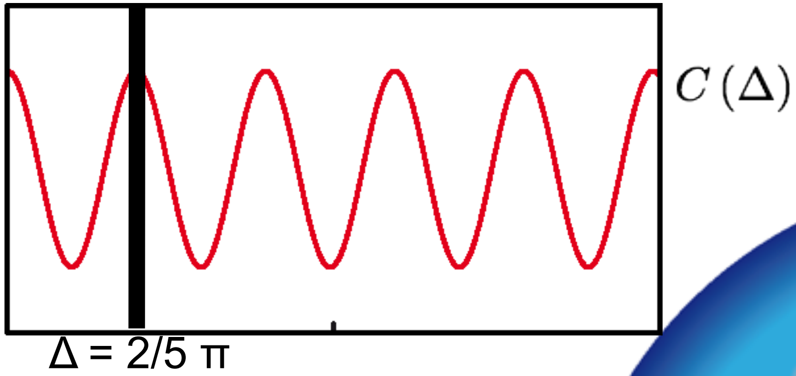
Coherent diffraction

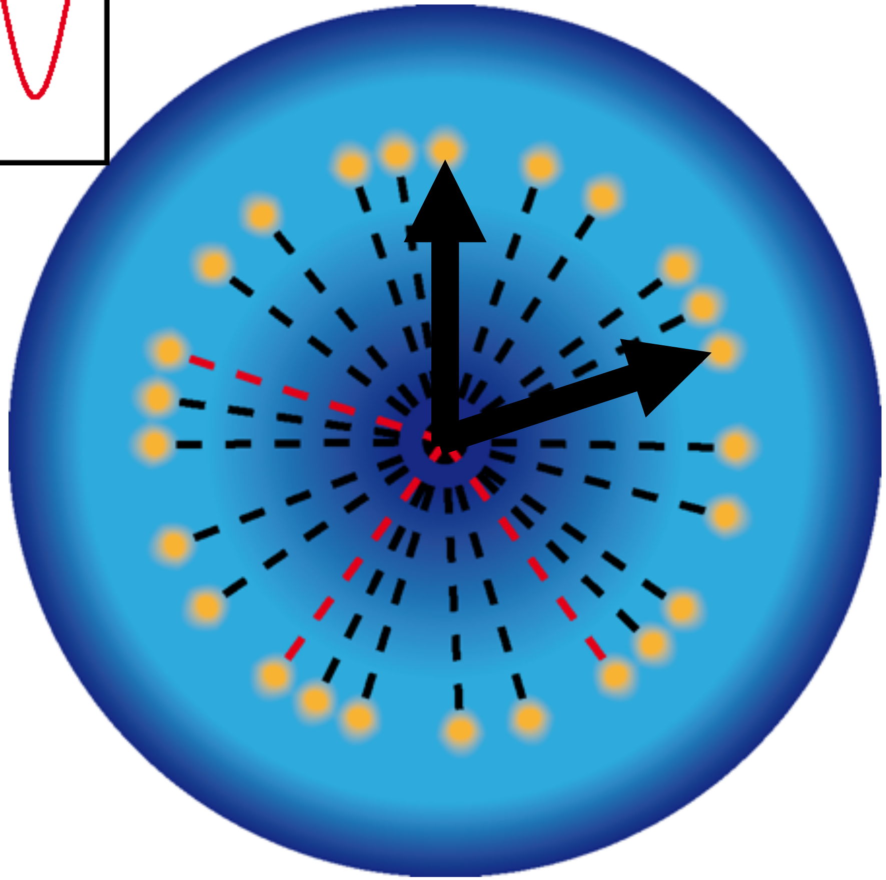




Speckle-Size ~ 1 / Beam-Size

= Volume of coherently illuminated sample


$C(\Delta)$
Δ = 2/5 π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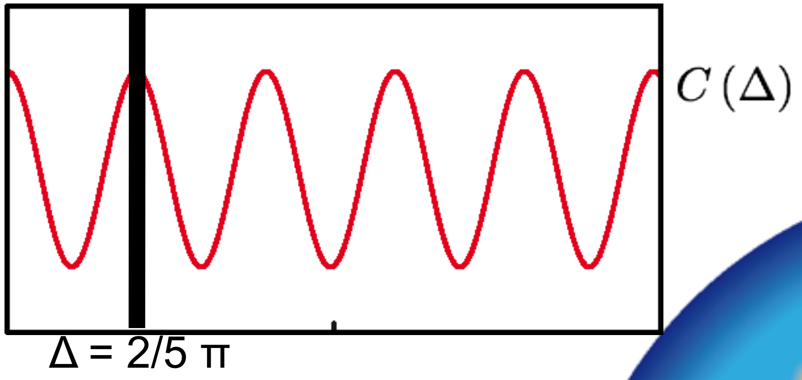
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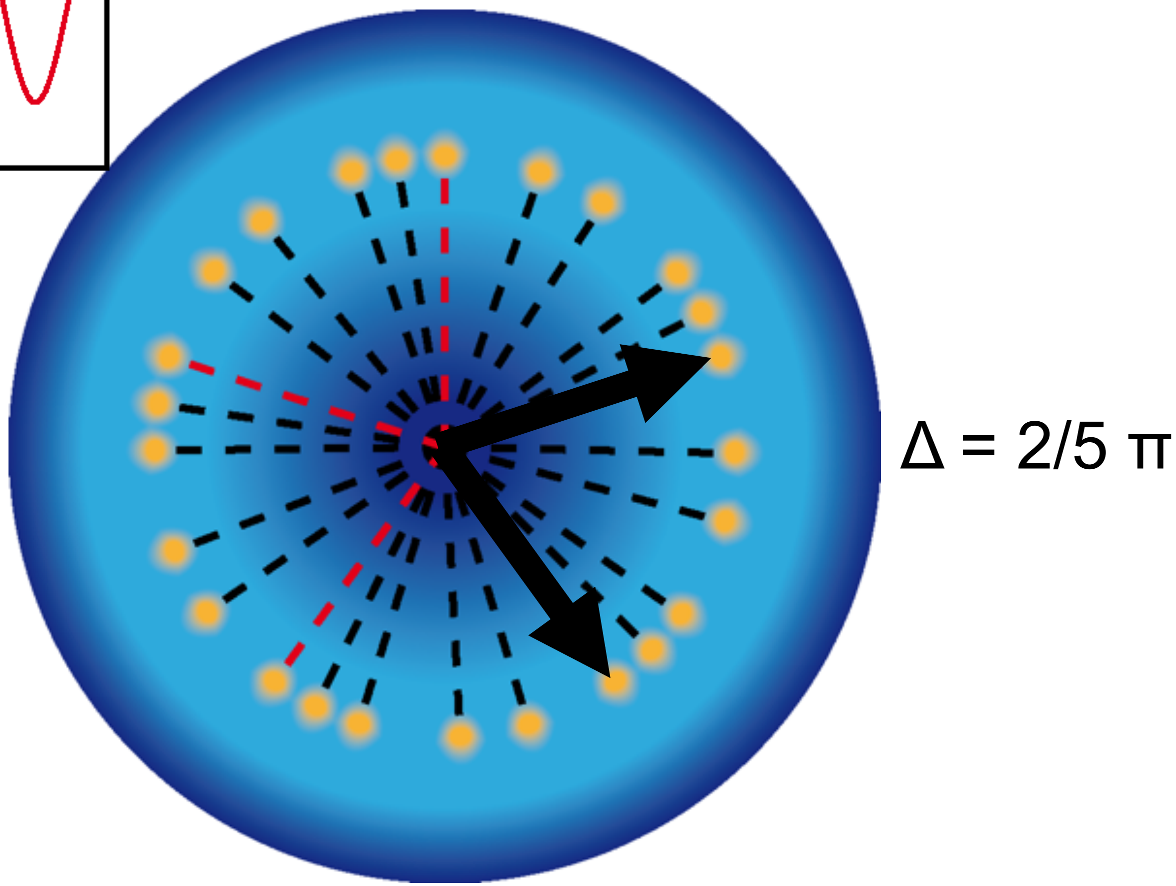
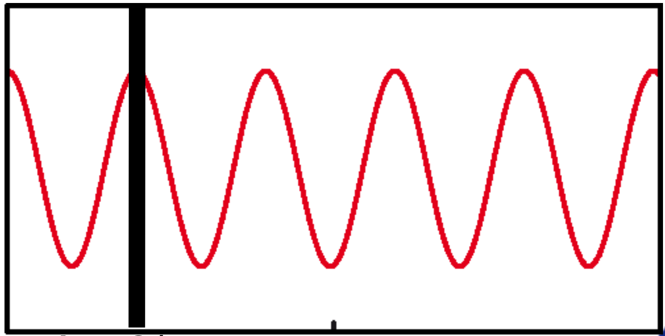

Δ = 2/5 π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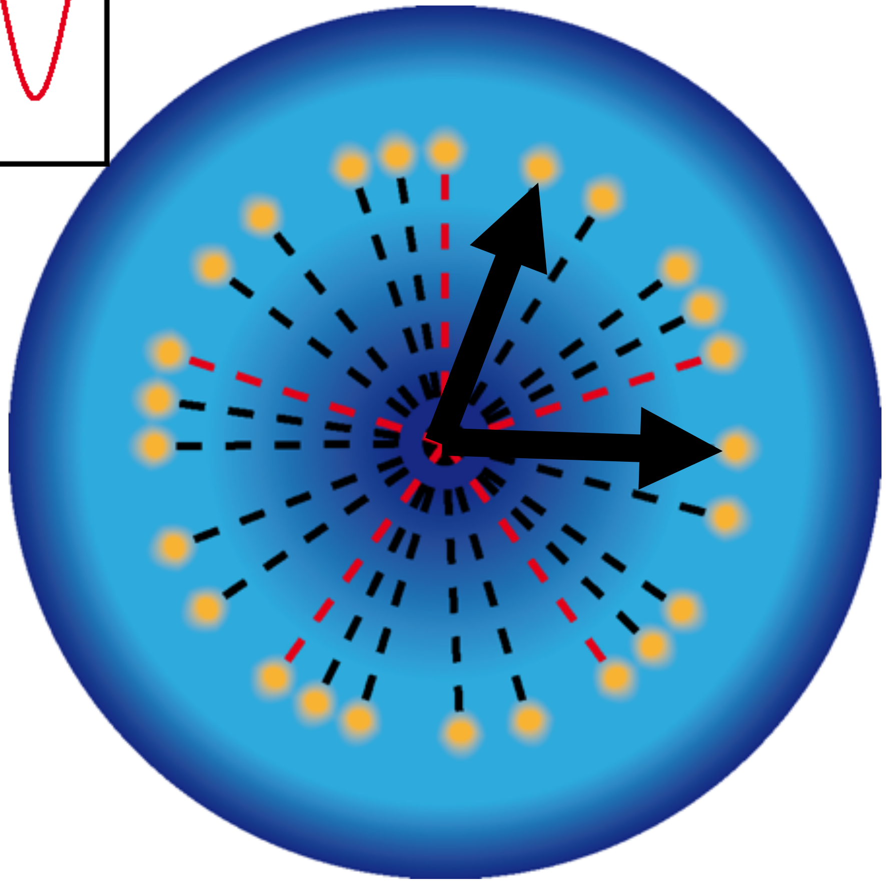
Δ = 2/5 π


Δ = 2/5 π

XCCA-averaging Considerations

Peter Wochner

MPI-MF DEPARTMENT DOSCH

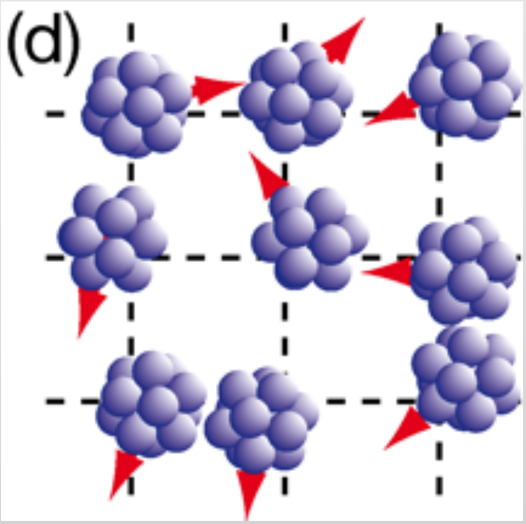
- Illuminated volume:
  - **10 μm x 10 μm x 800 μm ~ 6 x 10^6 PMMA particles**

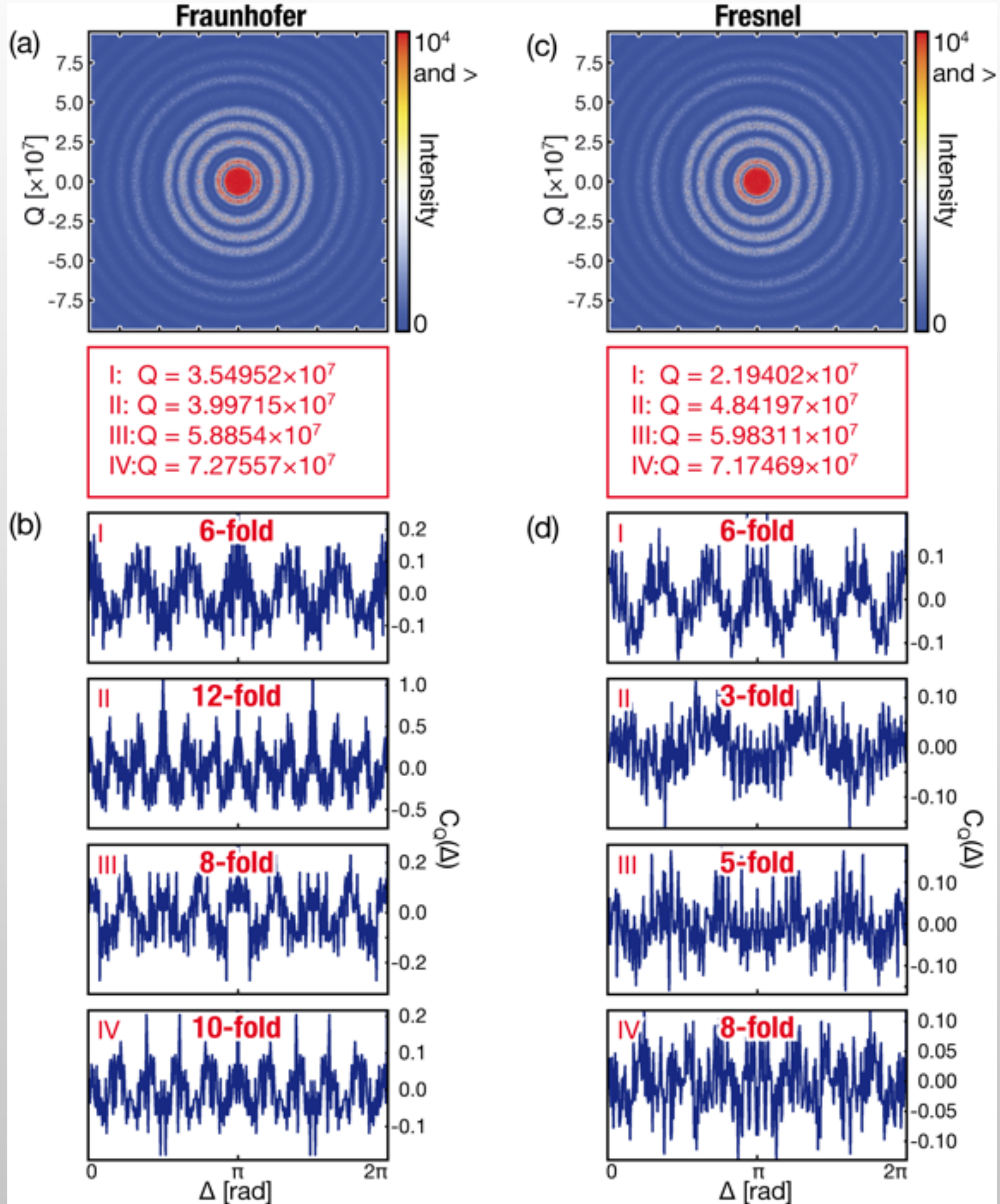
  $\longrightarrow$ **max. 500000 Icosahedra**

- XCCA symmetries: only subset of n-fold axes in beam direction contribute

- Analogy Powder Diffraction: Angular average selects subset of states lying on Debye-Scherrer Cone

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





Numerical Simulation

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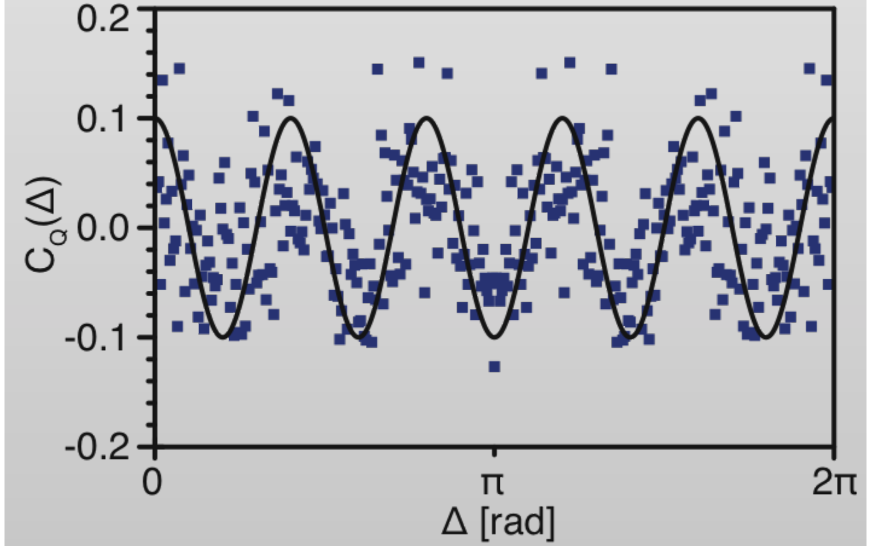
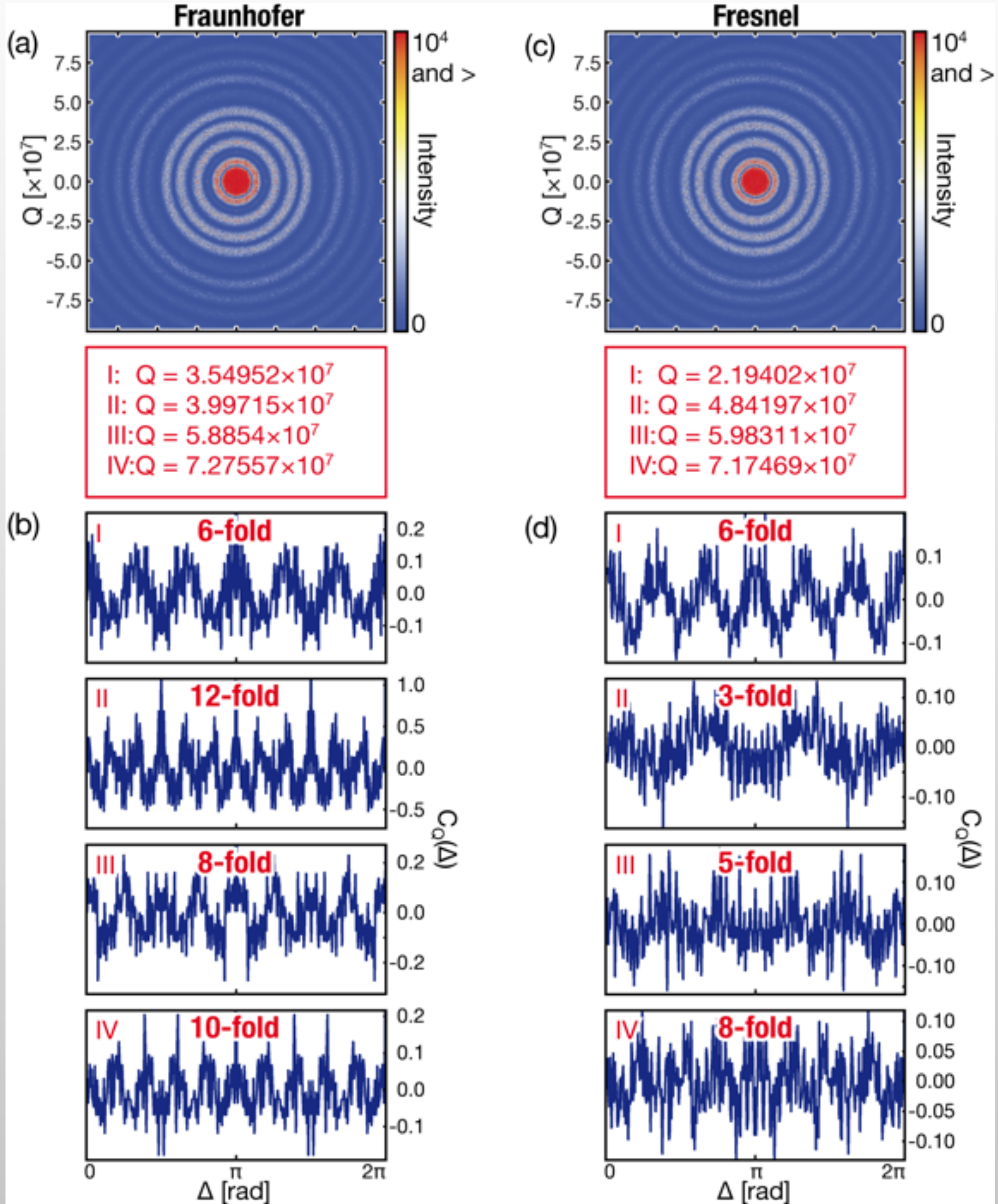
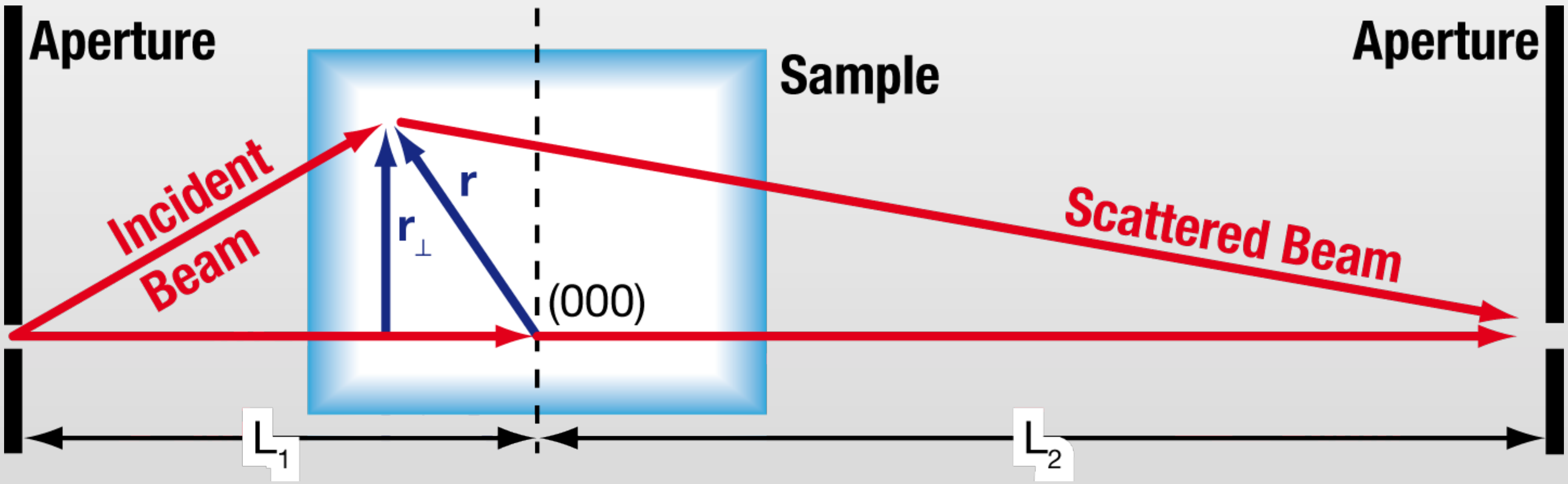
- **8000 random icosahedral cluster on a lattice**





Fresnel Approximation

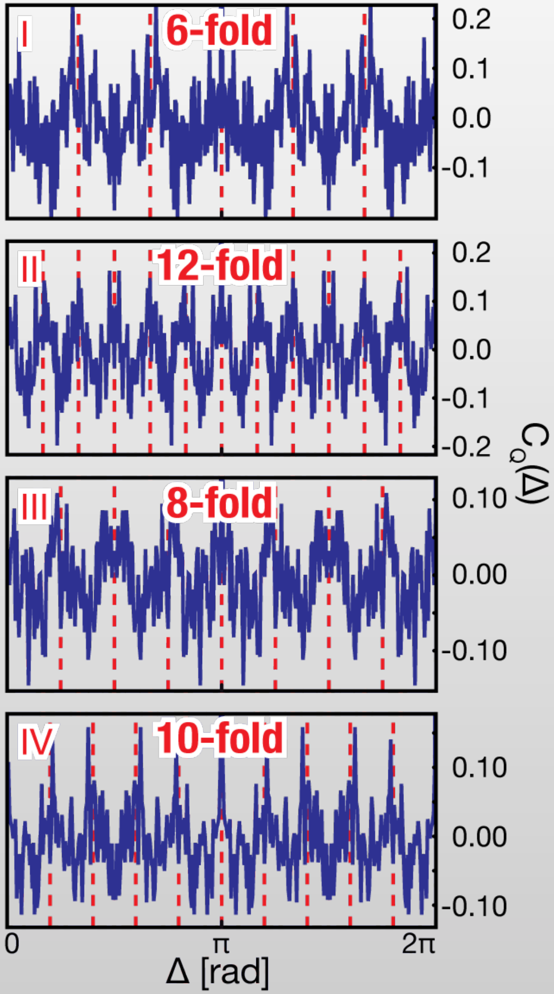
Peter Wochner



- **Fresnel Density: add imaginary phase factor**

$$\rho_F(\mathbf{r}) = \rho(\mathbf{r})\exp\left\{ i\frac{\Omega}{2}k_0\left(\frac{r_\perp^2}{L_1}+\frac{r_\perp^2}{L_2}\right)\right\}; \quad \Omega = 1+\Delta\lambda/\lambda$$

- **$C_Q(\Delta)$ with Fraunhofer approximation**

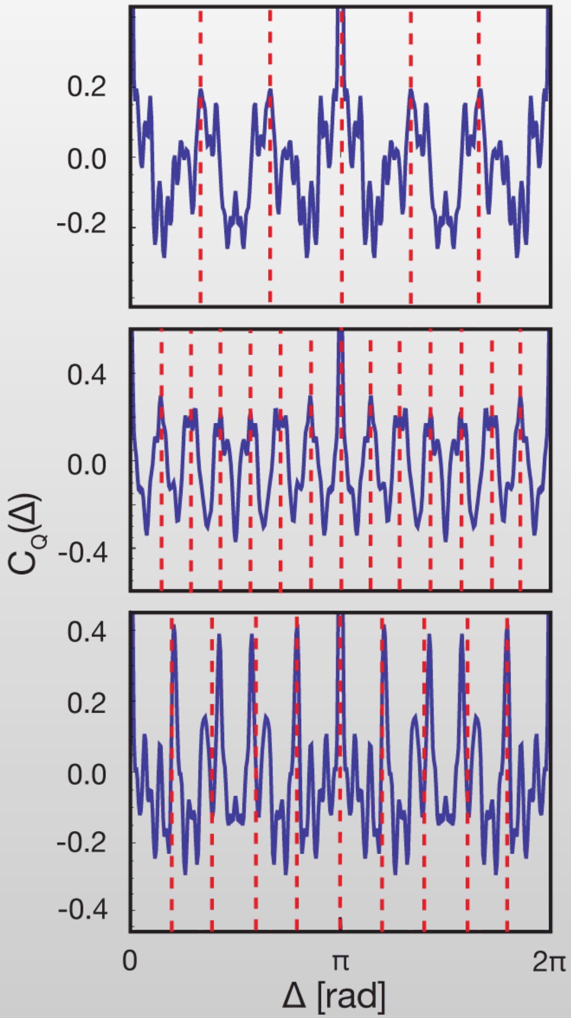


Q=16.43nm^{-1}

Q=18.07nm^{-1}

Q=18.44nm^{-1}

Q=18.79nm^{-1}



Q=13.14nm^{-1}

Q=15.35nm^{-1}

Q=13.50nm^{-1}

- **Mono-atomic glass**: Dzugutov potential
- 2•10^6 atoms in MD-simulation

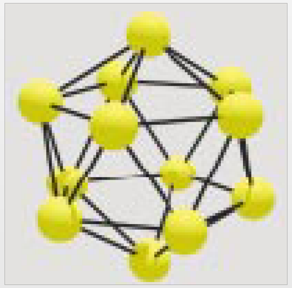
- **liquid H_2O**: 450000 particles SPC

Origin of Symmetries

Peter Wochner

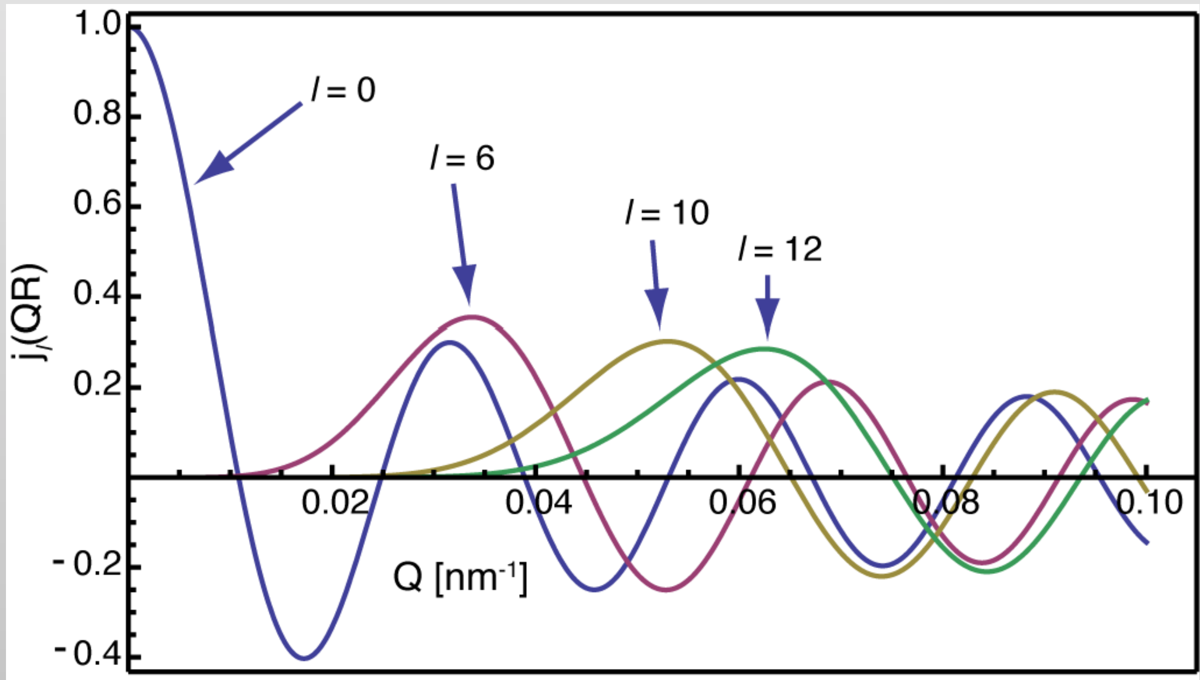
MPI-MF

- **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** ...



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

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



Summary and Outlook

- **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**

END

•Thanks to ESRF

•to A. Schofield for samples

•Thank you for your attention