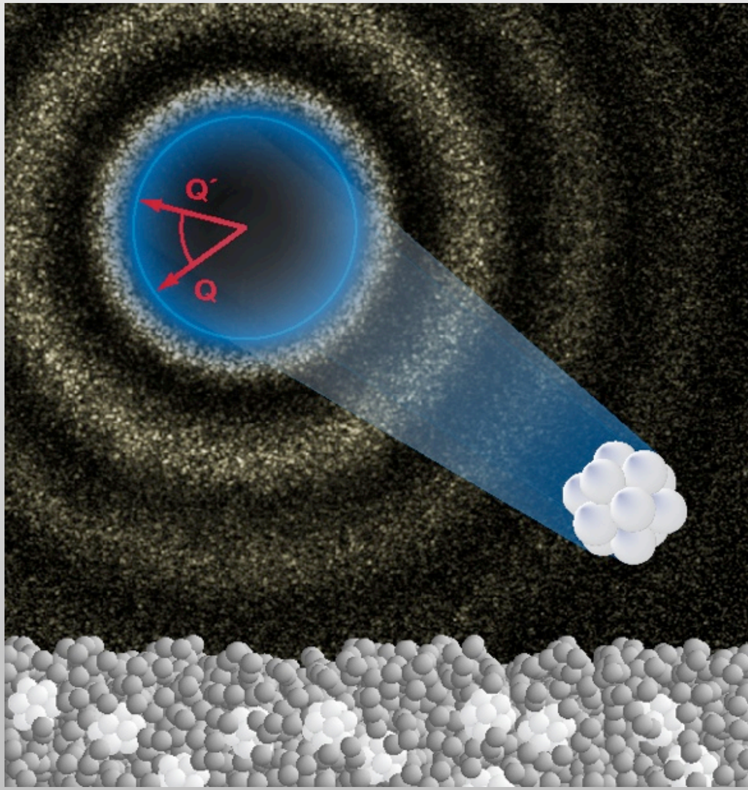
Hidden Symmetry in Disordered Matter

Peter Wochner



Disordered Materials in Synchrotron and XFEL X-ray light.
IX. Research Course on New X-ray Sciences February 17-19, 2010 at DESY, Hamburg

Acknowledgements

T. Demmer V. Bugaev A. Díaz Ortiz H. Dosch	MPI-MF
C. Gutt T. Autenrieth A. Duri G. Grübel	DESY
F. Zontone	ESRF
J. Roth	ITAP, University Stuttgart

Outline

- Motivation
- Structure Determination in Disordered Systems
- Properties of Glasses
- Higher Order Correlation Functions and XCCA
- Proof of Principle Experiment
- Results and Interpretation
- Conclusions and Outlook

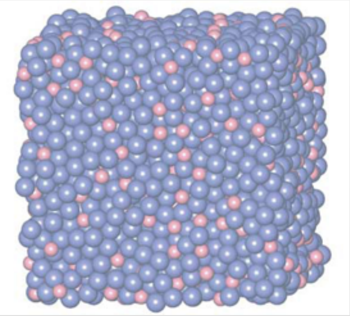
Motivation

Peter Wochner

- Materials of the future: disordered and far from thermal equilibrium

- Ultimate goal: living cell

- Already broad range of applications for amorphous materials:
  - from glassware to polymers
  - nano-particles
  - soft magnets with low coercivity and high electrical resistance
  - non-magnetic glassy steel with great strength
  - amorphous metals with high tensile strength and toughness, wear and corrosion resistance as well as high coefficient of restitution (shape memory).

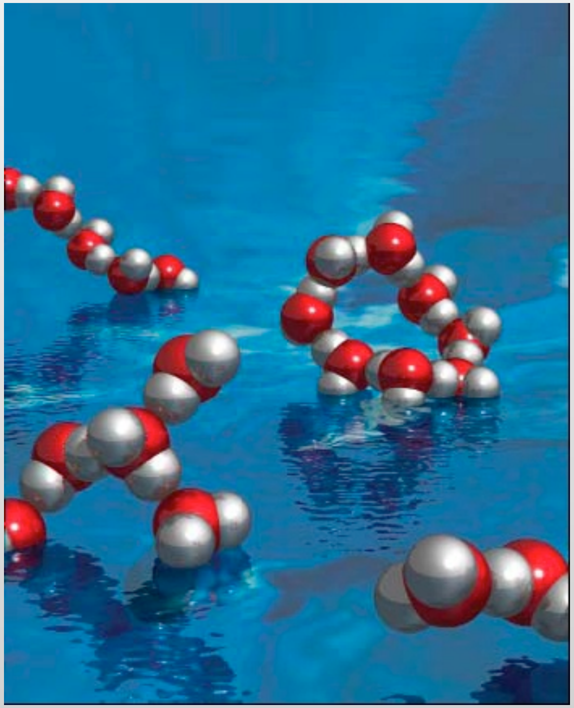


- Application of liquids: Numerous
  - Most chemical processing
  - Biological environment

- But: Knowledge of atomic structure not evolved significantly over the last 50 years.

Motivation

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



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

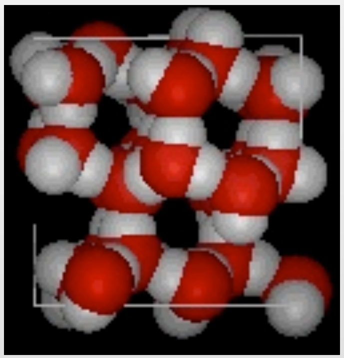
Y. Zubavicus, M. Grunze, Science **304**. 974 (2004)

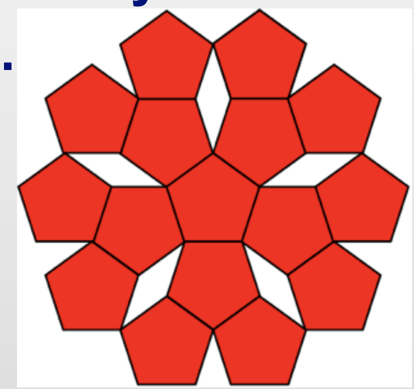
T. Head-Gordon, M.E. Johnson: “Tetrahedral structure or chains for liquid water”, PNAS (2006)
C. Huang et al.; "The Inhomogeneous Structure of Water at Ambient Conditions", PNAS (2009)

Difference: Crystal - Liquid/Glass

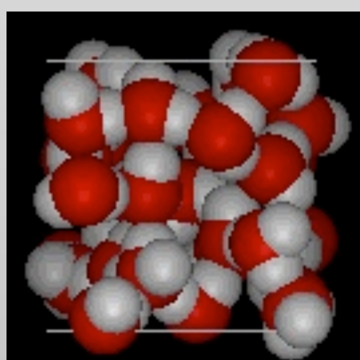
Peter Wochner

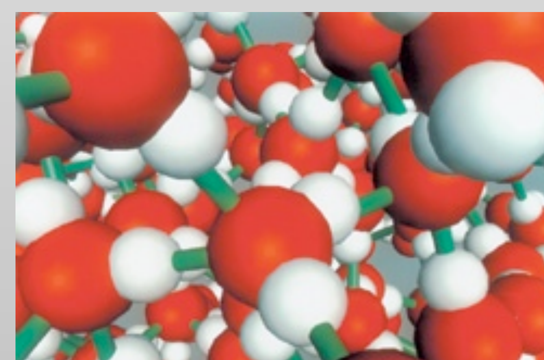
- **Crystal:**
- **Translational symmetry** ⟷ - only 2-, 3-, 4- & 6-fold rotational symmetry
  - NO 5-fold etc. symmetry





- **Liquid/Glass:**
- **NO translational symmetry, only local order** ⟷ ALL local rotational symmetries allowed

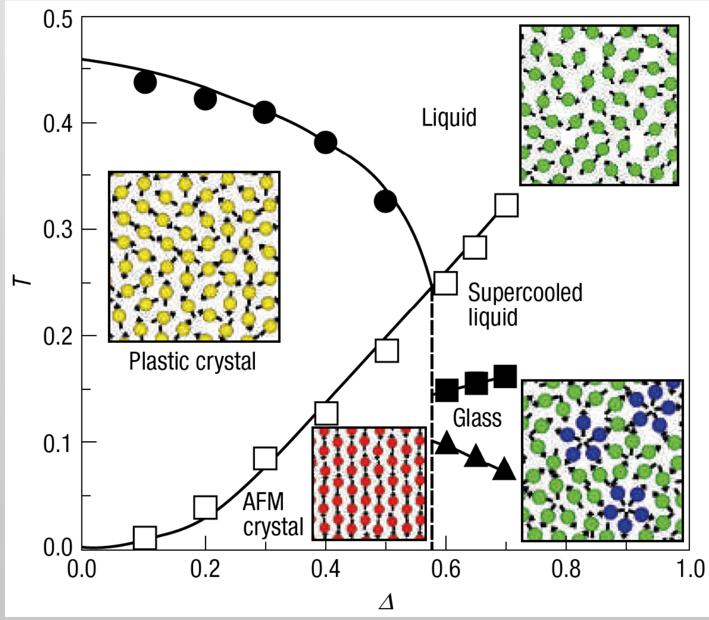




Molecular Glasses

- **2 popular glass forming scenarios:**
  - **tendency towards icosahedral order** with geometrical frustration: locally favored structures (LFS, icosahedral order) cannot fill up space
  - **tendency towards crystalline order**; frustration effect due to LFS (icosahedral short-range order) prevent crystallization

- **Microscopic insights so far only through simulation:**
  - e.g. spherical particles with directional anisotropy

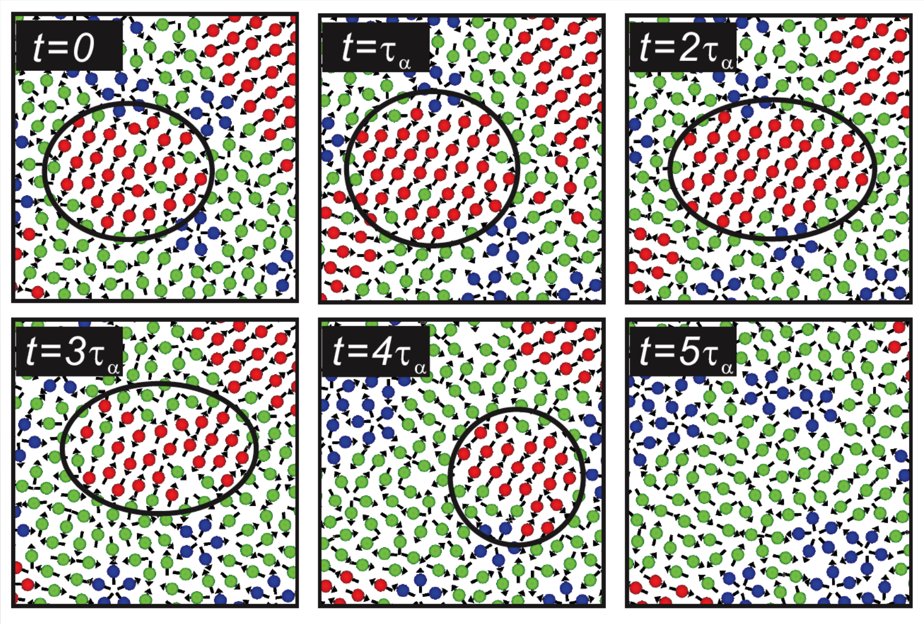


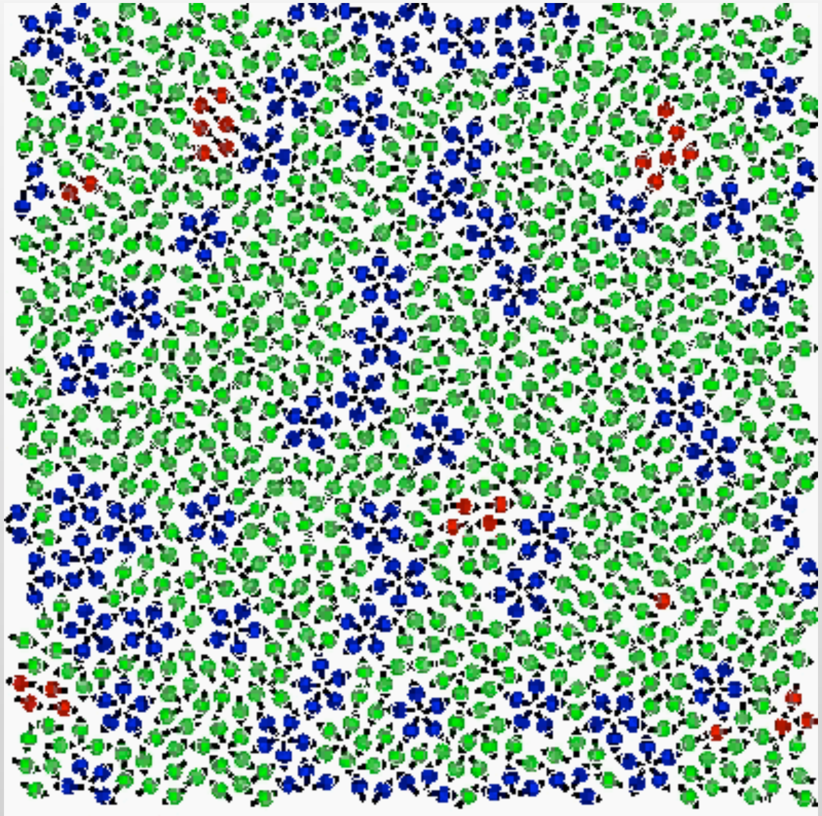
- 2-order-parameter model for liquid:
  - LFS (five-fold) and normal-liquid structure
- crystalline structure (hexagonal) key for supercooled state
- medium-range crystalline order and short-range bond order
- ‘dynamic heterogeneity’

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

Molecular Glasses

- temporal change of medium range crystalline order (MRCO)





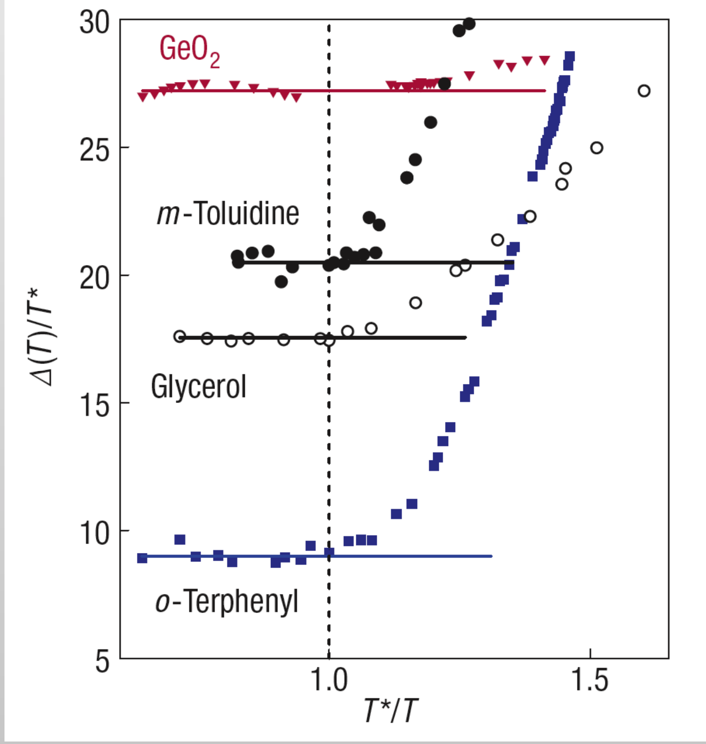
- weak frustration (strong fragility) → more MRCO (hexagonal)

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

Glass Dynamics

- **Glass transition**: most spectacular phenomenon in terms of dynamic range
- structural relaxation time τ_α increases 10^{15} by 30% change in T

- **Glassy questions:**
  - unique supermolecular length scale in supercooled liquids and polymers?
  - purely dynamic associated w/ ‘dynamic heterogeneities’?
  - or a corresponding thermodynamic correlation length?



✤ Strong glass formers (GeO_2):
  - slow relaxation, constant activation energy Δ

✤ ‘fragile’ glass formers (*ortho*-terphenyl)
  - fast relaxation, super-Arrhenius behaviour

S.A. Kivelson, G. Tarjus, Nature Materials **7**. 831 (2008)

- **Numerical experiments:**
  - dynamical heterogeneities:
    - long-lived dynamical structures
    - spatial correlations between temporarily localized (caged) particles
    - typical length scale , typical relaxation time (α, β)
  - decoupling of diffusion and relaxation

- **Light scattering (see L. Cipelletti, "Dynamical Heterogeneity")**

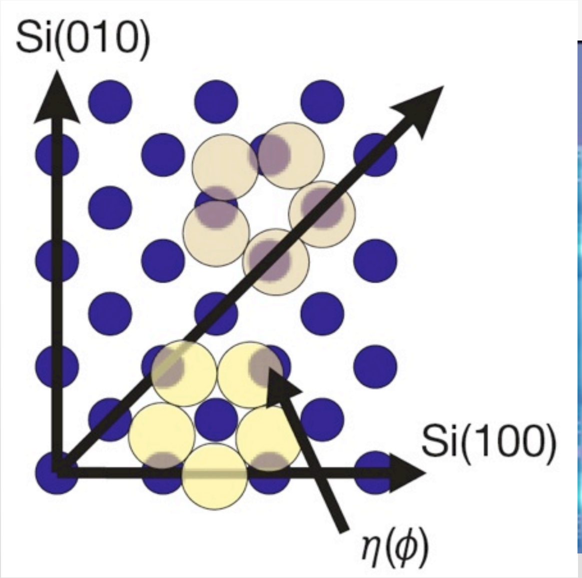
- **Theoretical description: (Parisi, Franz, Donati, Glotzer)**
  - Glass transition: freezing of density fluctuations $g_2(\mathbf{r}) = \left\langle \left(\rho(\mathbf{r}) - \rho_0\right)\left(\rho(0) - \rho_0\right) \right\rangle$
  - dynamical heterogeneities and correlation length treated as fluctuation of g_2:

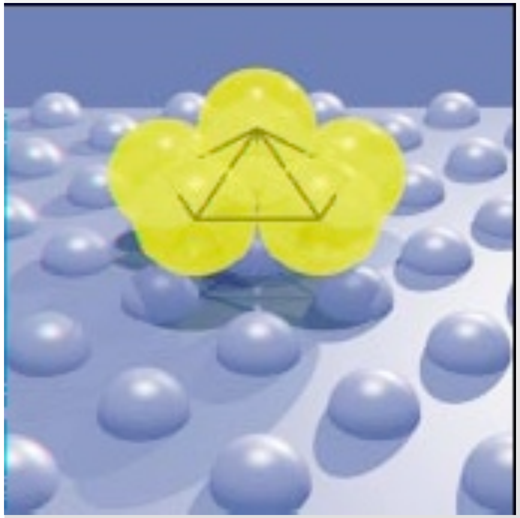
$$g_4(\mathbf{r}) = \left\langle \left[\left(\rho(\mathbf{r}) - \rho_0\right)\left(\rho(0) - \rho_0\right) \right]^2 \right\rangle - \left\langle \left(\rho(\mathbf{r}) - \rho_0\right)\left(\rho(0) - \rho_0\right) \right\rangle^2$$

Experimental Evidence

Peter Wochner

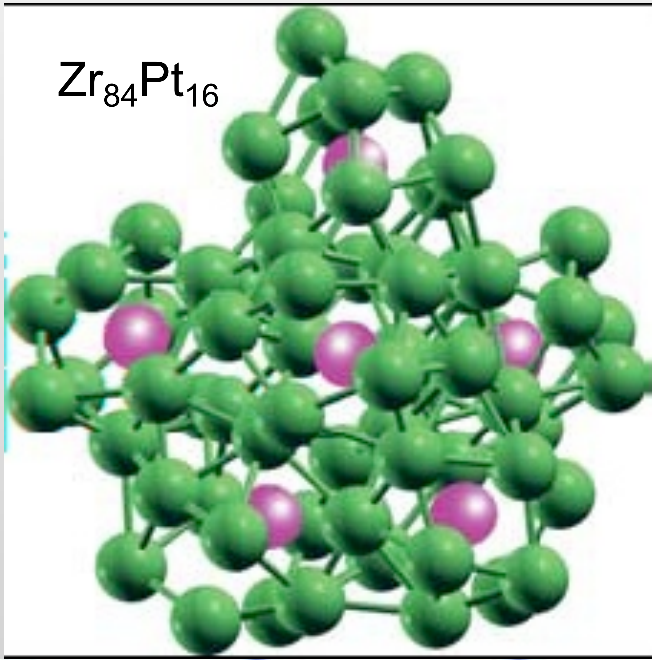
1. Five-fold symmetry in liquid Pb on Si(100)

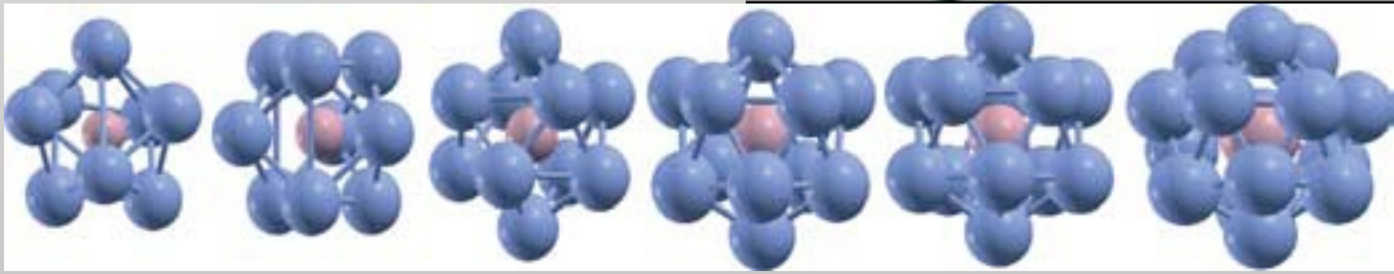




Reichert et al., Nature **408**. 839 (2000)

2. Short/medium-range order in metallic glasses (Kasper polyhedra)

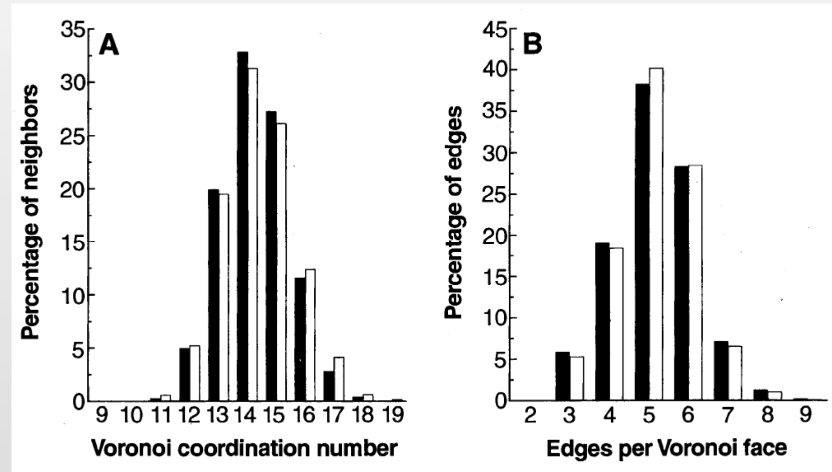




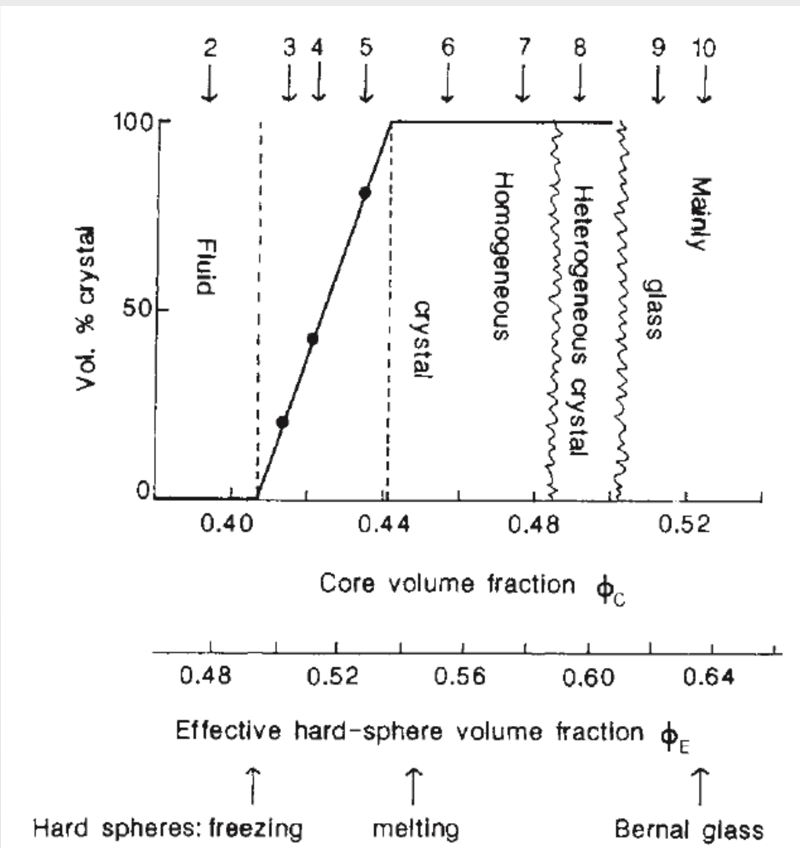
H.W. Sheng et al., Nature **439**. 419 (2006)

Colloidal Glasses

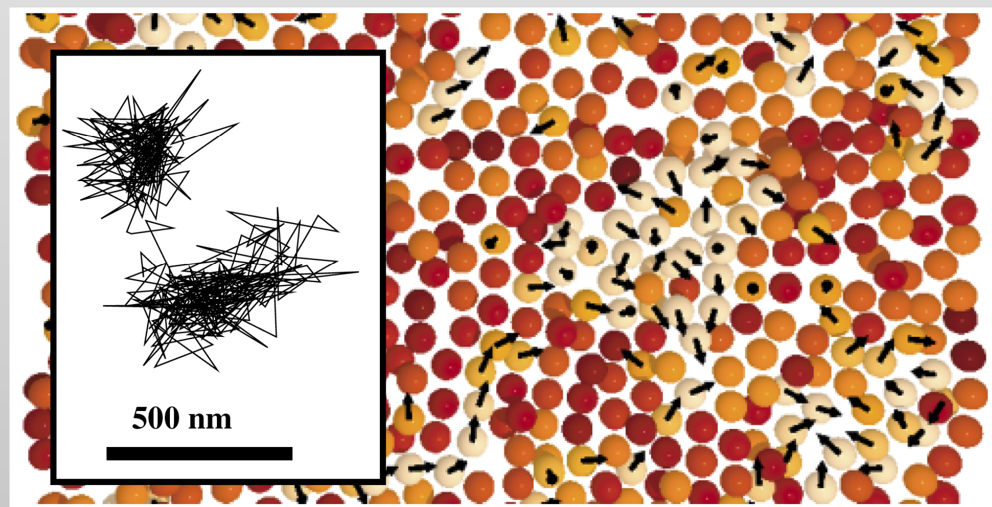
- nearly hard colloidal spheres (PMMA)
- ‘soft’ spheres (charge stabilized silica spheres)
- Thermodynamic variable: volume fraction



A. v. Blaaderen, P. Wiltzius, Science **270**, 1177 (1995)

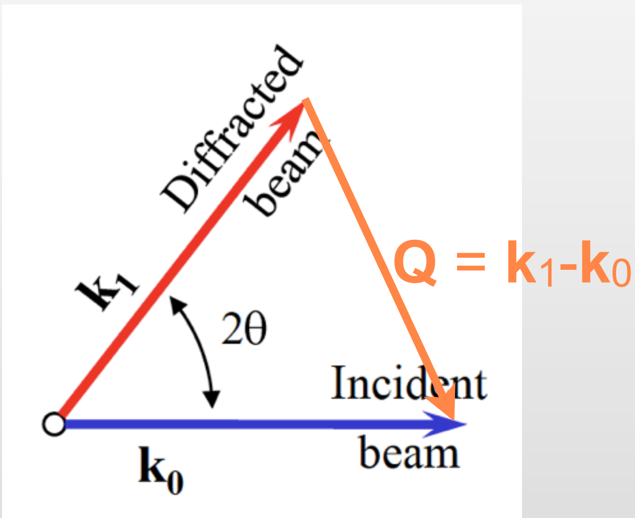


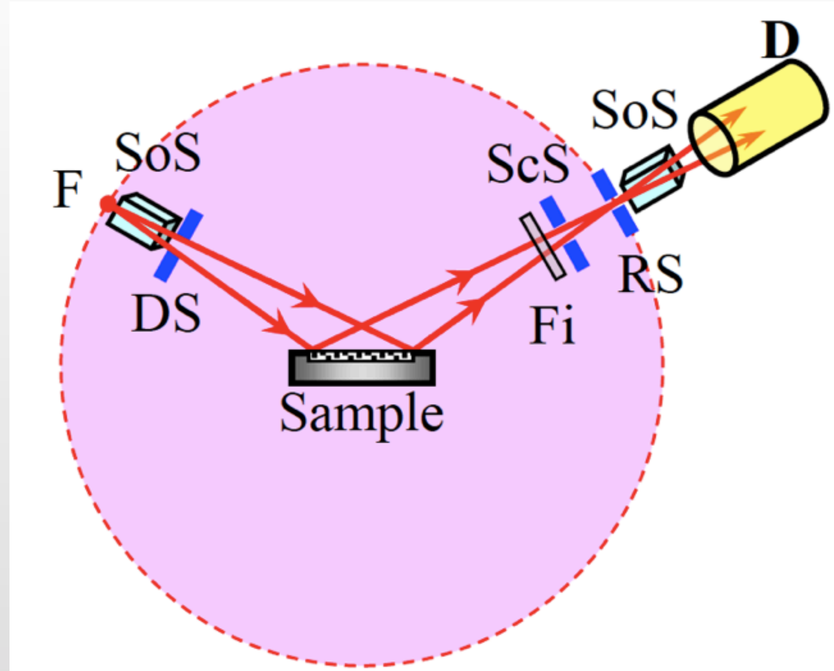
P.N. Pusey, W. van Megen, Nature **320**, 340 (1986)



E.R. Weeks, D.A. Weitz, PRL **89**, 095704 (2002)

Diffraction experiment:



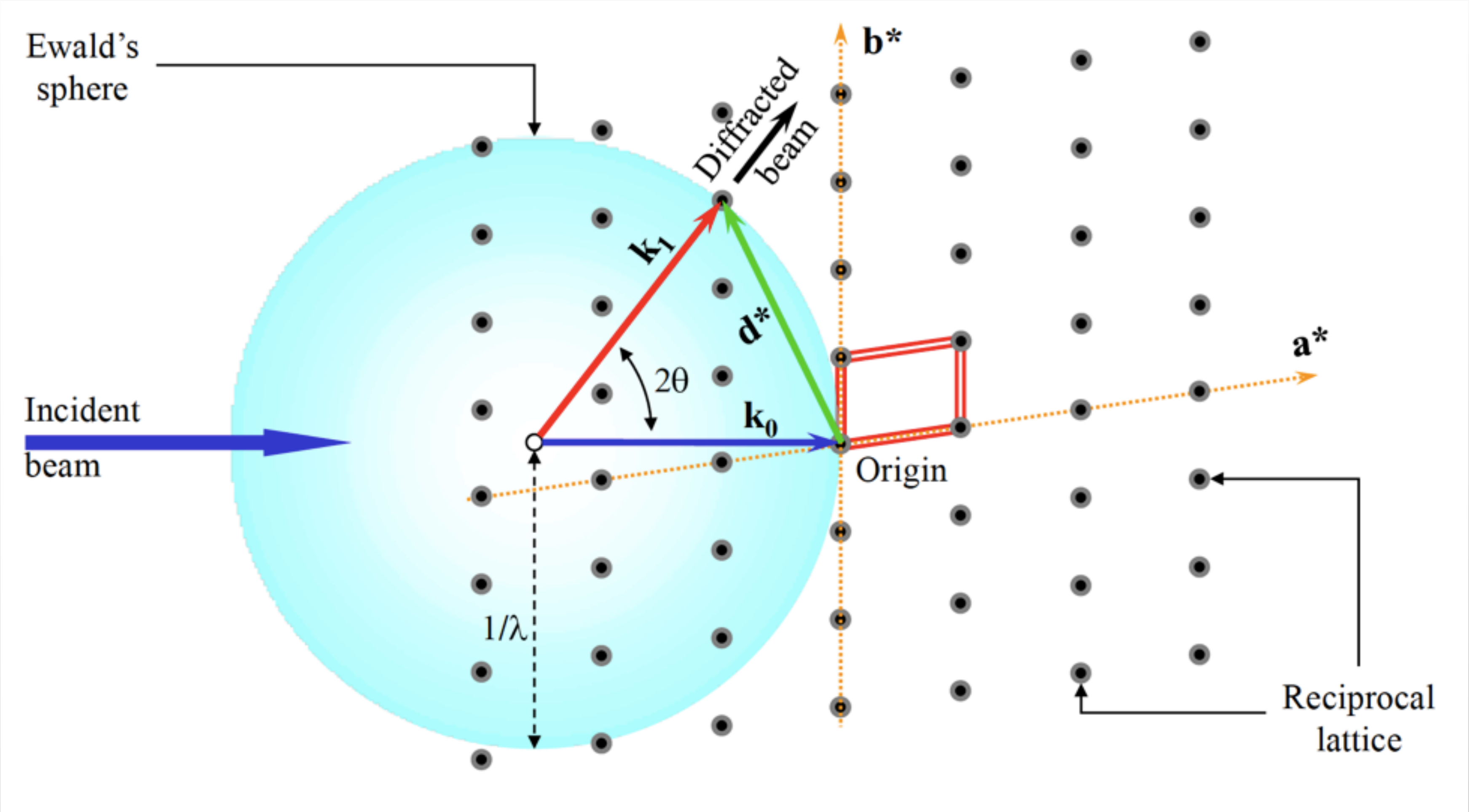


Traditional approach:

- **Intensity** $I(\mathbf{Q}) = \left|f_a(\mathbf{Q})\right|^2 \cdot N \cdot S(\mathbf{Q})$ **with** $S(\mathbf{Q}) = \left\langle \left| \int \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r} \right|^2 \right\rangle$
- **Fourier transform of single particle density function** $\rho(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{R}_i)$
- **Ensemble or configuration (and time) average <...>**

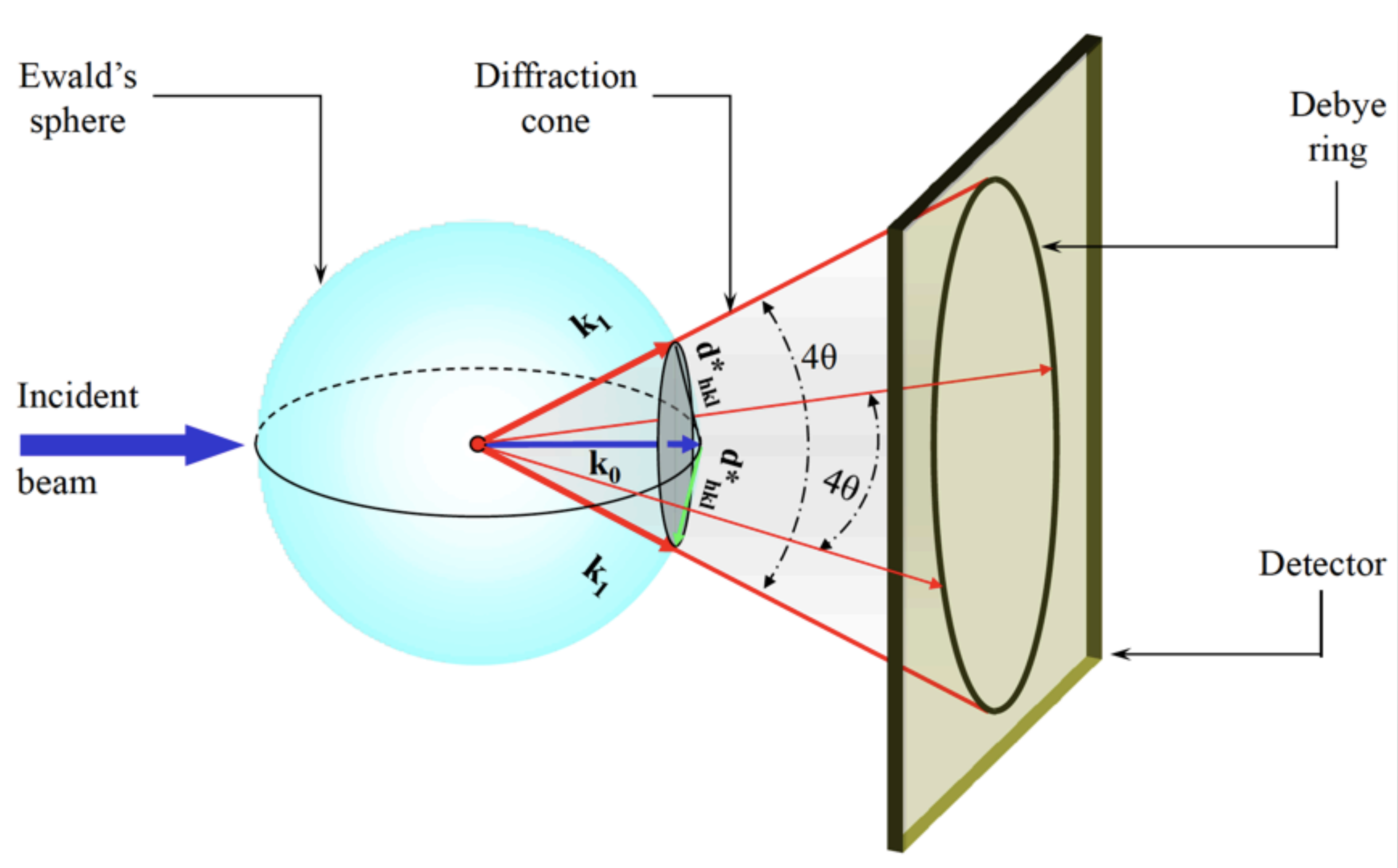
Single Crystal

Peter Wochner



Bragg's Law: d* = k$_1$-k$_0$ reciprocal lattice vector

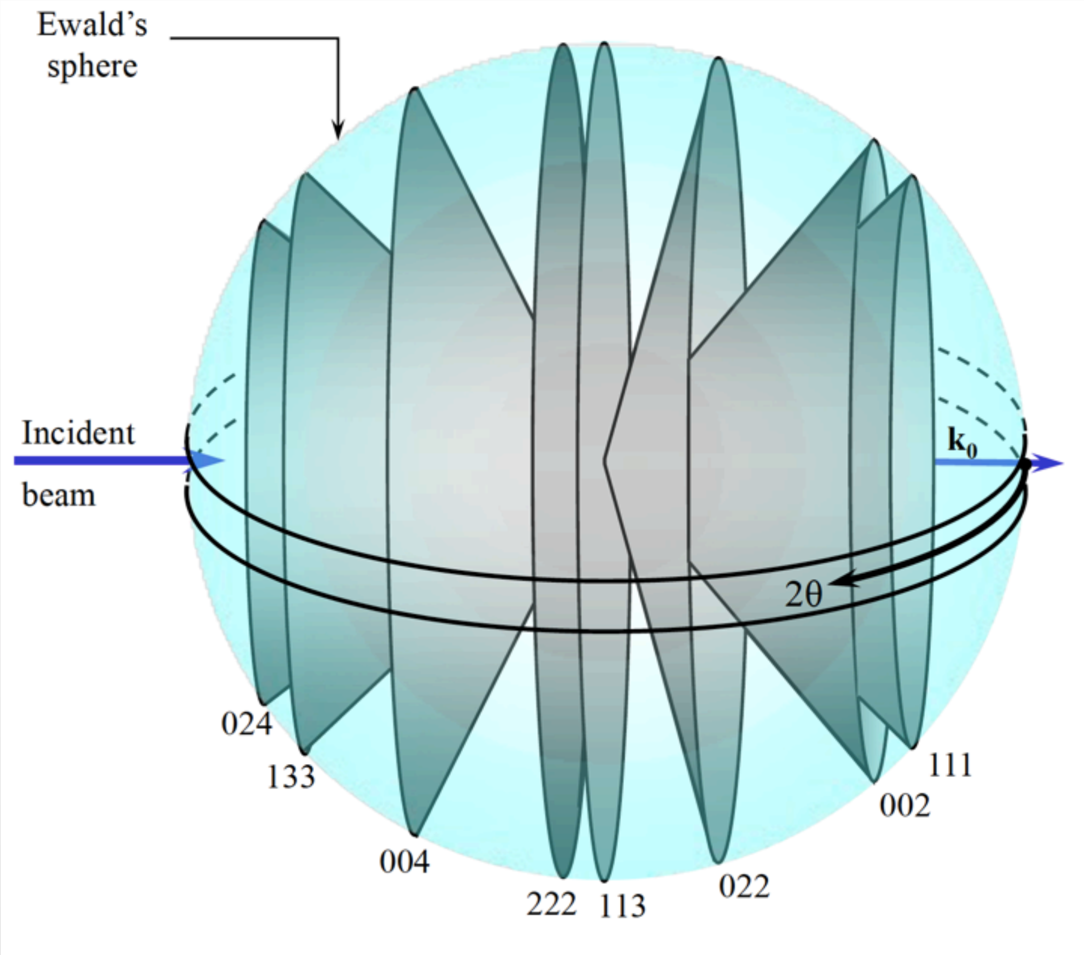
Vitalij K. Pecharsky • Peter Y. Zavalij
Fundamentals of Powder Diffraction and Structural Characterization of Materials.
Springer © 2008
Second Edition



spherically averaged crystallite orientations

Vitalij K. Pecharsky • Peter Y. Zavalij
Fundamentals of Powder Diffraction and Structural Characterization of Materials. Springer © 2008 Second Edition

Powder diffraction



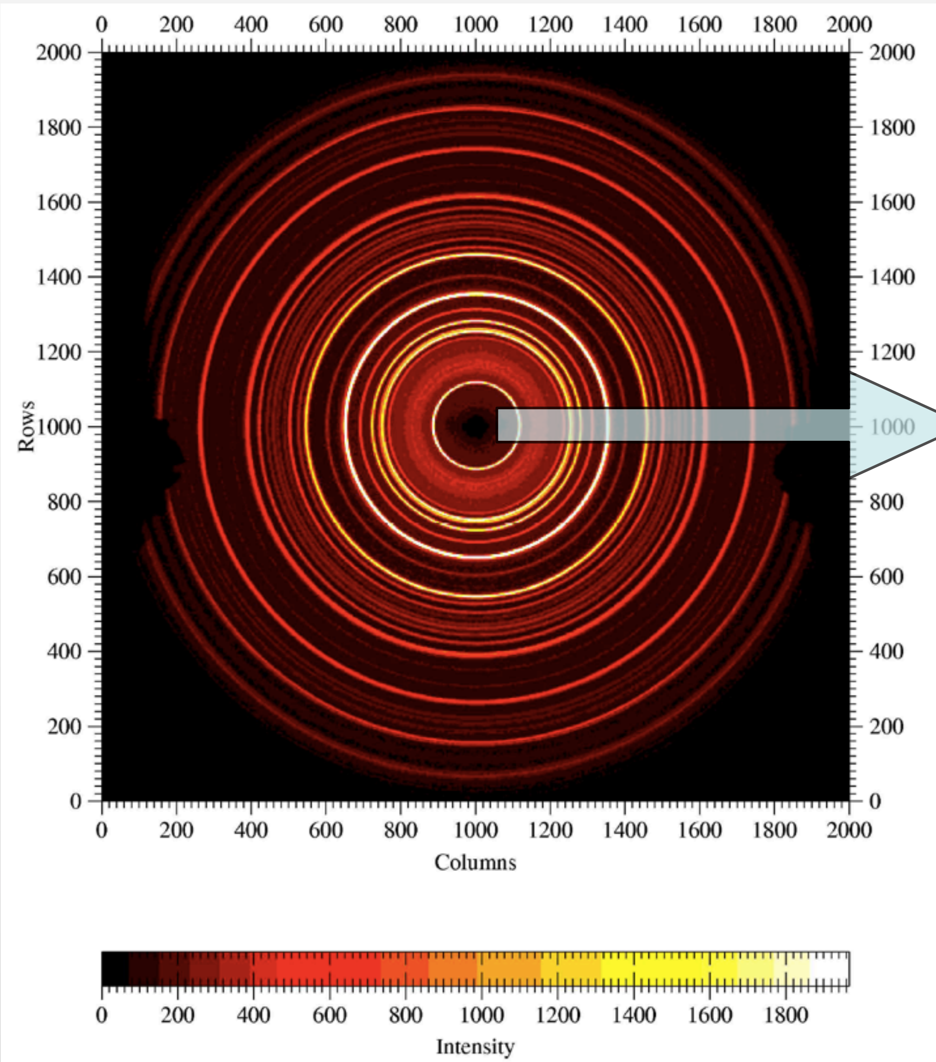
Debye-Scherrer Rings

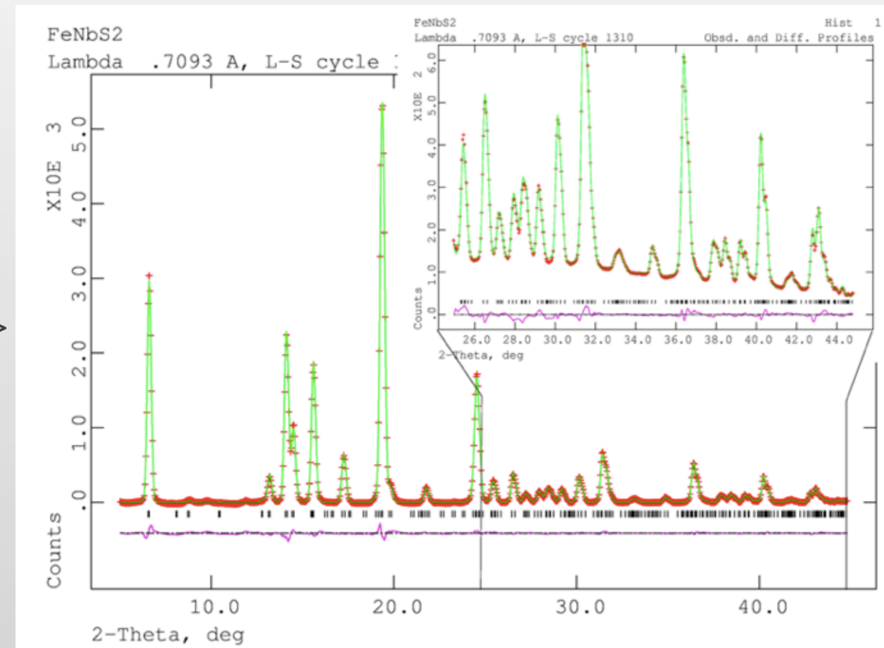
Vitalij K. Pecharsky • Peter Y. Zavalij
Fundamentals of Powder Diffraction and Structural Characterization of Materials.
Springer © 2008
Second Edition

Powder diffraction

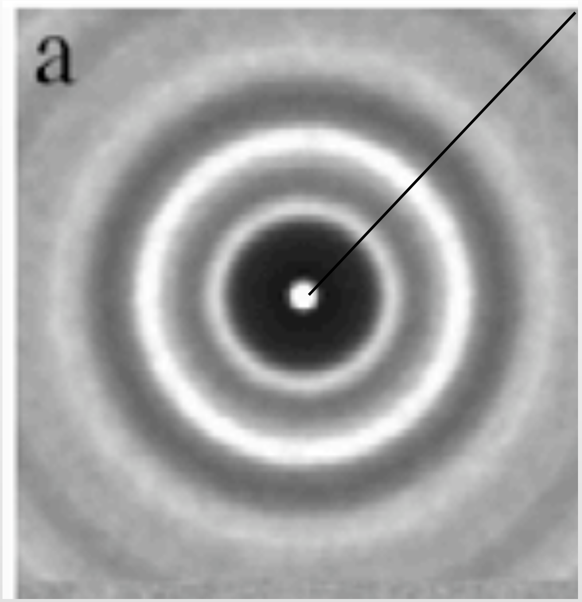
Peter Wochner

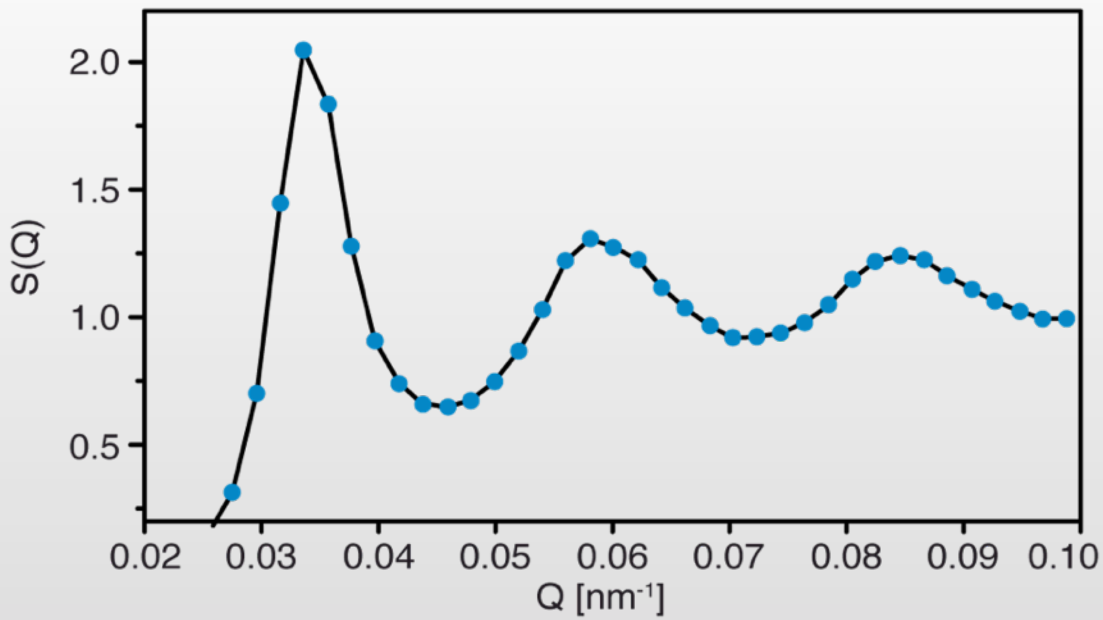
- **Typical diffraction image (2D-detector)**





S. Vogel et al., Adv. X-ray Anal. **45**, 31 (2002)





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

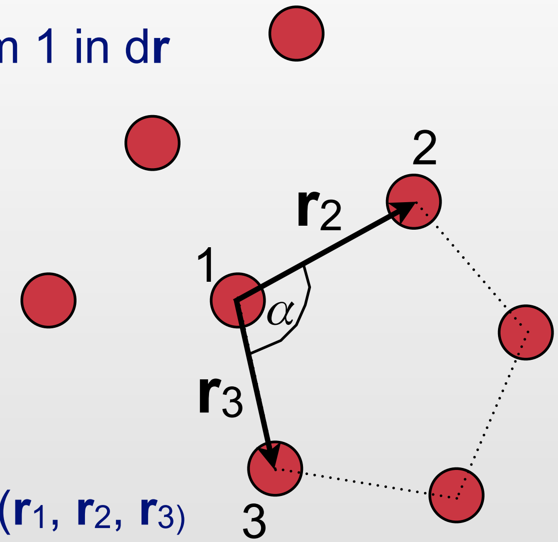
$$S(\mathbf{Q}) = 1 + \int (g_2(\mathbf{r}) - 1) e^{i\mathbf{Q}\cdot\mathbf{r}}\, d\mathbf{r}$$

- Major breakthrough: beyond 2-point correlation functions

N-Point Correlation Function

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

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

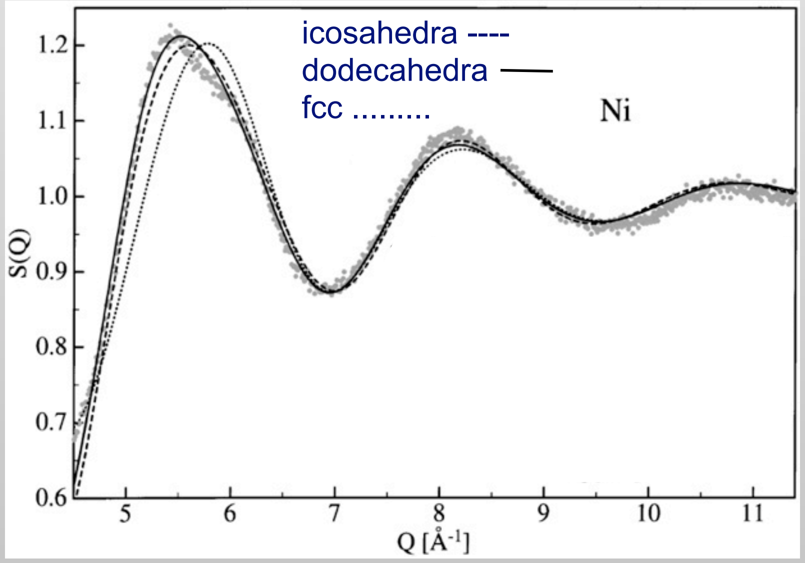


- $g_2(\mathbf{r})$ independent of bond angles

- 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)

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

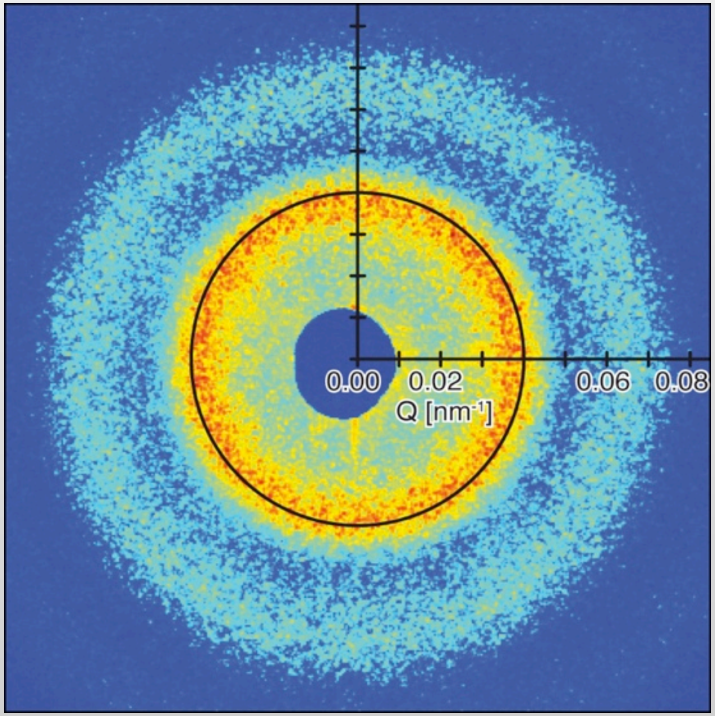
X-ray Cross-Correlation Analysis XCCA

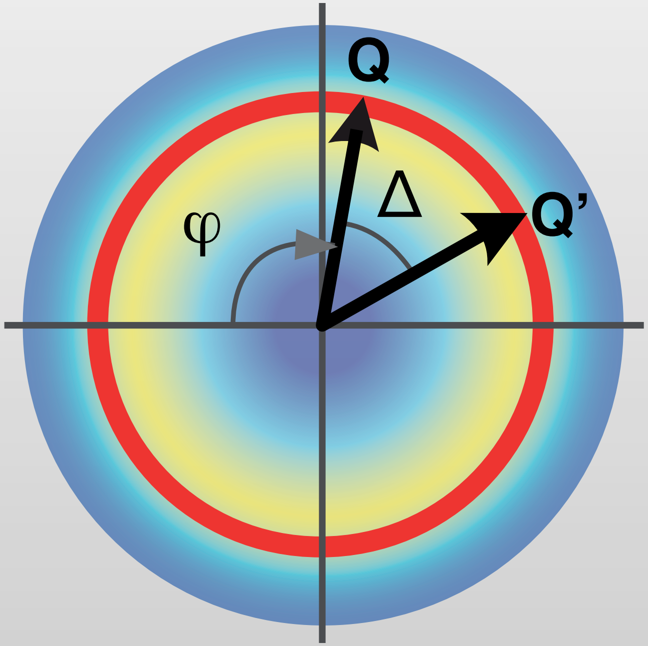
Peter Wochner

MPI-MF DEPARTMENT DOSCH

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

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





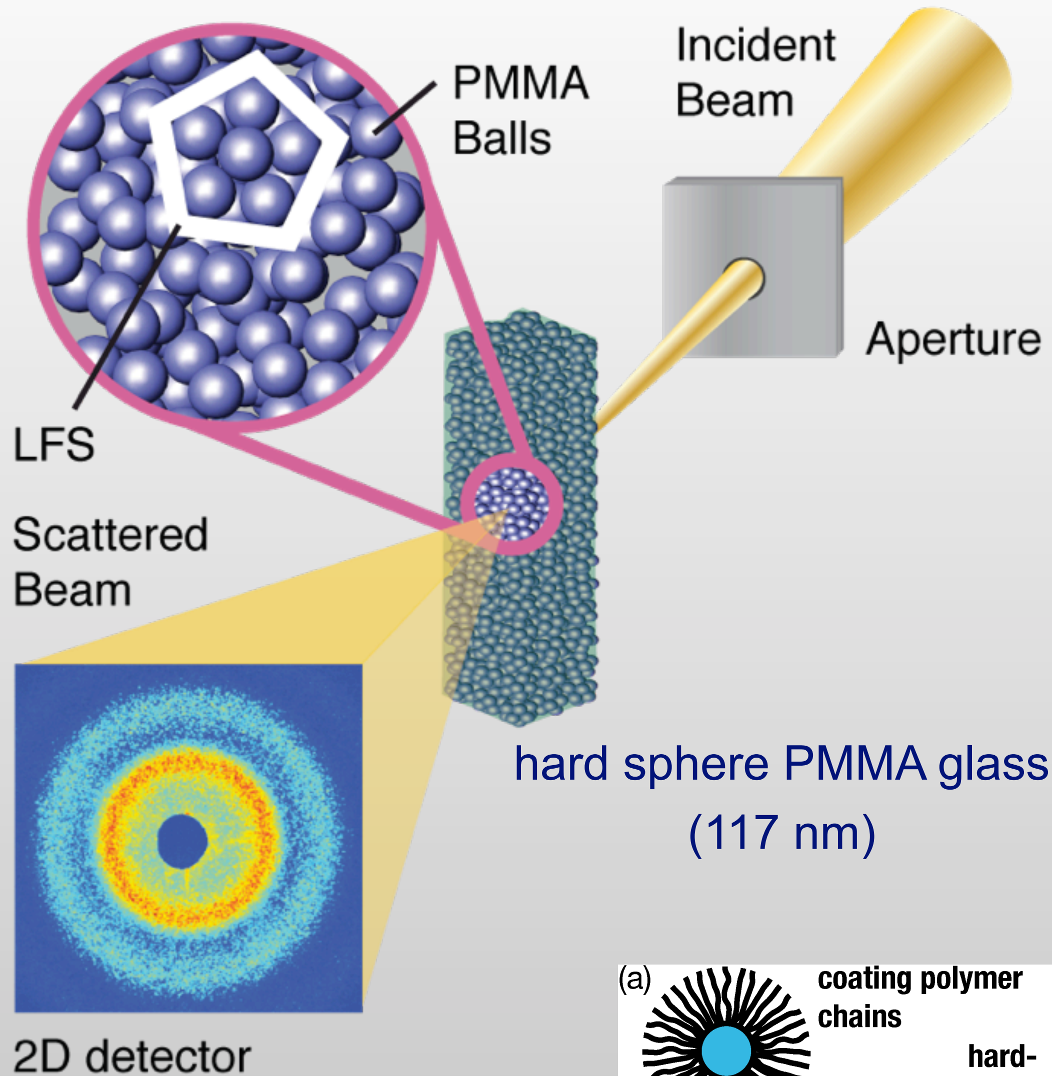
- **for medium range orientational correlations:** $|Q| \neq |Q'|$
- **time dependent:** $t \neq t'$

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

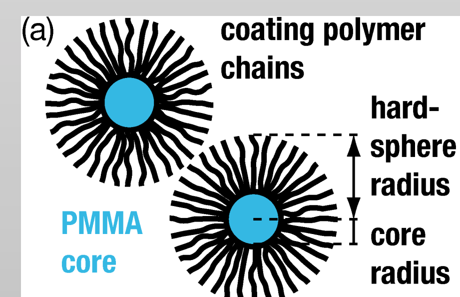
Proof of Principle: Colloidal Glass

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”

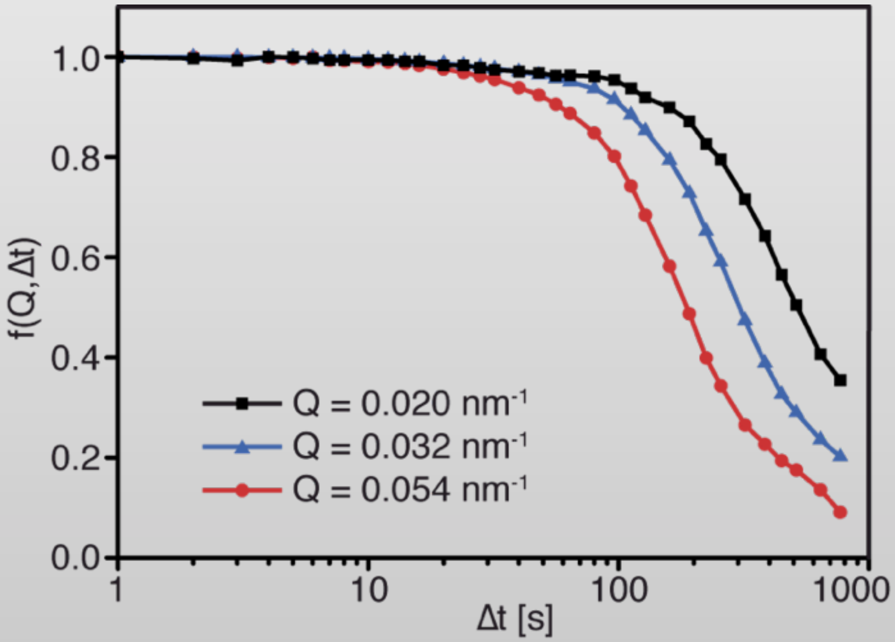


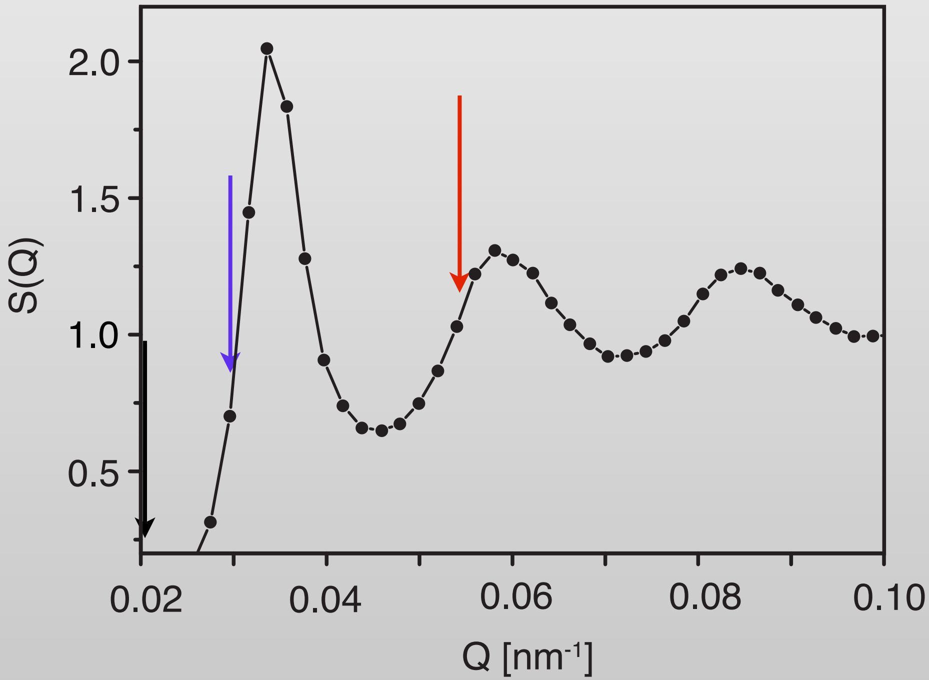
- **“Fast” hard sphere PMMA system (117 nm)**

Temporal auto-correlation function

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

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

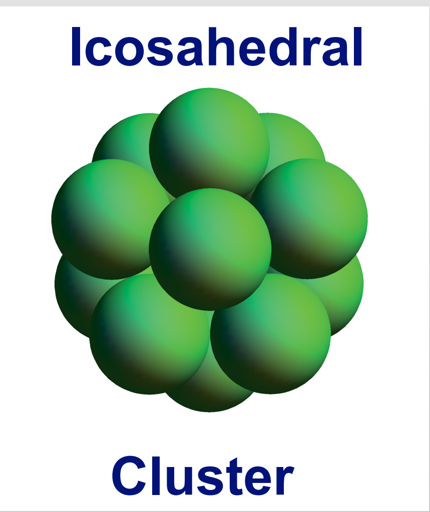


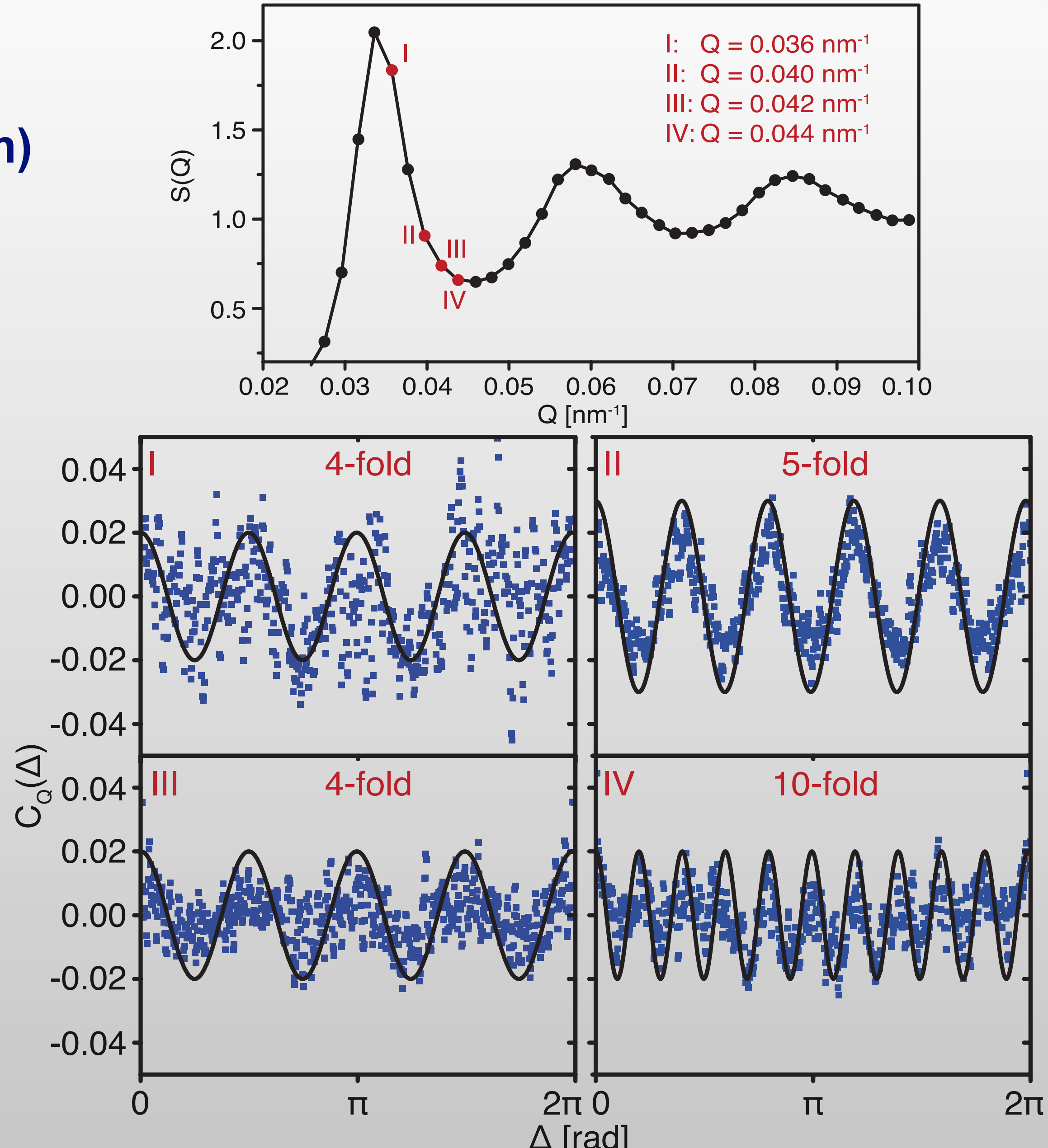


Typical angular dependence of $C_Q(\Delta)$

Peter Wochner

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

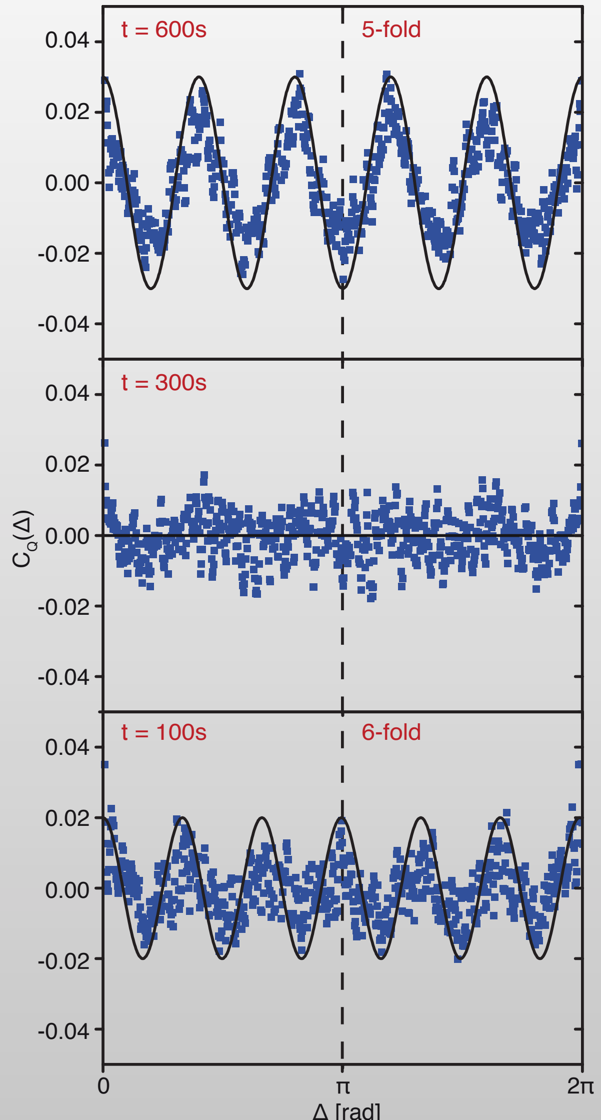




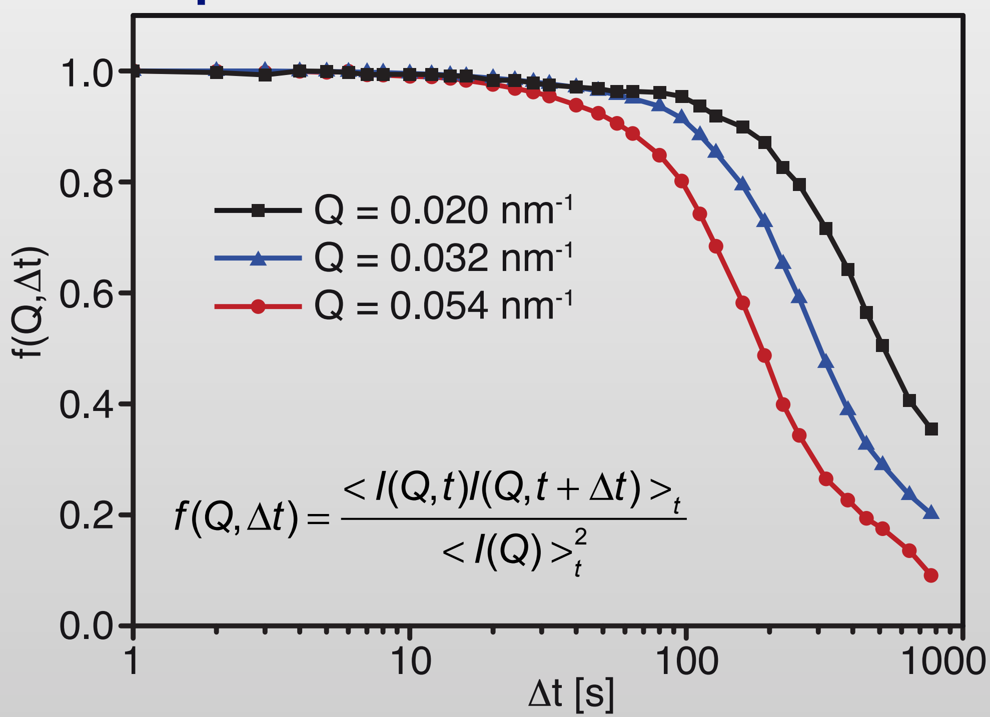
Time dependence of $C_Q(\Delta)$ in "fast" systems

Peter Wochner

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



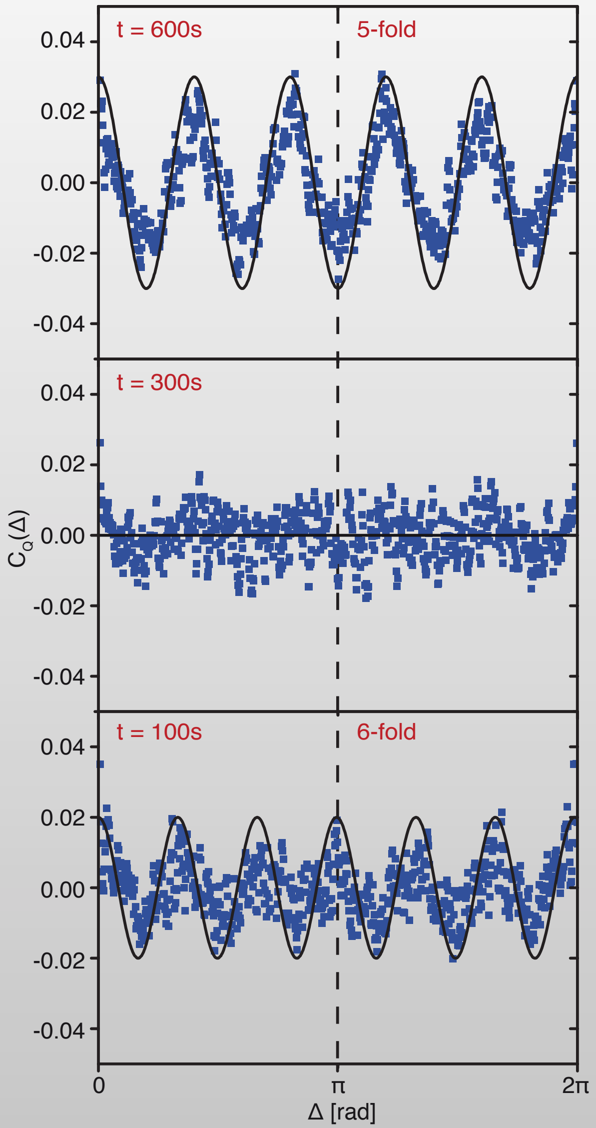
Temporal auto-correlation function

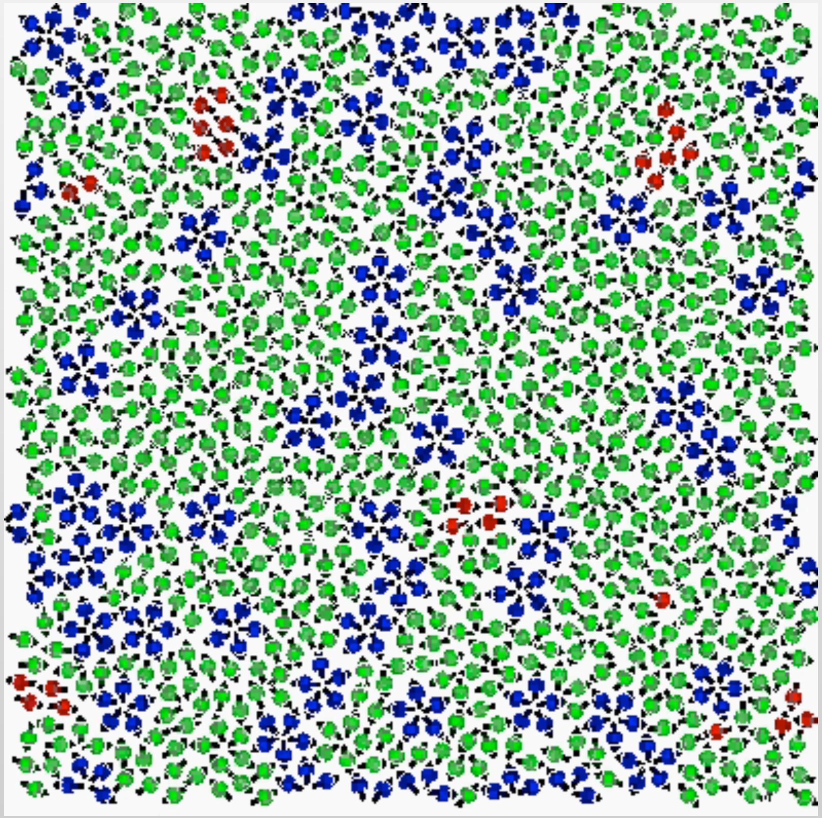


$$f(Q,\Delta t) = \frac{< I(Q,t) I(Q,t+\Delta t) >_t}{< I(Q) >_t^2}$$

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

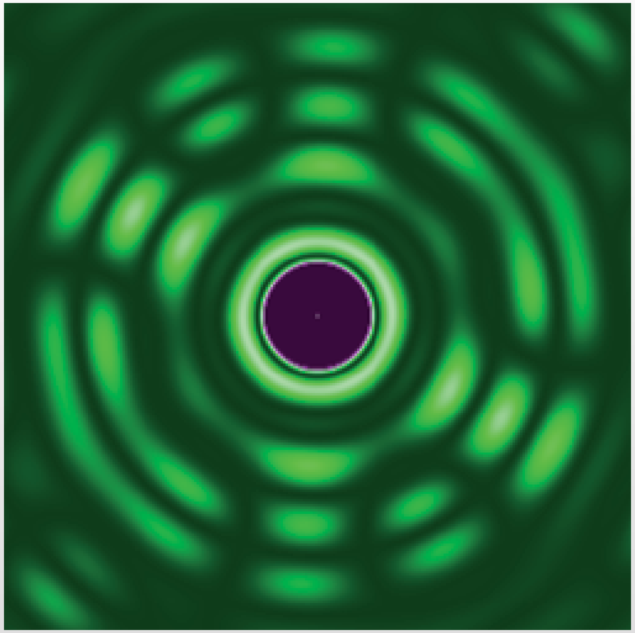
- **"Fast" hard sphere PMMA system (117 nm): dynamical heterogeneity**



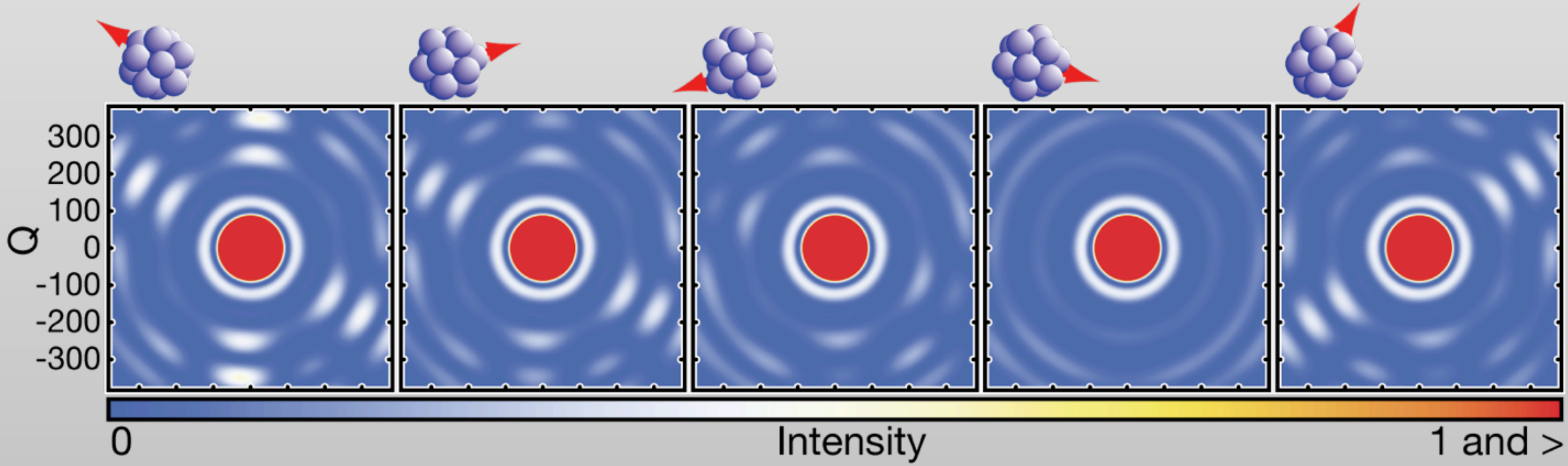


H.Shintani, H. Tanaka, Nature Physics **2**, 200 (2006)

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



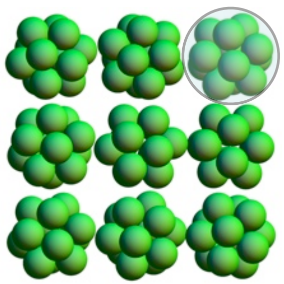
- **Wanted:** $< I(\varphi)I(\varphi+\Delta) >_{\varphi}$

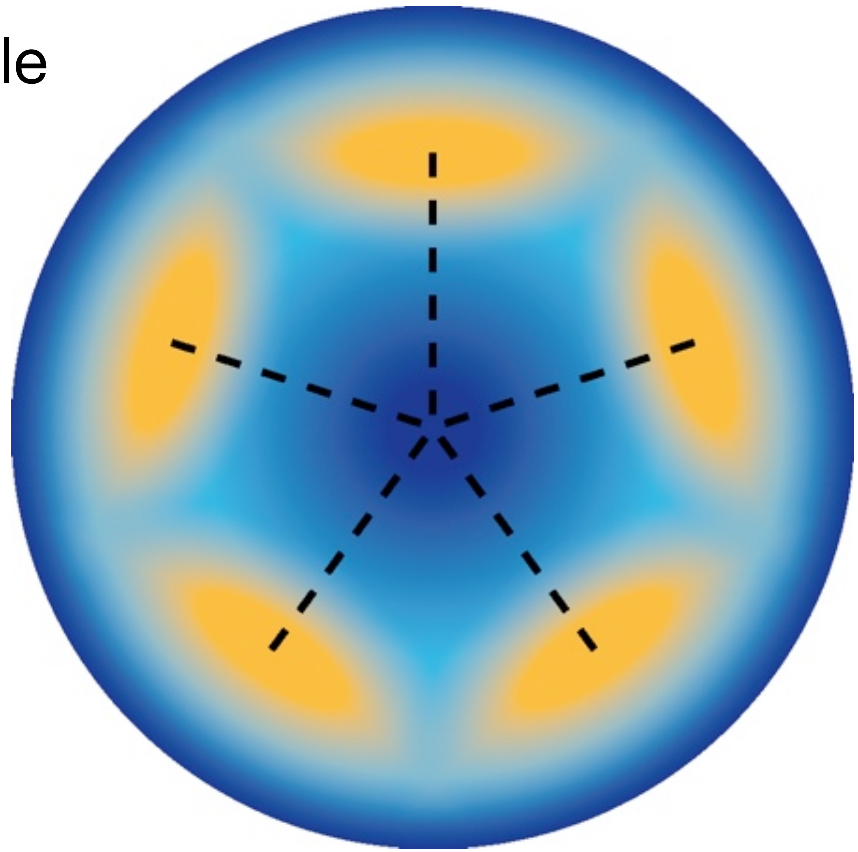


X-ray cross correlation analysis

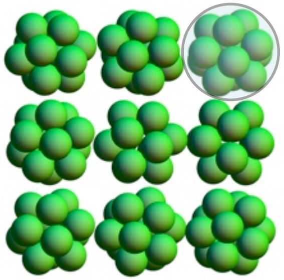
Peter Wochner

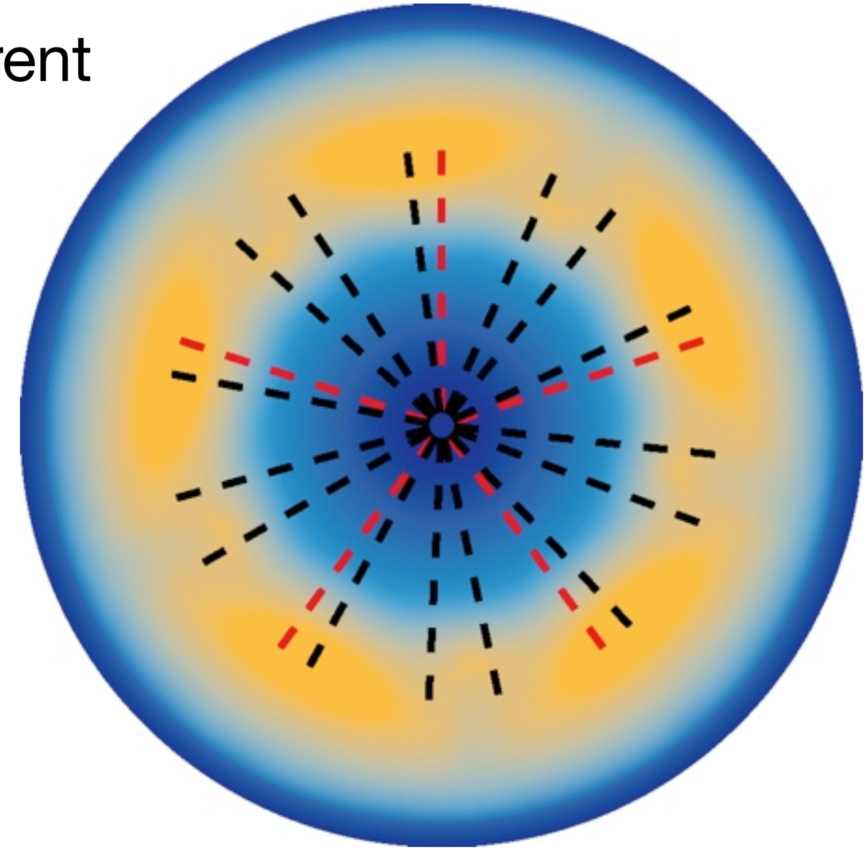
Single-molecule
diffraction





Partially coherent diffraction

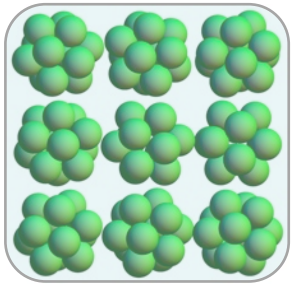


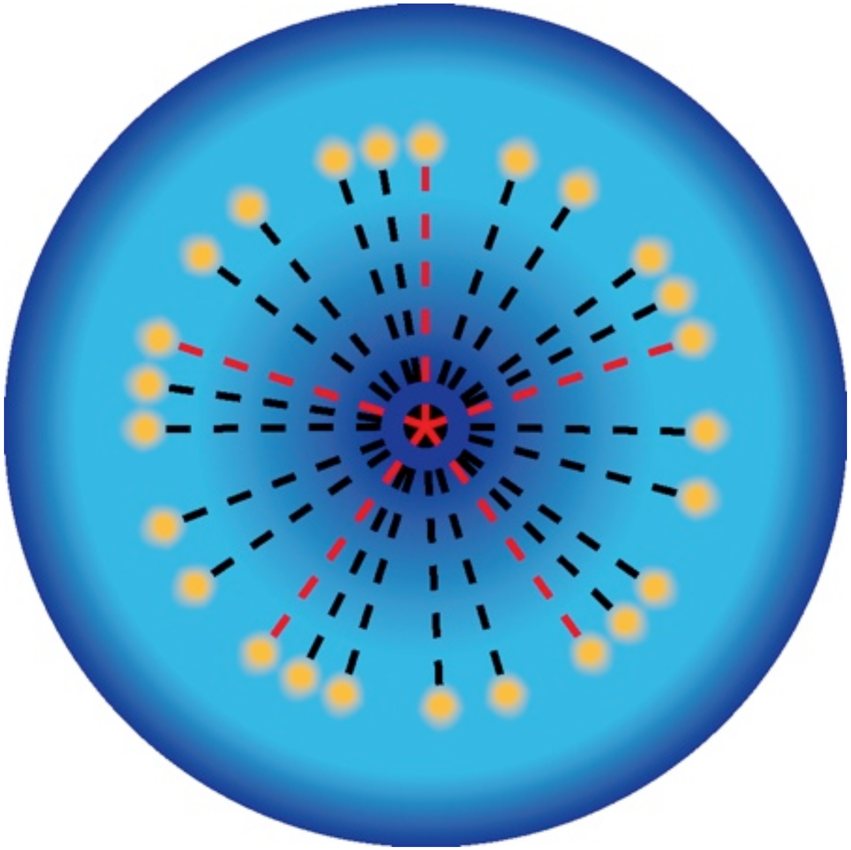


X-ray cross correlation analysis

Peter Wochner

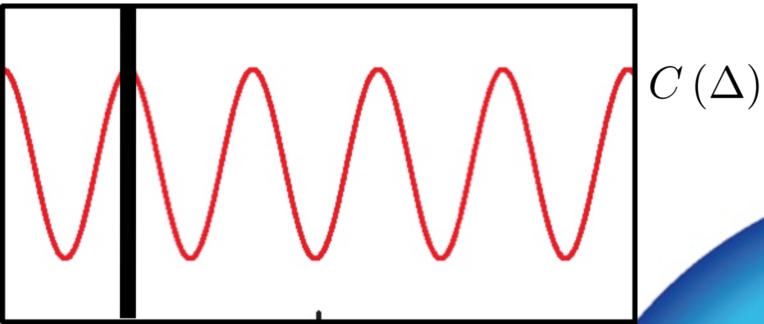
Coherent diffraction



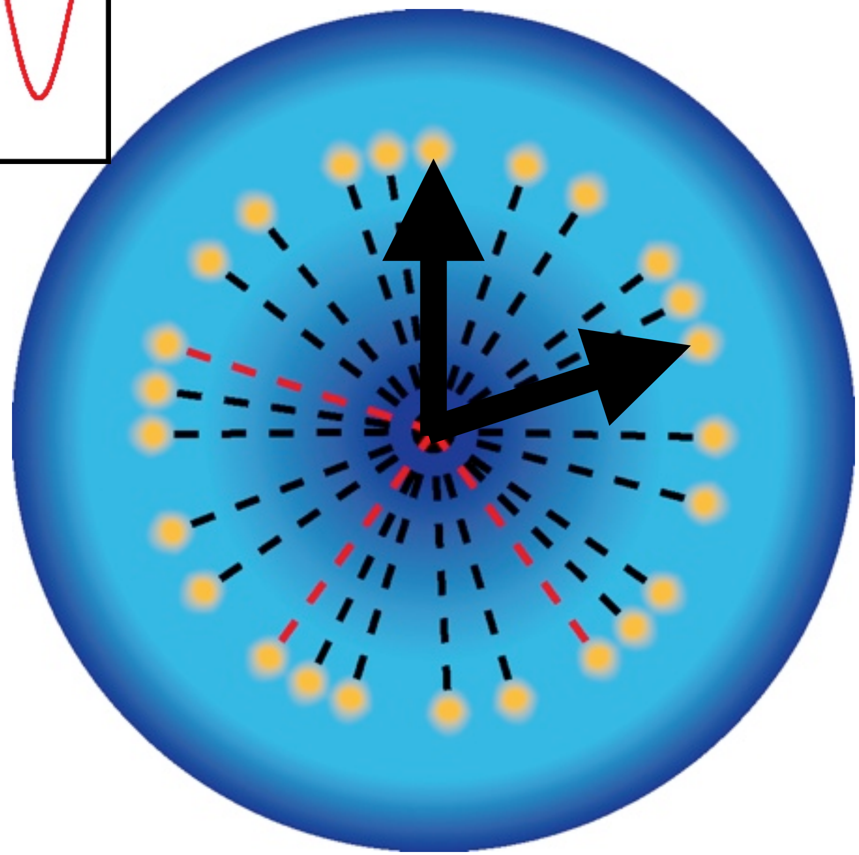


Speckle-Size ~ 1 / Beam-Size

= Volume of coherently illuminated sample



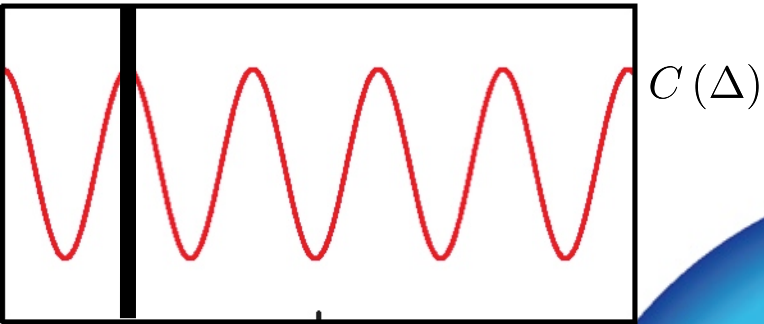
$\Delta = 2/5\ \pi$



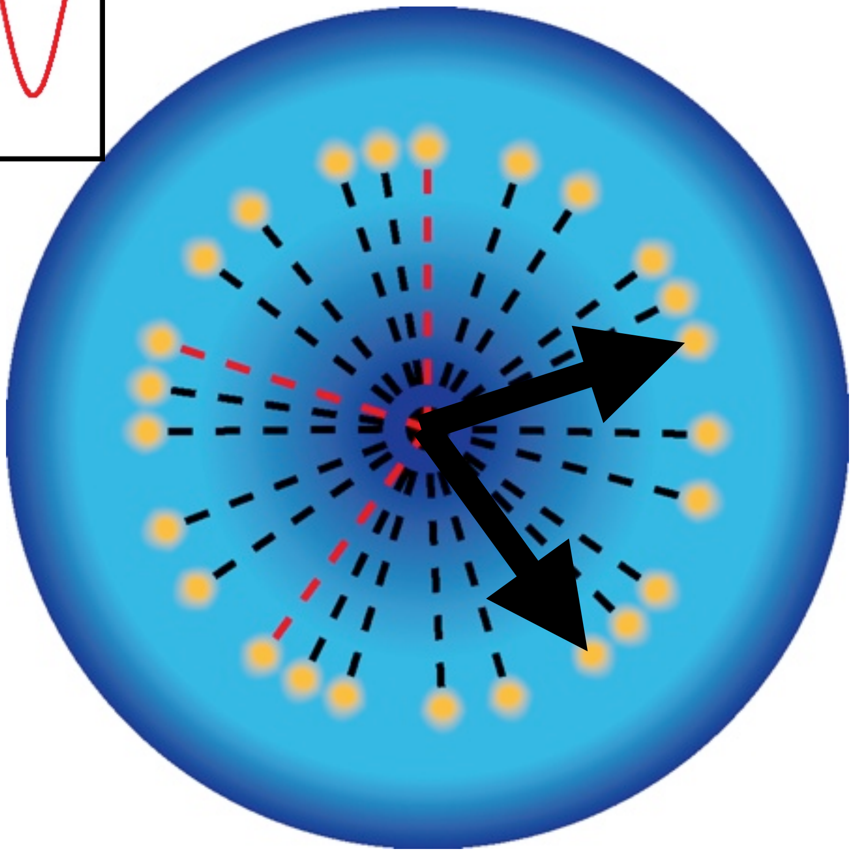
$\Delta = 2/5\ \pi$

X-ray cross correlation analysis

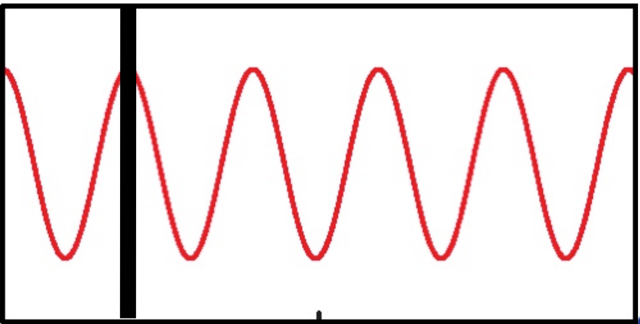
Peter Wochner

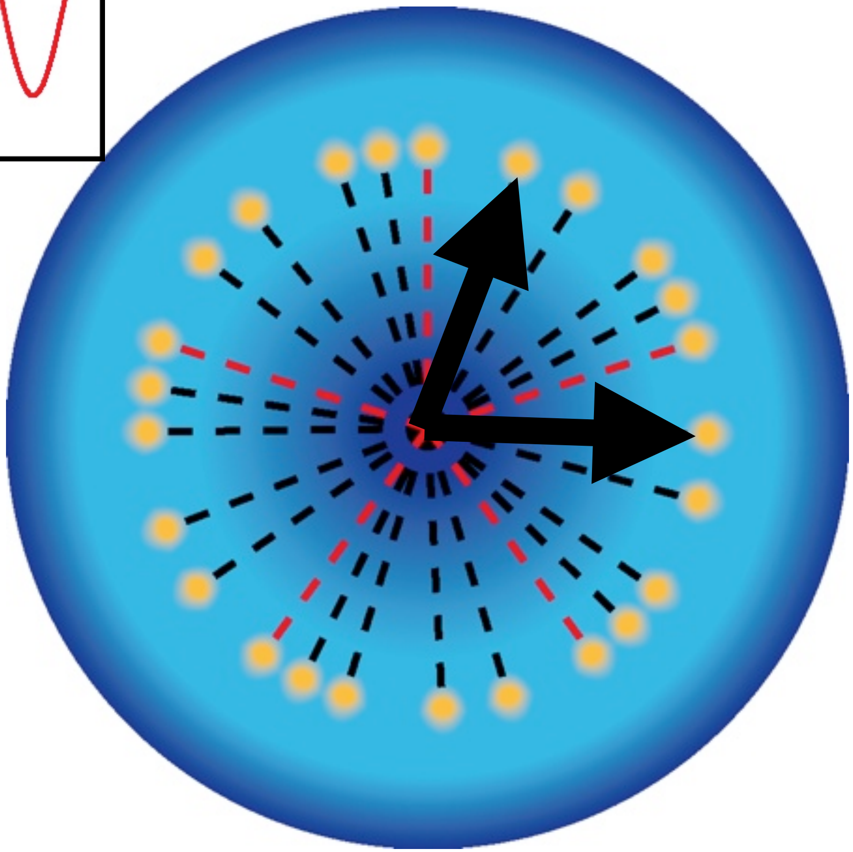


$\Delta = 2/5\ \pi$



$\Delta = 2/5\ \pi$


$C(\Delta)$
Δ = 2/5 π


Δ = 2/5 π

XCCA-averaging Considerations

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

  → max. 500000 Icosahedra

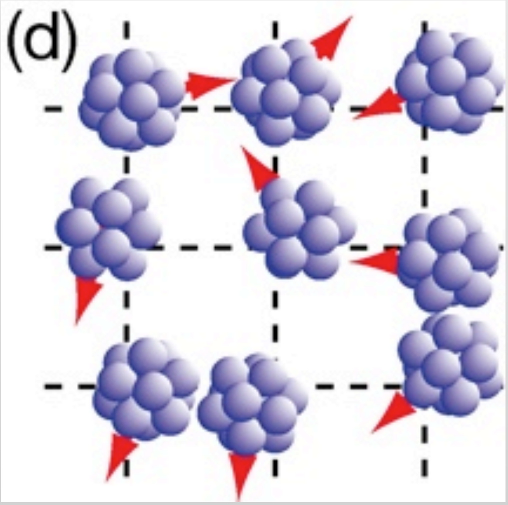
- XCCA symmetries: only subset of n-fold axes in beam direction contribute

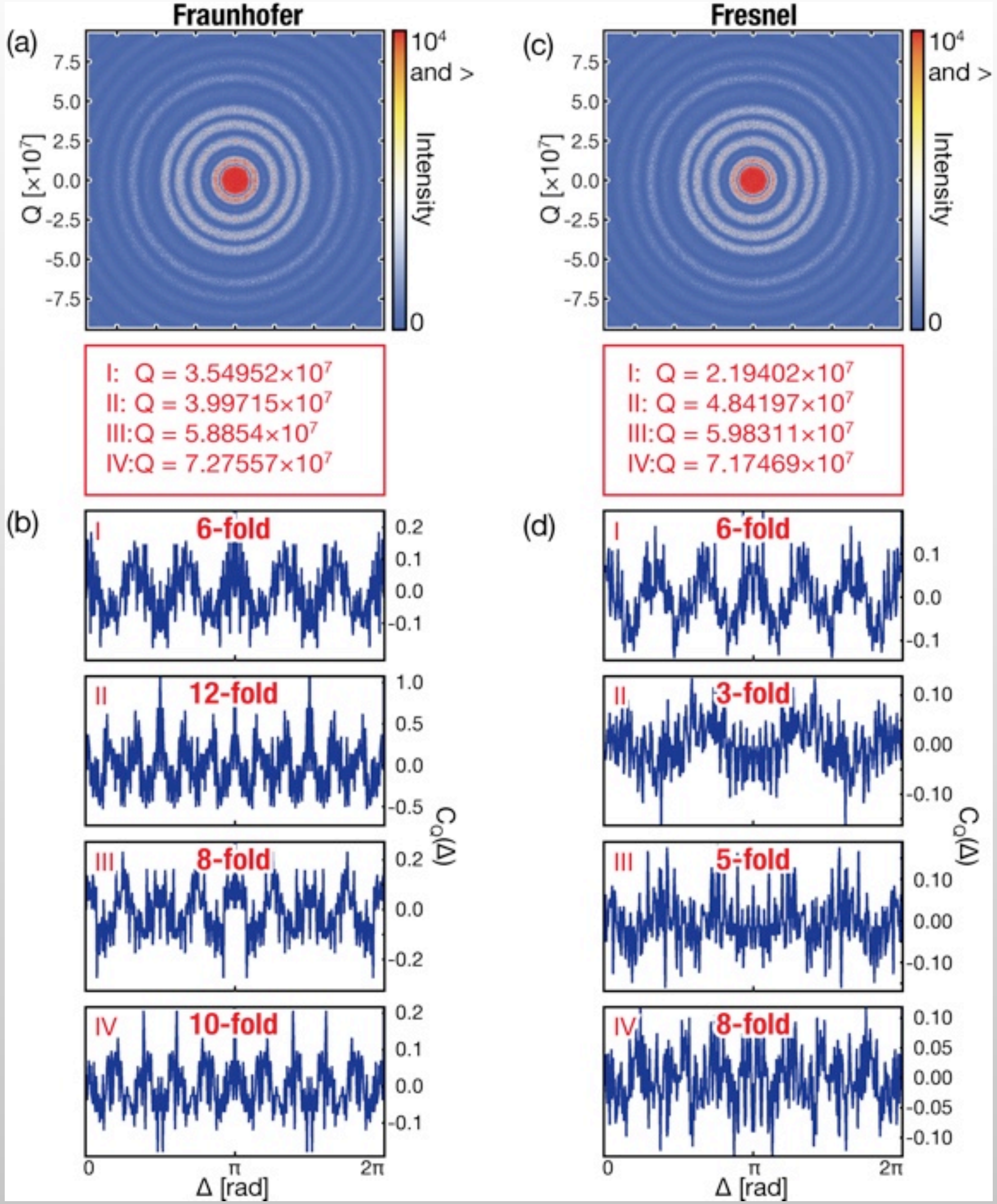
- Analogy Powder Diffraction: Angular average selects subset of states lying on Debye-Scherrer Cone

Numerical Simulation

Peter Wochner

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

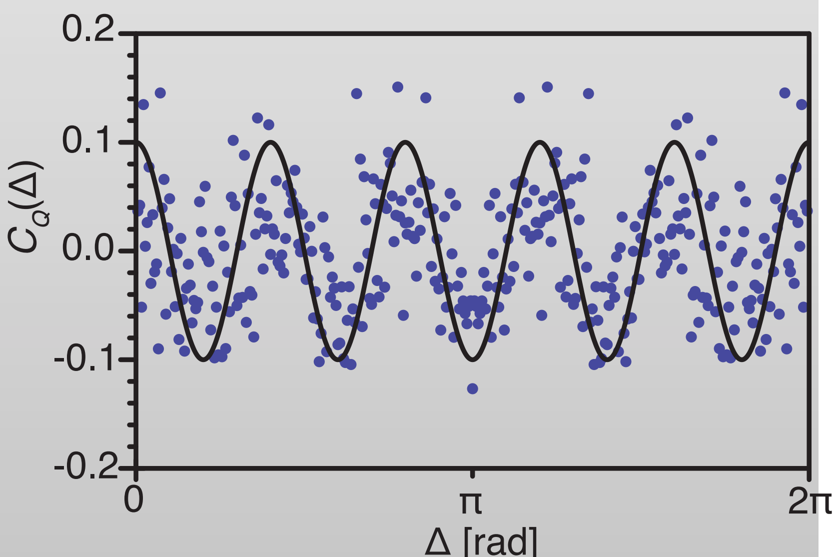


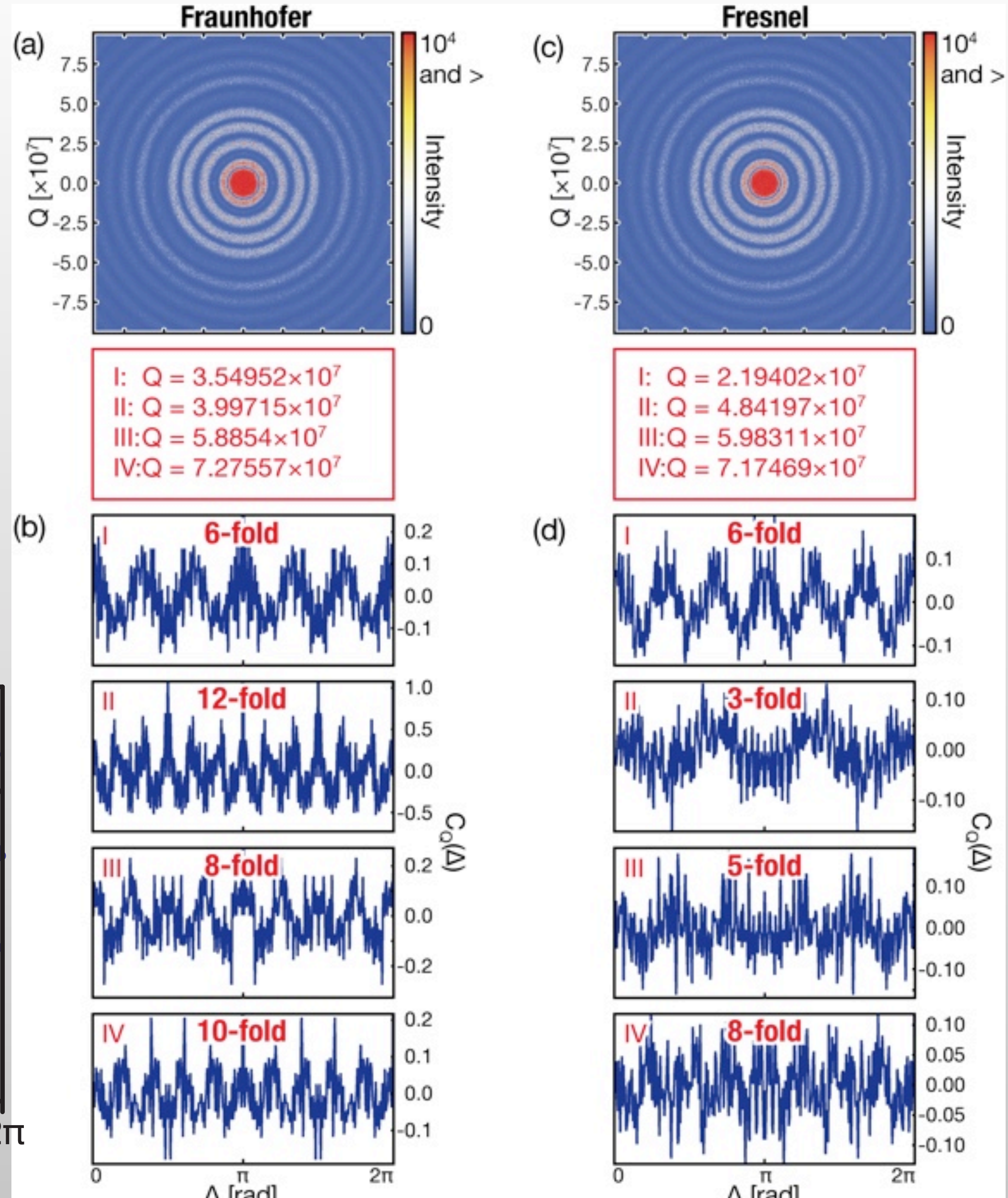


Numerical Simulation

Peter Wochner

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

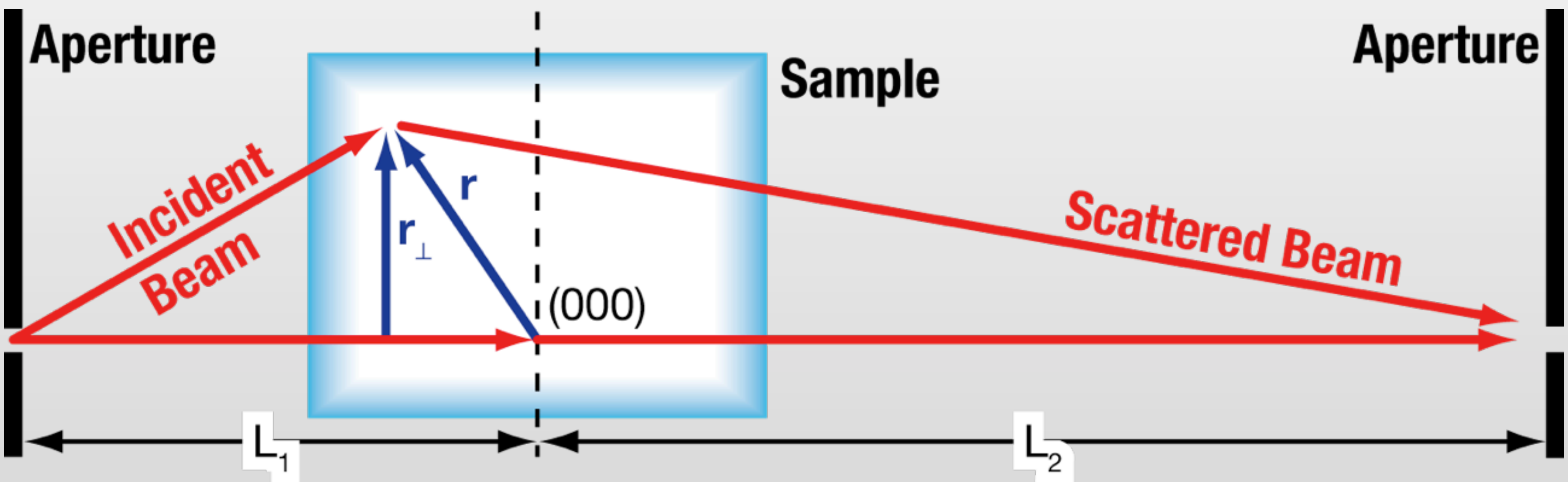




Fresnel Approximation

Peter Wochner

- Near field approximation for entrance wave front
- Far field for exit wave front



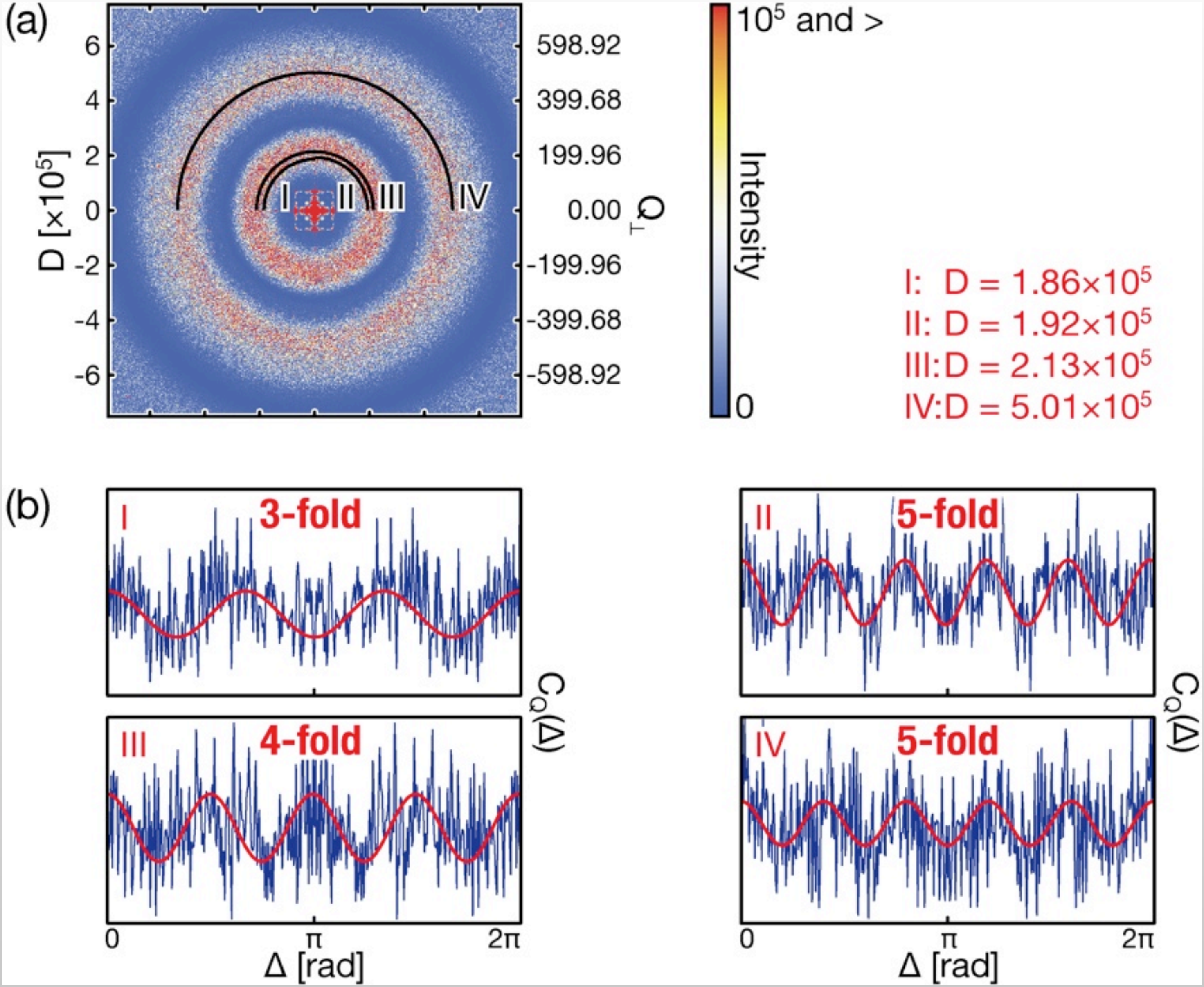
- Fresnel Density: add imaginary phase factor to real density

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

- Breaks inversion symmetry of I(Q) (Friedel's Law)

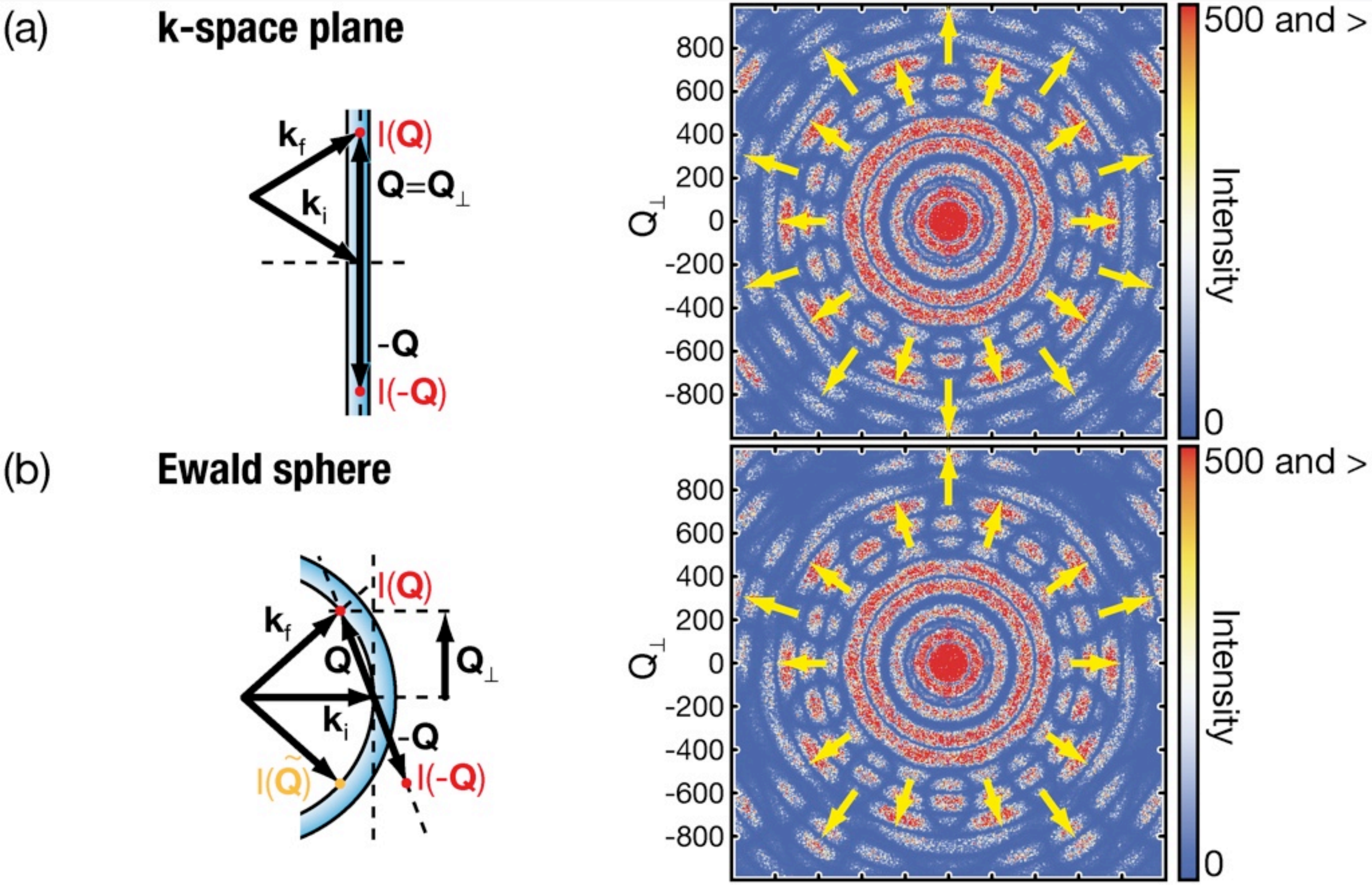
XCCA on Ewald sphere in the far field limit

Peter Wochner



Ewald sphere vs. plane through Origin

Peter Wochner

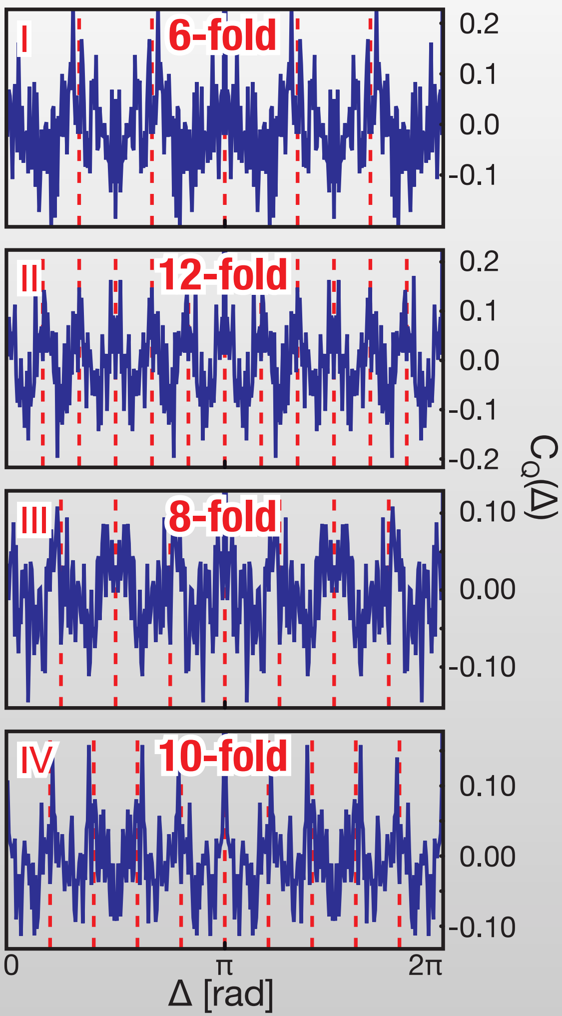


- **E= 8 keV and ΔE/E= 10^{-4} → Θ<0.4º**

MD Simulations

Peter Wochner

- $C_Q(\Delta)$ with Fraunhofer approximation

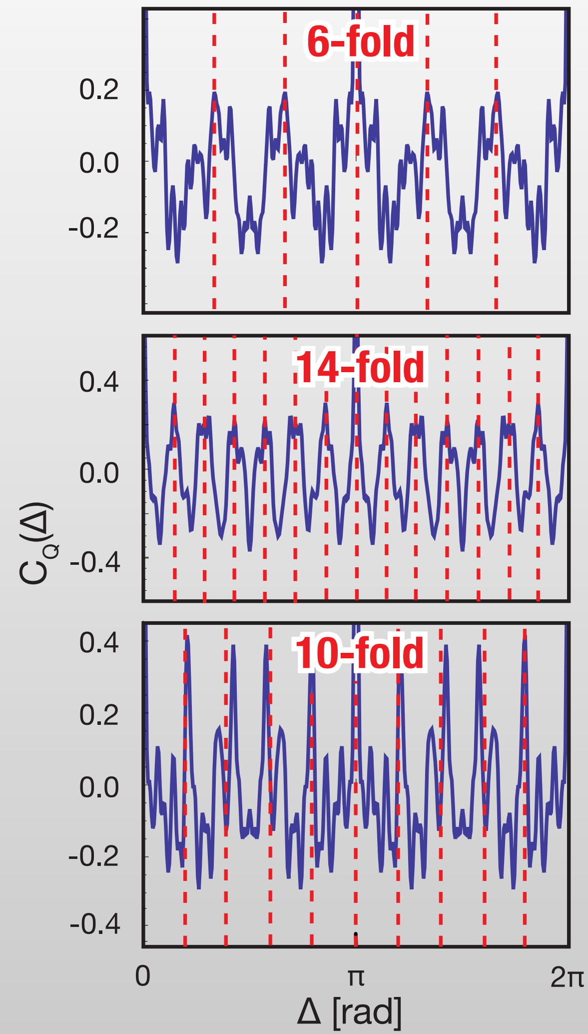


Q=16.43nm^{-1}

Q=18.07nm^{-1}

Q=18.44nm^{-1}

Q=18.79nm^{-1}



Q=13.14nm^{-1}

Q=15.35nm^{-1}

Q=13.50nm^{-1}

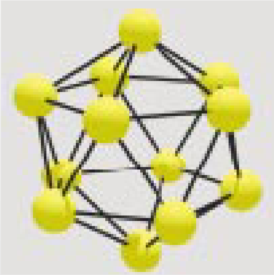
- **Monoatomic glass**: Dzugutov potential
- $2 \cdot 10^6$ atoms

- **liquid H_2O**: 450000 particles SPC

Origin of Symmetries

Peter Wochner
MPI-MF DEPARTMENT DOSCH

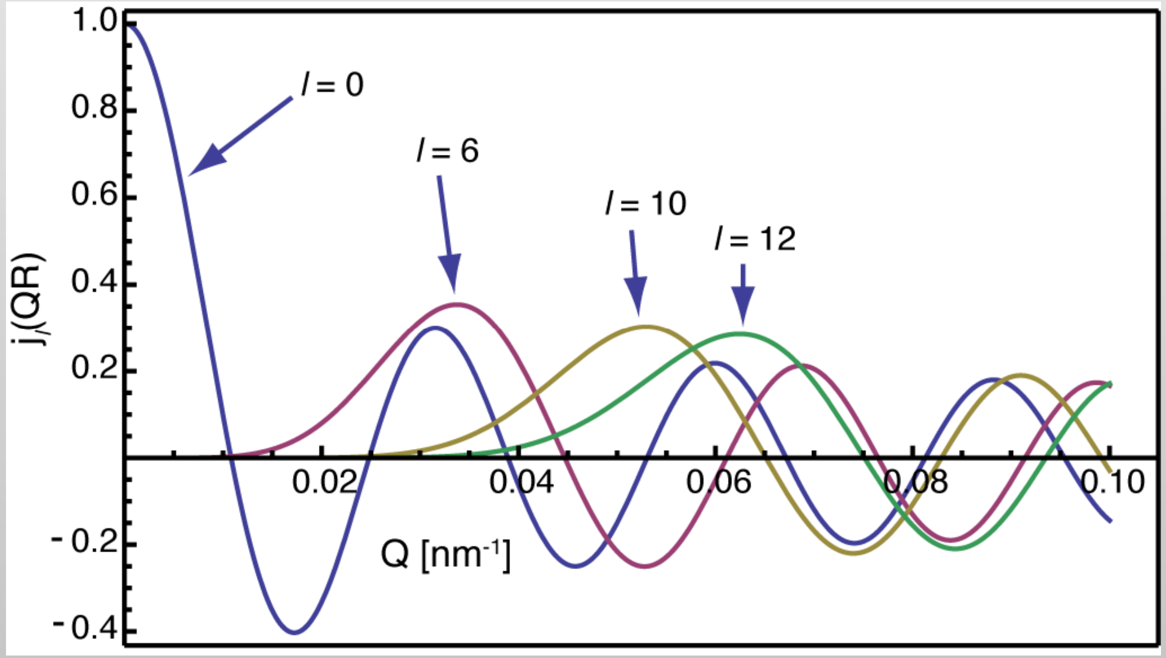
- **Hypothesis: Icosahedral clusters (LFS)**
- **form factor expansion**: in icosahedral harmonics and orthogonal rotator functions
  - e.g. icosahedron: l=0, **l=6, l=10, l=12** ...



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

Q-Range — 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**



Cluster Orientation : ω_i

Orientation of Q: Ω_Q

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**

END

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