Methoden moderner Röntgenphysik II: Streuung und Abbildung

Lecture 5	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2016 G. Grübel, M. Martins, S. Roth, O. Seeck, T. Schneider
Location	Lecture hall AP, Physics, Jungiusstraße
Date	Tuesday 12:30 - 14:00 Thursday 8:30 - 10:00

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Part I:
Basics of X-ray Physics
by Gerhard Grübel (GG)

Introduction
Overview, Introduction to X-ray Scattering

X-ray Scattering Primer
Elements of X-ray Scattering

Sources of X-rays, Synchrotron Radiation
Laboratory Sources, Accelerator Bases Sources

Reflection and Refraction from Interfaces
Snell's Law, Fresnel Equations

Kinematical Diffraction (I)
Diffraction from an Atom, a Molecule, from Liquids, Glasses, …

Kinematical Diffraction (II)
Diffraction from a Crystal, Reciprocal Lattice, Structure Factor, …

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Small Angle Scattering, and Soft Matter
Introduction, Form Factor, Structure Factor, Applications, ...

Anomalous Diffraction
Introduction into Anomalous Scattering, ...

Introduction into Coherence
Concept, First Order Coherence, ...

Coherent Scattering
Spatial Coherence, Second Order Coherence, ...

Applications of Coherent Scattering
Imaging and Correlation Spectroscopy, ...

Kinematical Diffraction

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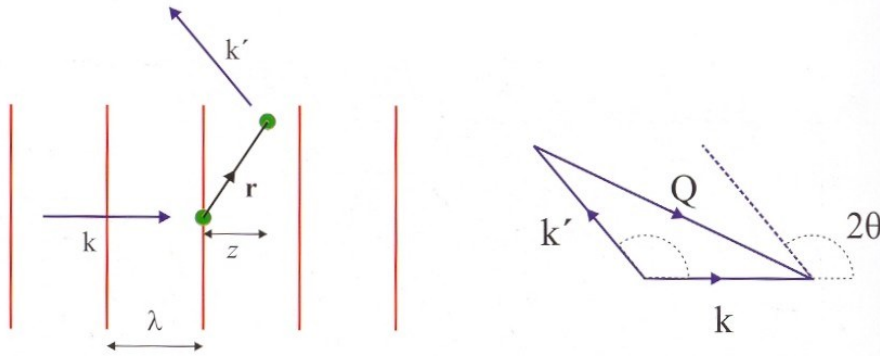
Kinematical Diffraction

One of the main applications of X-rays is the determination of structure(s) using diffraction.

Assume the scattering to be weak; multiple scattering effects are to be neglected: weak scattering limit ≡ kinematical approximation.

Consider a 2 electron system:

$z = r\cos\alpha;\ k\,z = k\,r\cos\alpha = \mathbf{k} \cdot \mathbf{r}$

$y = r\cos\beta;\ k'y = k'r\cos\beta = \mathbf{k'} \cdot \mathbf{r}$

Path- or phase difference:

$$\Delta\Phi = z - y = \mathbf{k} \cdot \mathbf{r} - \mathbf{k'} \cdot \mathbf{r} = \mathbf{Q} \cdot \mathbf{r}$$

with

$$Q = \left(\frac{4\pi}{\lambda}\right)\sin\theta$$

Elastic scattering
k = k'

Scattering amplitude for 2 electrons:

$$A(\mathbf{Q}) = -r_0\left[1 + e^{i\mathbf{Q}\mathbf{r}}\right]$$

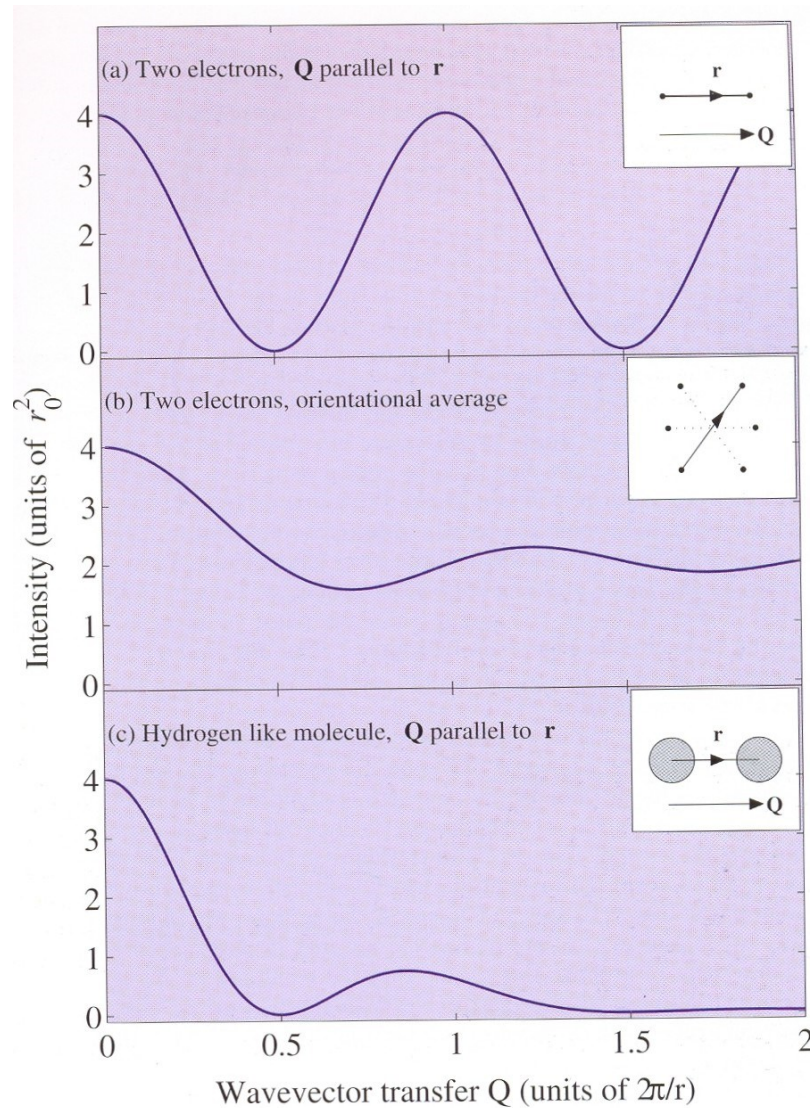$$I(\mathbf{Q}) = A(\mathbf{Q})A(\mathbf{Q})^*$$

$$= 2r_0{}^2\left[1 + \cos(Qr)\right]$$

see Fig. 4.2

For many electrons:

$$A(\mathbf{Q}) = -r_0 \sum_{r_{j'}} e^{i\mathbf{Q}\mathbf{r}_{j'}}$$

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Kinematical Diffraction

Intensity (units of r_0^2)

(a) Two electrons, **Q** parallel to **r**

(b) Two electrons, orientational average

(c) Hydrogen like molecule, **Q** parallel to **r**
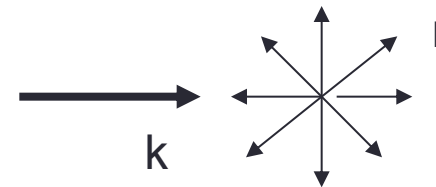
Wavevector transfer Q (units of $2\pi/r$)

Two electron system:

$$I(Q) = 2r_0{}^2[1 + \cos(Qr)]$$
$$Q \parallel r$$

orientational average

r

k

"smeared", no more "point-like" particles

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For many systems, e.g. molecules, the orientation of **r** will be random with respect to **k**

$$\int \exp(iQr\cos\theta)\, \sin\theta\, d\theta d\Phi$$

$$= 2\pi \int e^{iQr\cos\theta}\, \sin\theta\, d\theta$$

$$= 2\pi \left(-\frac{1}{iQr}\right) \int_{iQr}^{-iQr} e^{x}\, dx$$

$$= 4\pi \frac{\sin(Qr)}{Qr}$$
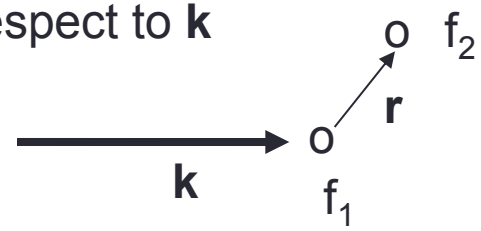
Orientational averaging:

Assume one electron at r=0, a second at r

$$A(\mathbf{Q}) = f_1 + f_2\, e^{i\mathbf{Qr}}$$
$$I(\mathbf{Q}) = f_1{}^2 + f_2{}^2 + f_1 f_2 e^{i\mathbf{Qr}} + f_1 f_2 e^{-i\mathbf{Qr}}$$

Orientational averaging:

$$\langle e^{i\mathbf{Qr}}\rangle = \langle e^{-i\mathbf{Qr}}\rangle$$

$$\langle I(Q)\rangle = f_1{}^2 + f_2{}^2 + 2 f_1 f_2 \langle e^{i\mathbf{Qr}}\rangle$$

$$\langle e^{i\mathbf{Qr}}\rangle = \frac{\int e^{iQr\cos\theta}\sin\theta\, d\theta}{\int \sin\theta\, d\theta d\phi} \quad \longleftarrow \quad 4\pi$$

$$\langle I(Q)\rangle = f_1{}^2 + f_2{}^2 + 4\pi f_1 f_2 \frac{\sin(Qr)}{Qr}$$

see figure 4.2 b

if the position of the electrons distributed or smeared: see Figure 4.2c

Orientational averaging
$\Rightarrow$ isotropic scattering signal
I(Q) instead of I(**Q**)

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Scattering From an Atom

Scattering amplitude of an atom $\equiv$ atomic form factor $f_0(\mathbf{Q})$ [in units of r_0]

$\rho(\mathbf{r})$: electronic number density $\equiv$ charge density

$$f_0(\mathbf{Q}) = \int \rho(\mathbf{r}) e^{i\mathbf{Qr}} d\mathbf{r} = \begin{cases} Z \text{ for } \mathbf{Q} \to 0 \\ 0 \text{ for } \mathbf{Q} \to \infty \end{cases}$$

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
C	2.3100	20.8439	1.0200	10.2075	1.5886	0.5687	0.8650	51.6512	0.2156
O	3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.8670	32.9089	0.2508
F	3.5392	10.2825	2.6412	4.2944	1.5170	0.2615	1.0243	26.1476	0.2776
Si	6.2915	2.4386	3.0353	32.333	1.9891	0.6785	1.5410	81.6937	1.1407
Cu	13.338	3.5828	7.1676	0.2470	5.6158	11.3966	1.6735	64.820	1.5910
Ge	16.0816	2.8509	6.3747	0.2516	3.7068	11.4468	3.683	54.7625	2.1313
Mo	3.7025	0.2772	17.236	1.0958	12.8876	11.004	3.7429	61.6584	4.3875

Table 4.1: J. Als-Nielsen & D. McMorrow

Note: atomic form factor is FT of electronic charge distribution

$f_0\left(\dfrac{Q}{4\pi}\right)$ tabulated:

$$f_0\left(\frac{Q}{4\pi}\right) = \sum_{j=1}^{4} a_j e^{-b_j\left(\frac{Q}{4\pi}\right)^2} + c$$

Note:

$$f = f_0(Q) + f' + f''$$

corrections f' and f'' arise from the fact that the electrons are bound in the atom

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Scattering from a Molecule

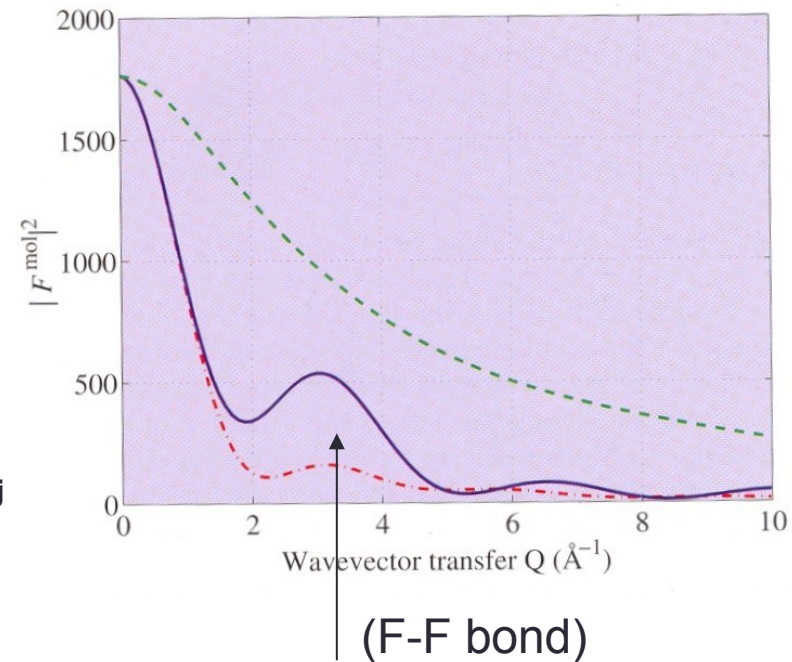$$F^{mol}(Q) = \sum_{r_j} f_j(Q) e^{iQr_j}$$

——— CF_4

-.-.- CF_4 Q not || C-F

- - - - - molybdenum

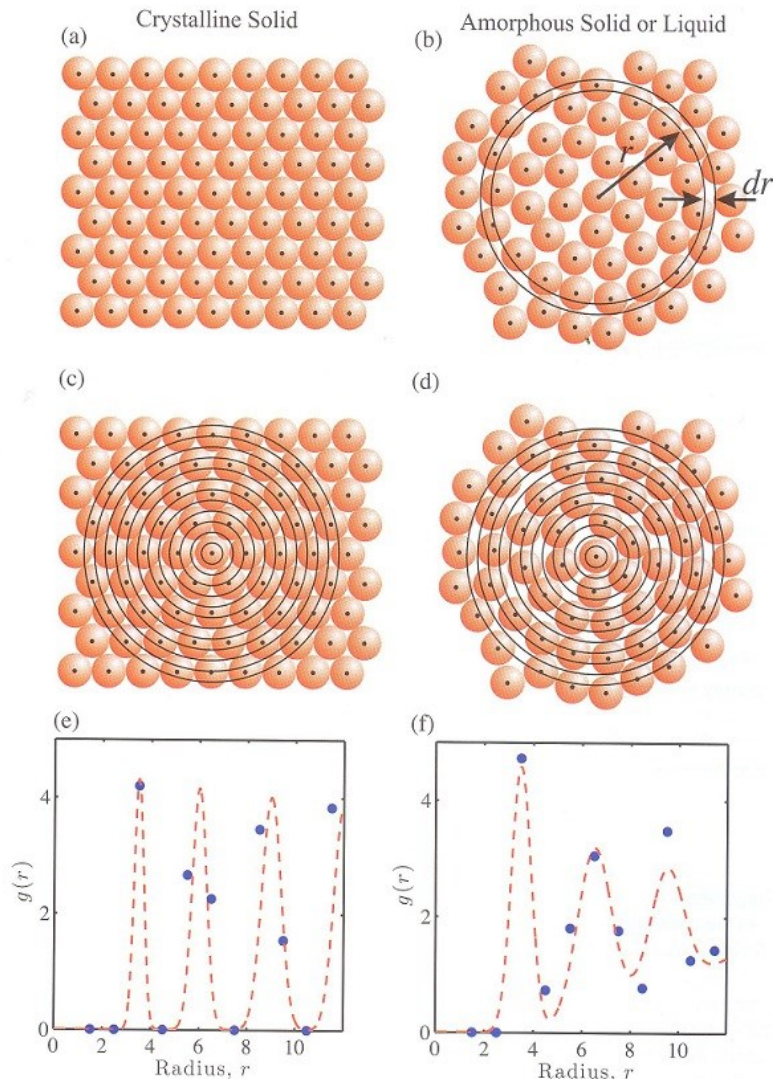(also 42 electrons)

Example: CF_4 (tetraeder)

assume $OA = OB = OC = OD = 1$; $z = OO' = \cos(u) = \dfrac{1}{3}$

(109.5deg)

$$\mathbf{Qr_j} = Qr_j \cos(u) = \left(\frac{1}{3}\right)Qr_j$$

(F-F bond)
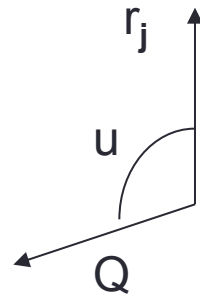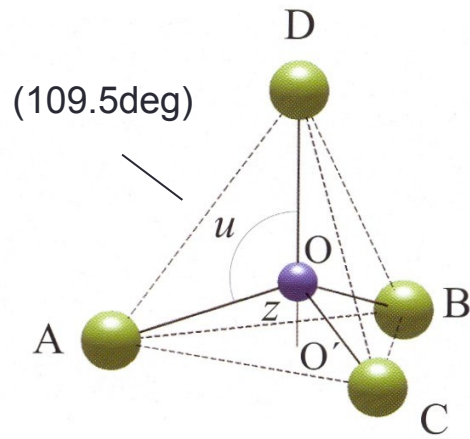
Scattering From Liquids and Glasses

(a) Crystalline Solid

(b) Amorphous Solid or Liquid

(c)

(d)

(e)

(f)

The positions of atoms in non-crystalline materials change over a wide range of timescales (from nanoseconds in the case of liquids to millennia or more in the case of glasses).

X-rays are a fast probe delivering snapshots of the structure as shown schematically in the figure.

Radial density:
$$\rho(r) = \frac{N(r)}{2\pi r dr}$$

with $N(r)$ number of atoms in annulus r+dr , with $2\pi r dr$ being the annulus' area

Radial distribution function:
$$g(r) = \frac{\rho(r)}{\rho_{at}}$$

ρ_a average areal number density

The radial distribution function of a non-crystalline material damps and broadens as a function of r with g(r) tending to unity.

The Liquid Structure Factor

Consider mono-atomic or mono-molecular systems:

$$I(\mathbf{Q}) = f(\mathbf{Q})^2 \ _n\sum e^{i\mathbf{Q}\mathbf{r}_n} \ _m\sum e^{i\mathbf{Q}\mathbf{r}_m} = f(\mathbf{Q})^2 \ _n\sum_m\sum e^{i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)}$$

with f($\mathbf{Q}$) form factor

separate summations

$$I(\mathbf{Q}) = Nf(\mathbf{Q})^2 + f(\mathbf{Q})^2 \ _{n,\,m}\sum_{m\neq n}\sum e^{i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)}$$

Replace m≠n sum by integral and separate out average density ρ_{at}:

$$I(\mathbf{Q}) = \underline{Nf(\mathbf{Q})^2 + f(\mathbf{Q})^2 \ _n\sum \ _V\!\int [\rho_n(\mathbf{r}_{nm}) - \rho_{at}\ e^{i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)}dV_m} + \underline{f(\mathbf{Q})^2\ \rho_{at}\ _n\sum\ _V\!\int e^{i\mathbf{Q}(\mathbf{r}_n-\mathbf{r}_m)}dV_m}$$

$$I_{SRO}\,(Q) \qquad\qquad\qquad\qquad I_{SAXS}\,(Q)$$

measures short-range order (SRO) since

$\rho_n(\mathbf{r}_{nm}) \rightarrow \rho_{at}$ after few atomic spacings

and the term oscillates then towards zero

contributes only for Q → 0

(otherwise oscillates to zero)

where $\rho_n(\mathbf{r}_{nm})\ dV_m$ is the number of atoms in element dV_m located at $\mathbf{r}_m$ - $\mathbf{r}_n$ relative to $\mathbf{r}_n$.

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The Liquid Structure Factor

Average over different choices for the origin $\langle \rho_n(\mathbf{r}_{nm}) \rangle \rightarrow \rho(r)$

Isotropy: $\rho(\mathbf{r}) = \rho(r)$:

$$I(Q) = Nf(Q)^2 + Nf(Q)^2 \int_0^\infty [\rho(r) - \rho_{at}] \, 4\pi r^2 \left(\frac{\sin(Qr)}{Qr}\right) dr$$

$$\Rightarrow \quad S(Q) = \frac{I^{SRO}(Q)}{Nf(Q)^2} = 1 + \frac{4\pi}{Q} \int_0^\infty r \, [\rho(r) - \rho_{at}] \sin(Qr) \, dr$$

For $Q \rightarrow \infty$: $\quad S(Q) \rightarrow 1$

For $Q \rightarrow 0$:

$$\frac{\sin(Qr)}{Q} \rightarrow r \Rightarrow S(Q) = 1 + 4\pi \int_0^\infty r^2 dr \, [\rho(r) - \rho_{at}]$$

$$S(Q) \propto [\rho(r) - \rho_{at}] \quad \text{proportional to the density fluctuations}$$

Density fluctuations become strong when the compressibility κ_T is large. If, at a critical point, the compressibility diverges, S(0) might become so strong that the sample becomes opaque: critical opalescence.

For an ideal gas: $\quad P = \rho_{at} k_B T$ and $\kappa_T = \dfrac{1}{(\rho_{at} k_B T)}$ $\qquad\qquad$ since $\kappa_T = \dfrac{1}{\rho}\left(\dfrac{\partial \rho}{\partial P}\right)_T$

For interacting gas: κ_T diverges at critical point

Actually: $S(0) = \rho_{at} \kappa_T k_B T = 1$ (for all Q) for an ideal gas

The Pair Correlation Function g(r):

$$S(Q) = 1 + \frac{4\pi}{Q} \int_o^\infty r \, [\rho(r) - \rho_{at}] \, \sin(Qr) \, dr$$

$\Rightarrow$ Radial distribution function for a liquid or glass:

$$g(r) = 1 + \left(\frac{1}{2\pi^2 r \rho_{at}}\right) \int_o^\infty Q \, [S(Q) - 1] \, \sin(Qr) \, dQ$$

Note:

It was assumed that the scattering is dominated by elastic scattering events. This holds for a glass but not for a liquid. However e.g. 10 keV photons are far more energetic than any relevant excitation in a liquid (typically 10 meV); thus any inelastic effect is negligibly small.

However this does not hold for neutrons.

Example: Hard sphere system
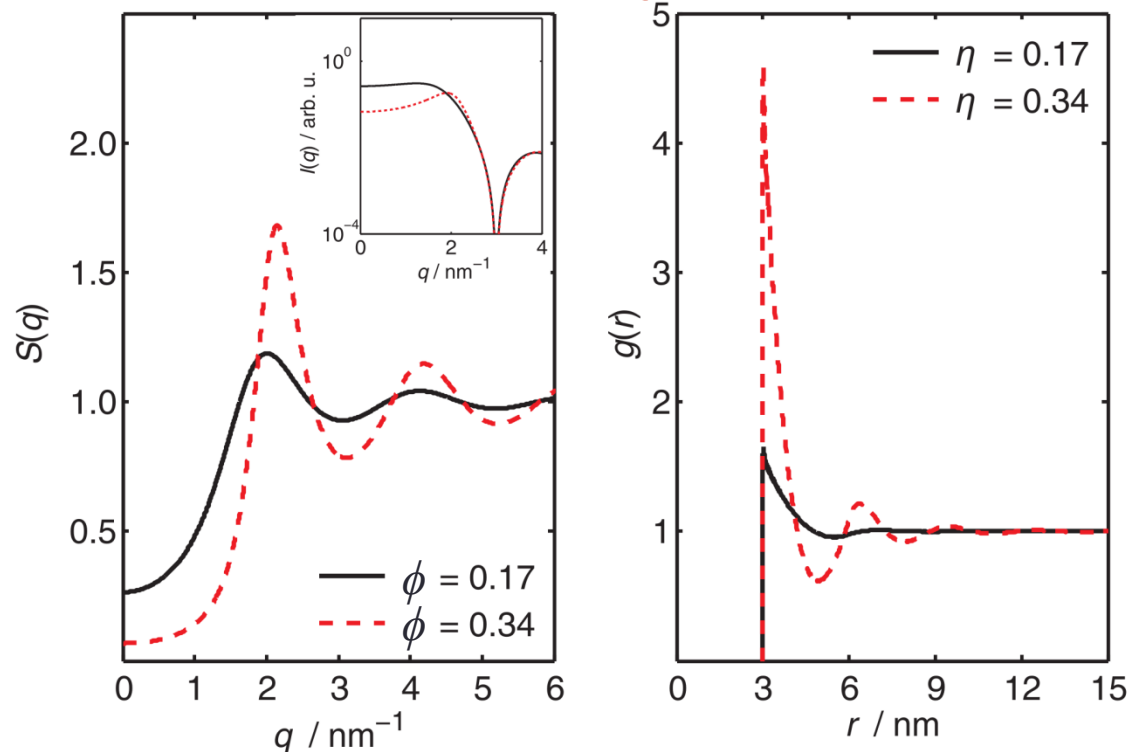
- Interaction only via steric repulsion

- model system for liquids, colloids, glasses

- only dependent on volume fraction $\phi = 1/6 \, \pi \, n \, \sigma^3$ (σ: particle diameter)
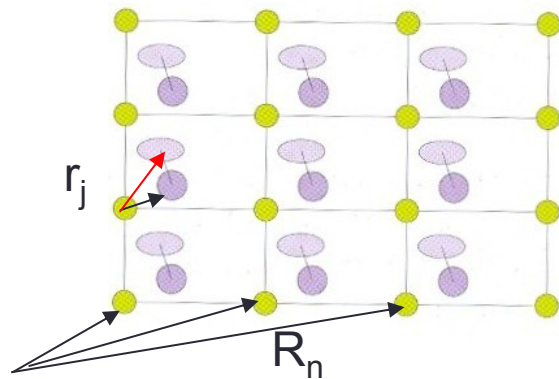
More realistic models use van-der Waals interactions, Coulomb interactions,…

Scattering From a Crystal

$$A(\mathbf{Q}) = -r_0 \sum_{r_j} e^{i\mathbf{Q}r_{j'}}$$

An extension to crystalline matter is simplified since there is translational symmetry.

Crystalline matter: $\mathbf{r}_j' = \mathbf{R}_n + \mathbf{r}_j$

$$A(\mathbf{Q}) = -r_0 \underbrace{\sum_{R_n} e^{i\mathbf{Q}\mathbf{R}_n}}_{\text{lattice sum}} \underbrace{\sum_{r_j} e^{i\mathbf{Q}\mathbf{r}_j}}_{\text{unit cell structure factor}}$$

Crystallography:

Determine electron density within unit cell

> **Note:** one does measure
> $I(Q) = A(Q)\, A^*(Q)$
> and is thus not sensitive to phase shifts