Methoden moderner Röntgenphysik II: Streuung und Abbildung

Lecture 5

Vorlesung zum Haupt/Masterstudiengang Physik

SS 2014

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Today: 1st exercises !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

Location: Hörs AP, Physik, Jungiusstrasse

Tuesdays 12.45 – 14.15

Thursdays 8:30 – 10.00

Methoden moderner Röntgenphysik II: Streuung und Abbildung

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
Snell's law, Fresnel equations,
Kinematical Diffraction (I)
Diffraction from an atom, molecule, liquids, glasses,..

Kinematical Diffraction (II)
Diffraction from a crystal, reciprocal lattice, structure factor,..

Methoden moderner Röntgenphysik II: Streuung und Abbildung

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,..
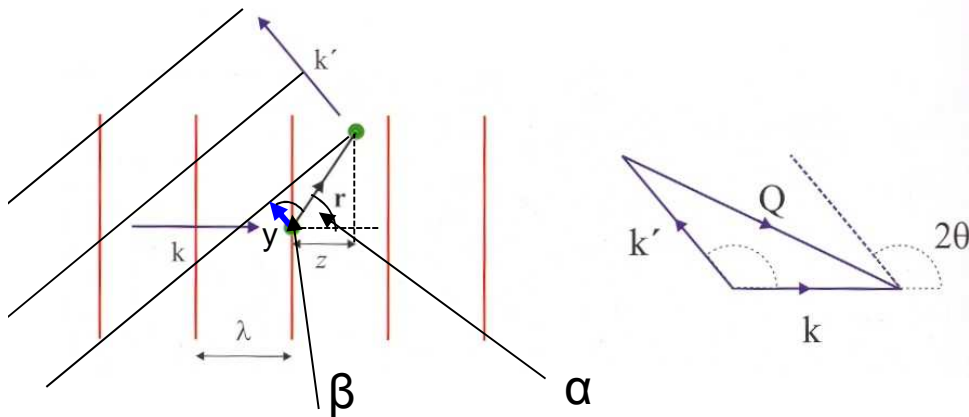
Kinematical Diffraction

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.

Alos called "Born-Approximation"

Consider a 2 electron system:

β   α

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

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

path- or phase difference:

$\Delta\Phi = kz - ky = \mathbf{k} \cdot \mathbf{r} - \mathbf{k'} \cdot \mathbf{r} = \mathbf{Q} \cdot \mathbf{r}$

with

$Q = (4\pi/\lambda)\sin\theta$

scattering amplitude for 2 electrons (one sitting at 0):

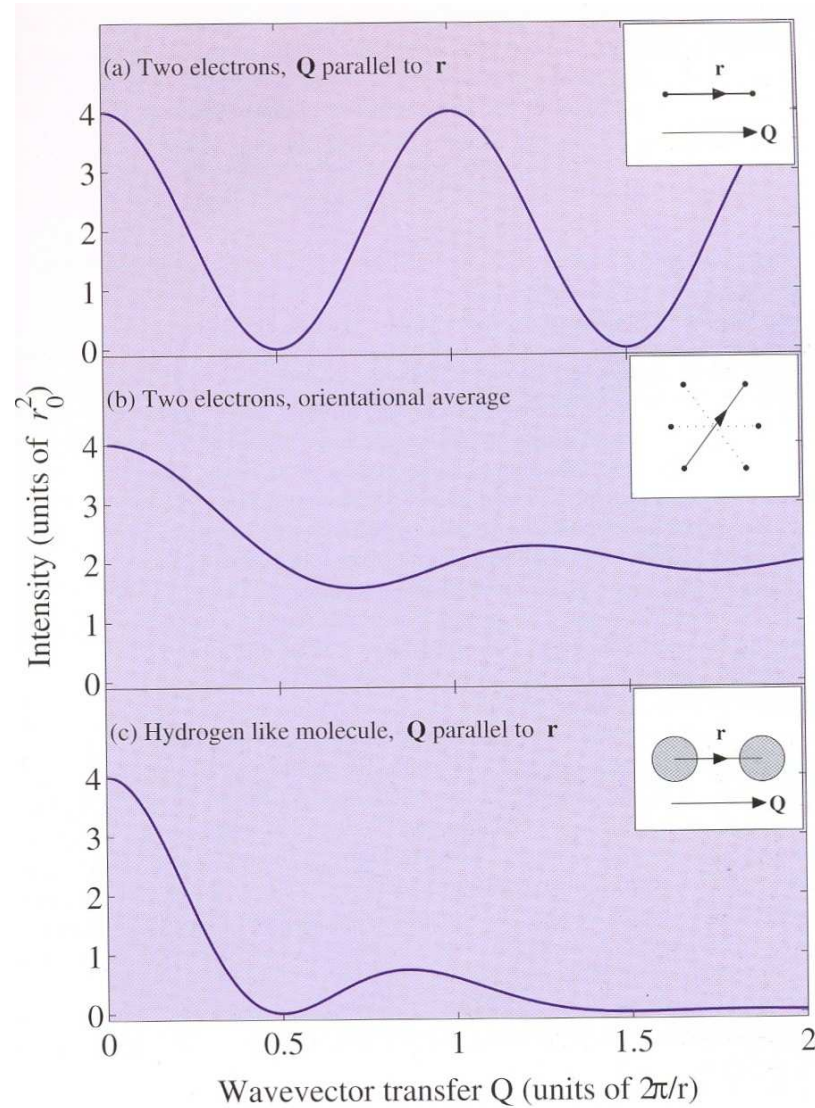$A(\mathbf{Q}) = -r_0 [1 + \exp(i\mathbf{Q}\mathbf{r})]$

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

$\qquad = 2r_0^2 [1 + \cos(Qr)]$

see Fig. 4.2

for many electrons:

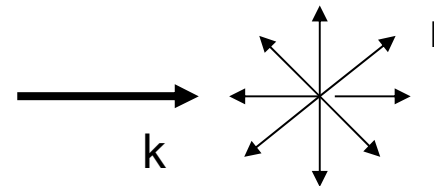$A(\mathbf{Q}) = -r_0 \sum r_{j'} \exp(i\mathbf{Q}\mathbf{r}_{j'})$

Kinematical Diffraction

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

(b) Two electrons, orientational average

(c) Hydrogen like molecule, **Q** parallel to **r**

Intensity (units of r_0^2)

Wavevector transfer Q (units of $2\pi/r$)

Two electron system:

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

Q || r

orientational average

r

k

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

for many systems, e.g. molecules the orientation of **r** will be random wrt **k**

o f_2

o **r**

k f_1
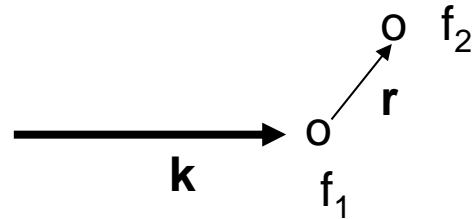
Orientational averaging: assume one electron at r=0, a second at r

$A(Q) = f1 + f_2 \exp(i\mathbf{Qr})$

$I(Q) = f_1^2 + f_2^2 + f_1f_2 \exp(i\mathbf{Qr}) + f_1f_2\exp(-i\mathbf{Qr})$

orientational averaging: $\langle\exp(i\mathbf{QR})\rangle = \langle\exp(-i\mathbf{Qr})\rangle$

$\langle I(Q)\rangle = f_1^2 + f_2^2 + 2f_1f_2\langle\exp(i\mathbf{Qr})\rangle$

$$\langle\exp(i\mathbf{Qr})\rangle = \frac{\int \exp(iQr\cos\theta)\sin\theta\, d\theta d\Phi}{\int \sin\theta\, d\theta d\Phi} \longleftarrow 4\pi$$

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

$= 2\pi \int\exp(iQr\cos\theta)\sin\theta\, d\theta$

$= 2\pi\, (-1/iQr) \int_{iQr}^{-iQr}\exp(x)\, dx$

$= 4\pi \sin(Qr)/Qr$

$\langle I(Q)\rangle = f_1^2 + f_2^2 + 4\pi f_1f_2 \sin(Qr)/Qr$

see figure 4.2 b

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

Scattering from an atom:

scattering amplitude of an atom ≡ atomic form factor $f_0(Q)$ [in units of r_0]

$\rho(r)$: electronic number density ≡ charge density

$$f_0(\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{Qr}) \, d\mathbf{r}$$

$$= \begin{cases} Z & Q \to 0 \\ 0 & Q \to \infty \end{cases}$$

	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

$f_0(Q/4\pi)$ tabulated:

$$f_0(Q/4\pi) = \sum_{j=1}^{4} a_j \exp -b_j (Q/4\pi)^2 + c$$

note:

$$f = f_0(Q) + f' + f''$$
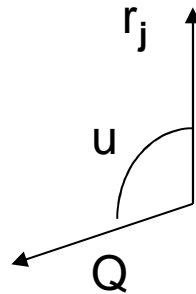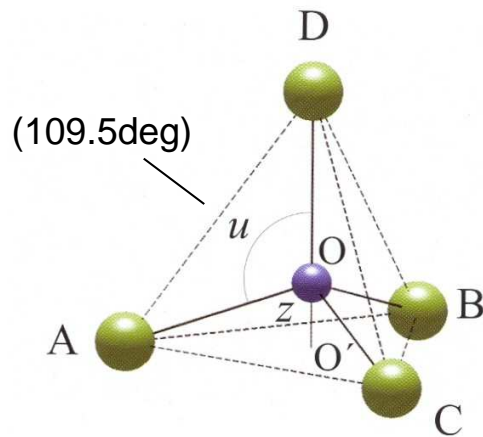
corrections f' and f'' arise from the fact that the electrons are bound in the atom

- # Scattering from a molecule:

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

——	CF_4
-.-.-	CF_4 Q not || C-F
- - - - -	molybdenum
	(also 42 electrons)

example: CF_4:
assume OA=OB=OC=OD=1; z=OO'=cos(u) =1/3

(109.5deg)
u
r_j
u
Q

$$Qr_j = Qr_j \cos(u) = (1/3)Qr_j$$

(F-F bond)

Assume: Q \|\| C-F bond

$$F^{mol} = f^C(Q) + f^F(Q) [\exp(iQR) + 3\exp(iQr_j)\}$$
$$= f^C(Q) + f^F(Q) [3\exp(-/+iQR/3) + \exp(+/-iQR)]$$
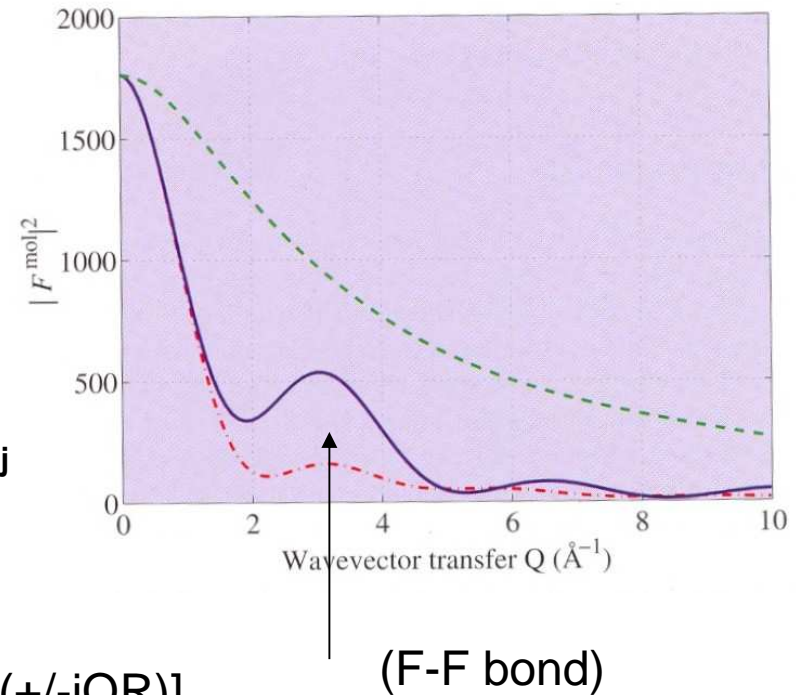
Scattering from liquids and glasses

Crystalline Solid — (a) / Amorphous Solid or Liquid — (b)
(c) / (d)
(e) / (f)
$g(r)$ vs Radius, r
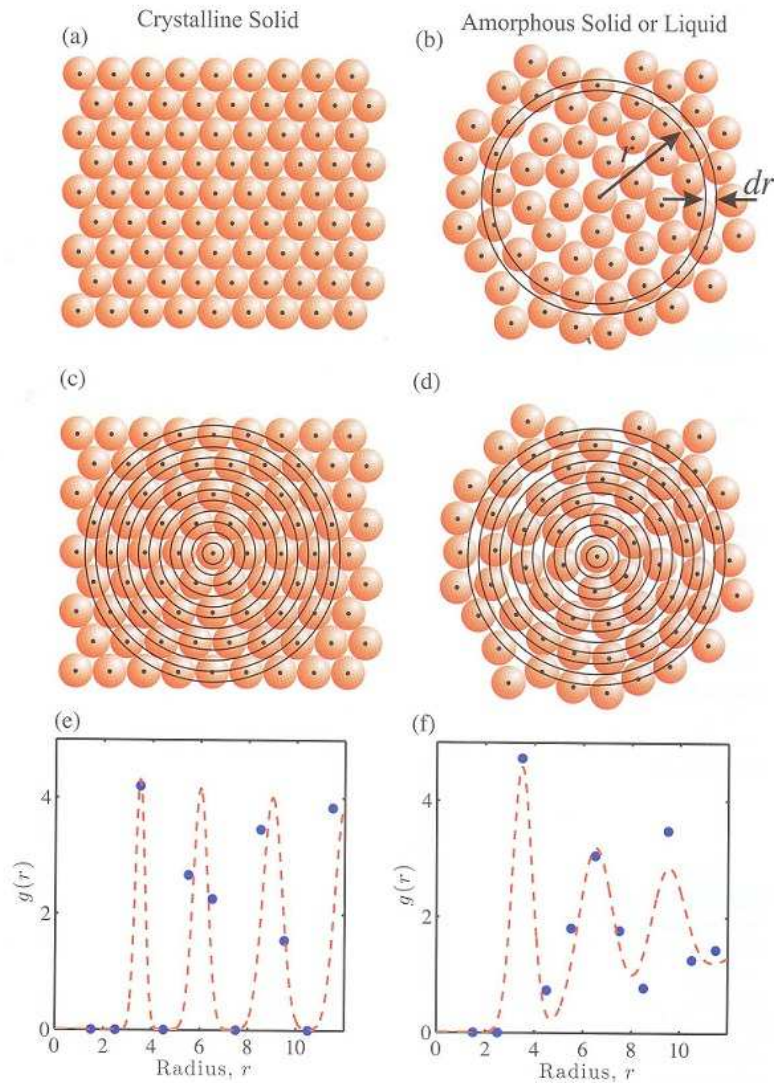
The positions of atoms in non-crystalline materials changes over a wide range of timescales (from nanoseconds in the case of liquids to millennia or more in the case of glasses.

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

Radial density: $\rho(r) = N(r) / (2\pi r dr)$

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

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

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 system:

$$I(\mathbf{Q}) = f(\mathbf{Q})^2 \; {}_n\!\sum \exp(i\mathbf{Q}\mathbf{r}_n) \; {}_m\!\sum \exp(i\mathbf{Q}\mathbf{r}_m) = f(\mathbf{Q})^2 \; {}_n\!\sum {}_m\!\sum \exp i\mathbf{Q}(\mathbf{r}_n\text{-}\mathbf{r}_m)$$

with f($\mathbf{Q}$) formfactor

separate summations

$$I(\mathbf{Q}) = Nf(\mathbf{Q})^2 \; + \; f(\mathbf{Q})^2 \; {}_n\!\sum {}_{m\neq n}\!\sum \exp i\mathbf{Q}(\mathbf{r}_n\text{-}\mathbf{r}_m)$$

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

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

I_{SRO} (Q)	I_{SAXS} (Q)
measures short-range order 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 volume element dV_m located at $\mathbf{r}_m\text{-}\mathbf{r}_n$ relative to $\mathbf{r}_n$.

The liquid structure factor

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

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

$$I(Q) = Nf(Q)^2 + Nf(Q)^2 \, {}_o\!\int^\infty [\, \rho(r)-\rho_{at}) \, 4\pi r2 \, (\sin(Qr)/(Qr) \, dr$$

$\Rightarrow \qquad S(Q) = I^{SRO}(Q)/Nf(Q)^2 = 1 + 4\pi/Q \, {}_o\!\int^\infty r \, [\, \rho(r)-\rho_{at}] \sin(Qr) \, dr$

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

For $Q \rightarrow 0$: $\qquad \sin(Qr)/Q \rightarrow r \Rightarrow \quad S(Q) = 1+ 4\pi \, {}_o\!\int^\infty r^2 dr \, [\, \rho(r)-\rho_{at}]$

$\qquad\qquad S(Q) \propto [\, \rho(r)-\rho_{at}]$ 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.

Ideal gas: $\quad dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \quad$ and with isothermal compressibility $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ and the

$\qquad\qquad\qquad$ thermal expansion coefficient $\quad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad$ follows

$dV = -V\kappa dp + V\beta dT \qquad$ Also: from $\rho V = const \qquad$ follows $\rho dV + V d\rho = 0 \quad$ and $\quad dV = -V\frac{d\rho}{\rho}$

Therefore, for const. temperature, $-V\kappa dp = -V\frac{d\rho}{\rho} \quad$ so $\quad \kappa = \frac{1}{\rho}\frac{d\rho}{dp} \quad$ (density fluctuations : $\frac{d\rho}{dp}$)

For an ideal gas: $\qquad pV=Nk_BT \Rightarrow p=\rho_{at}k_BT \Rightarrow \rho_{at}=p/k_BT \quad$ and $\kappa = 1/(\rho_{at} \, k_BT)$
Actually: $\quad S(Q\rightarrow 0) = \rho_{at} \, \kappa \, k_BT = 1 \qquad$ for an ideal non-interacting gas: no correlation and $S(Q) = 1$
For interacting gas: $\quad \kappa$ diverges at critical point

The pair correlation function g(r):

$$S(Q) = 1 + 4\pi/Q \ _o\!\int^\infty r \ [\ \rho(r) - \rho_{at}] \sin(Qr) \ dr$$

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

$$g(r) \ 1 + (1/2\pi^2 r\rho_{at}) \ _o\!\int^\infty Q \ [\ S(Q) - 1] \sin(Qr) \ dQ$$

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 (typically10 meV); thus any inelastic effect is negligibly small.
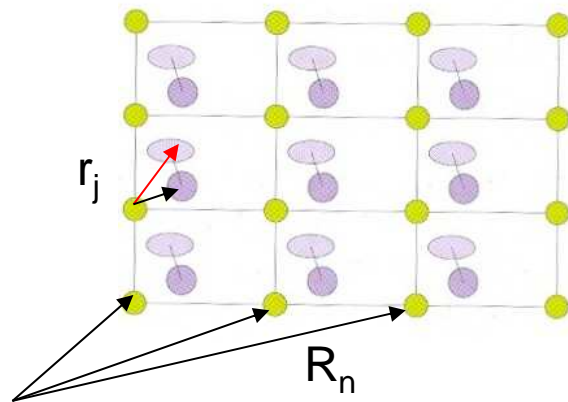
However this does not hold for neutrons.

Scattering from a crystal

$A(\mathbf{Q}) = -r_0 \sum_{rj} \exp(i\,\mathbf{Q}\mathbf{r}_j')$

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

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

r_j

R_n

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

$A(\mathbf{Q}) = -r_0 \sum_{Rn} \exp(i\,\mathbf{Q}\mathbf{R}_n) \sum_{rj} \exp(i\,\mathbf{Q}\mathbf{r}_j)$

lattice sum   unit cell structure factor