Coherence and Correlation in neutron scattering

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Basic Concepts (diffraction case)

Distinction: Coherence versus Correlation

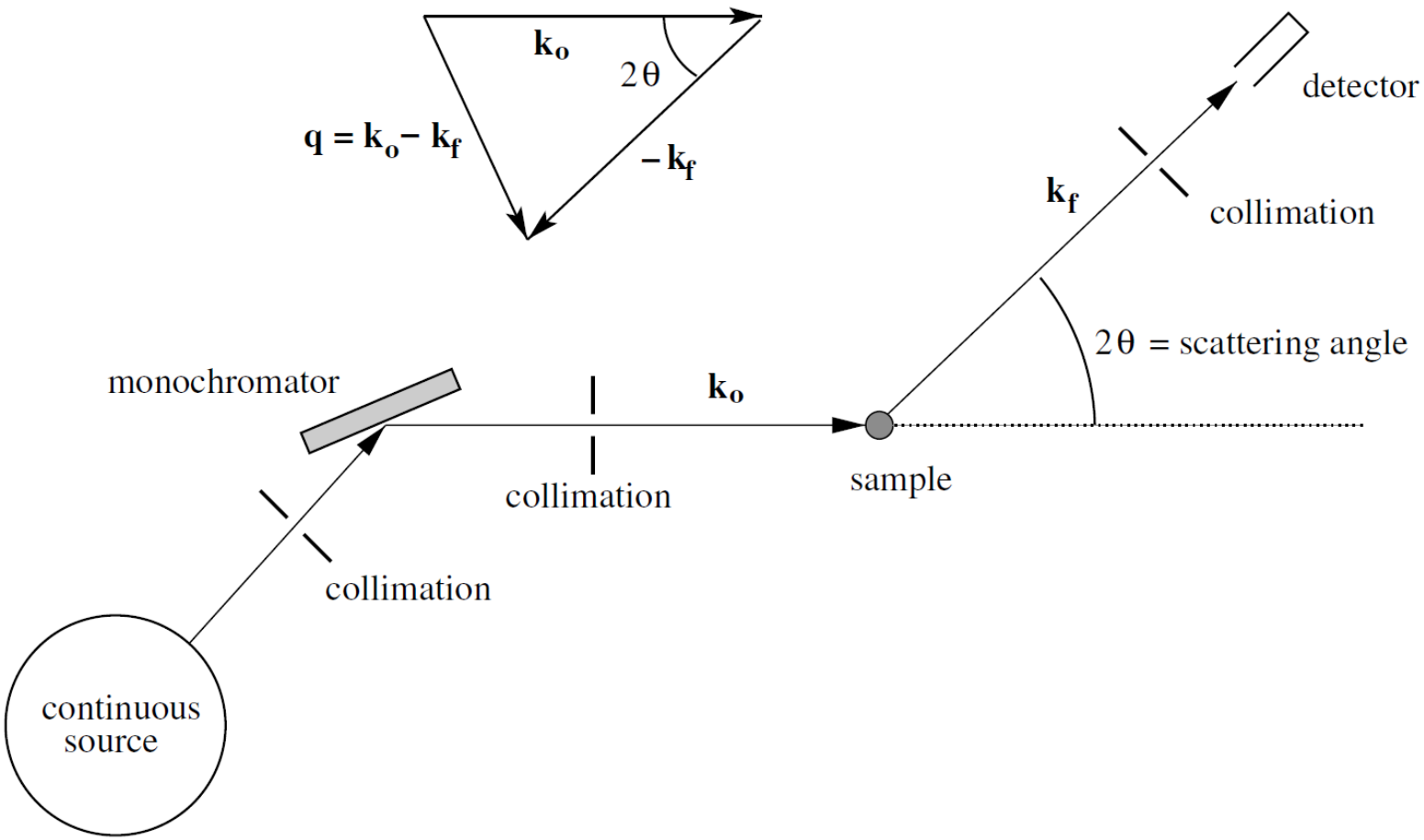
Coherence lengths and times are properties of the wavefunctions of quantum particules/waves as scattered by a sample.
The coherence properties of neutron beams are determined by the optics of the spectrometer or diffractometer.

Correlation lengths and times are parameters describing the structure and dynamics of scattering centers in the sample, *e.g.* as expressed in terms of a van Hove correlation function $G(\mathbf{r}, t)$.

In a neutron scattering experiment, the interference of neutron waves scattered by the atoms of a sample leads to a Fourier transform of $G(\mathbf{r}, t)$ to the measured $S(\mathbf{q}, \omega)$. The *q*-resolution and ω-resolution of a neutron diffractometer or spectrometer are inversely proportional to the relevant coherence lengths and times, respectively.

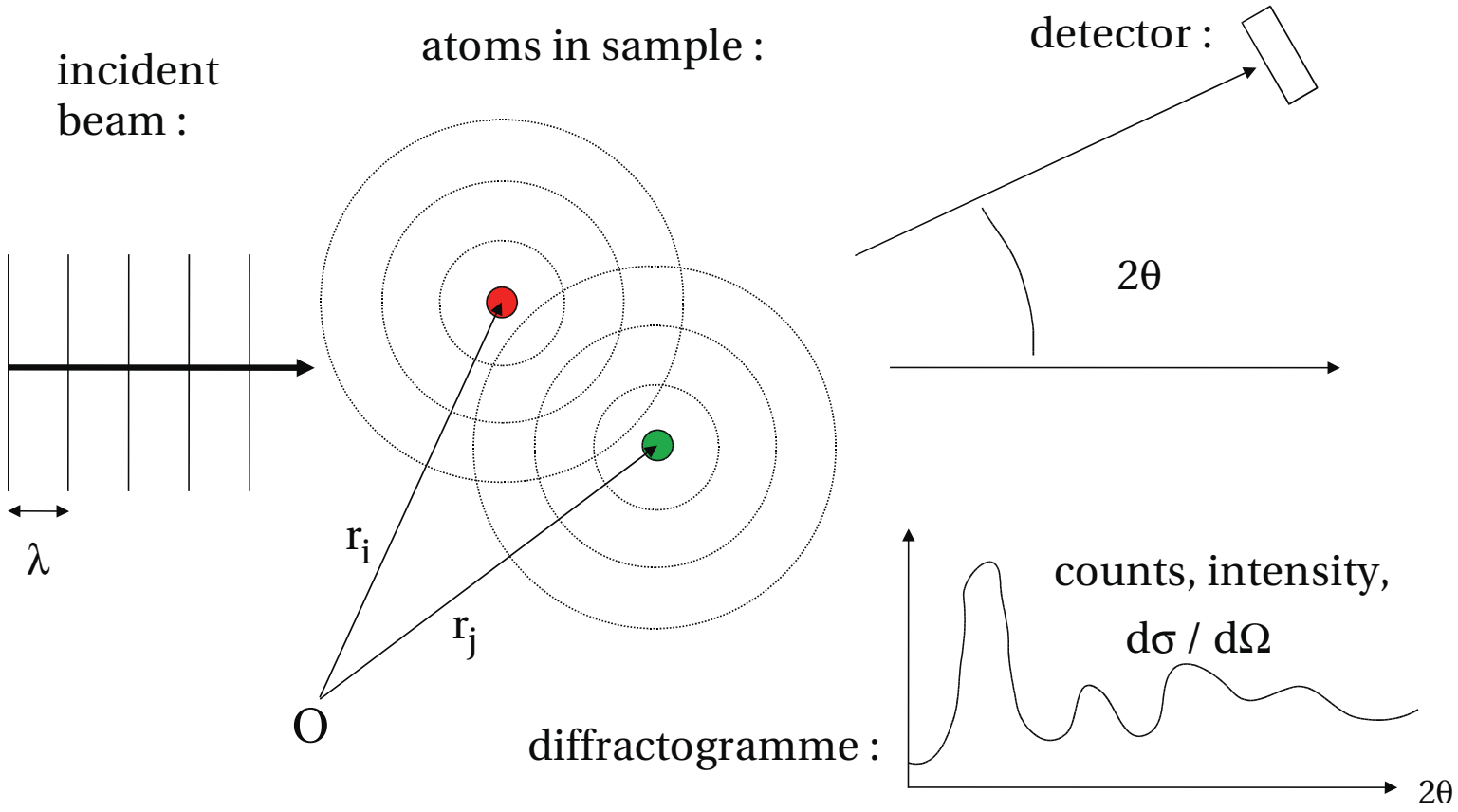
If a neutron coherence length ξ is smaller than the corresponding correlation length ζ (*e.g.* crystallographic grain size) of the sample's structure, then the diffraction experiment is *q-resolution-limited*.
And if a neutron coherence time τ_{coh} is smaller than the corresponding correlation time τ_{correl} (*e.g.* phonon lifetime) of the sample's dynamics, then the inelastic scattering experiment is $\hbar\omega$*-resolution-limited*.

Schematic of a diffraction measurement (mono-λ)



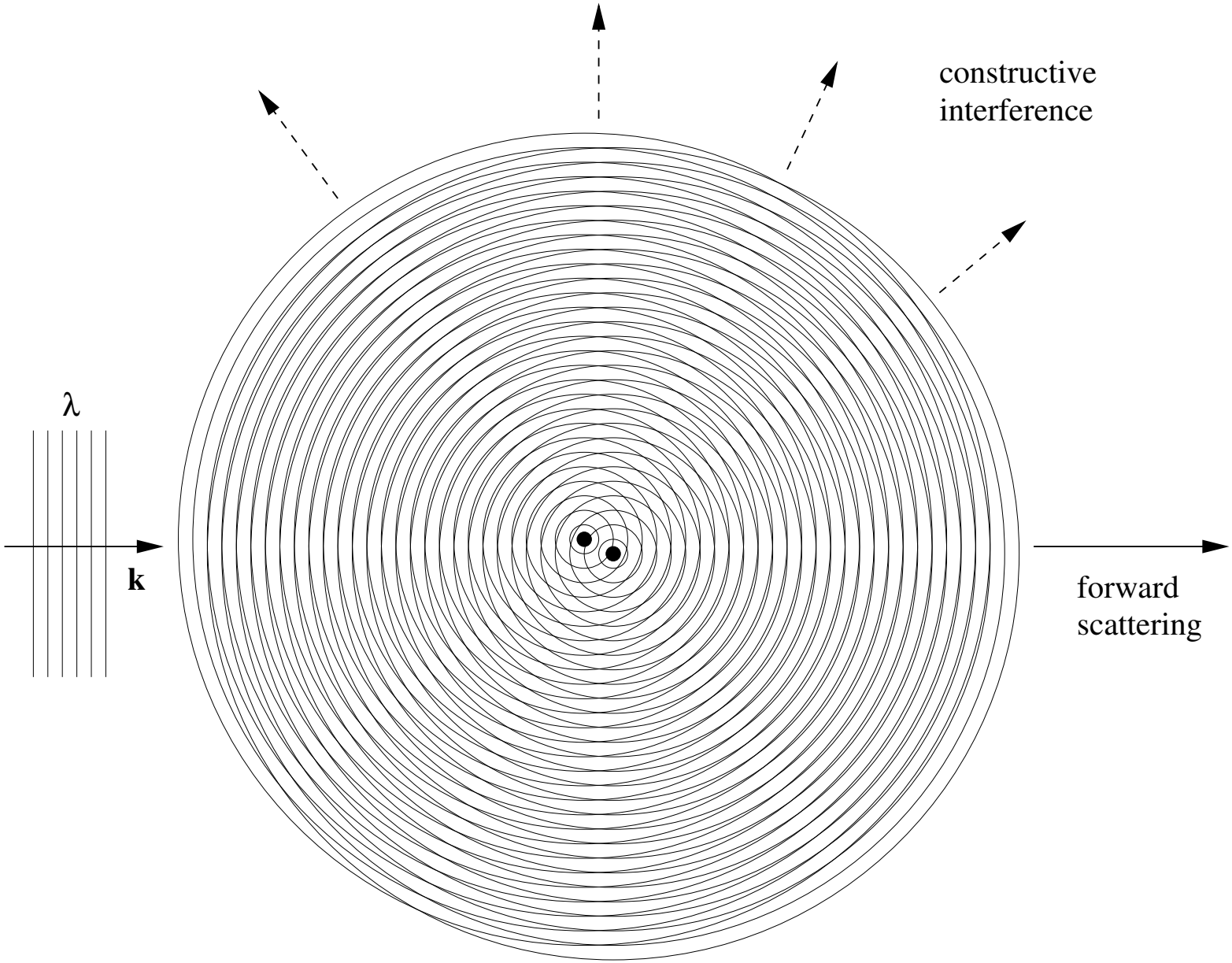
A detector counts *all* neutrons of incident wavevector $\mathbf{k}_o$ and kinetic energy E_o that are scattered by a sample through a scattering angle 2θ with wavevector transfer $\mathbf{q} = \mathbf{k}_o - \mathbf{k}_f$, *regardless of energy loss* $\hbar\omega = E_o - E_f$ *, which in fact defines a diffraction measurement*.

Schematic of a diffraction measurement (mono-λ)

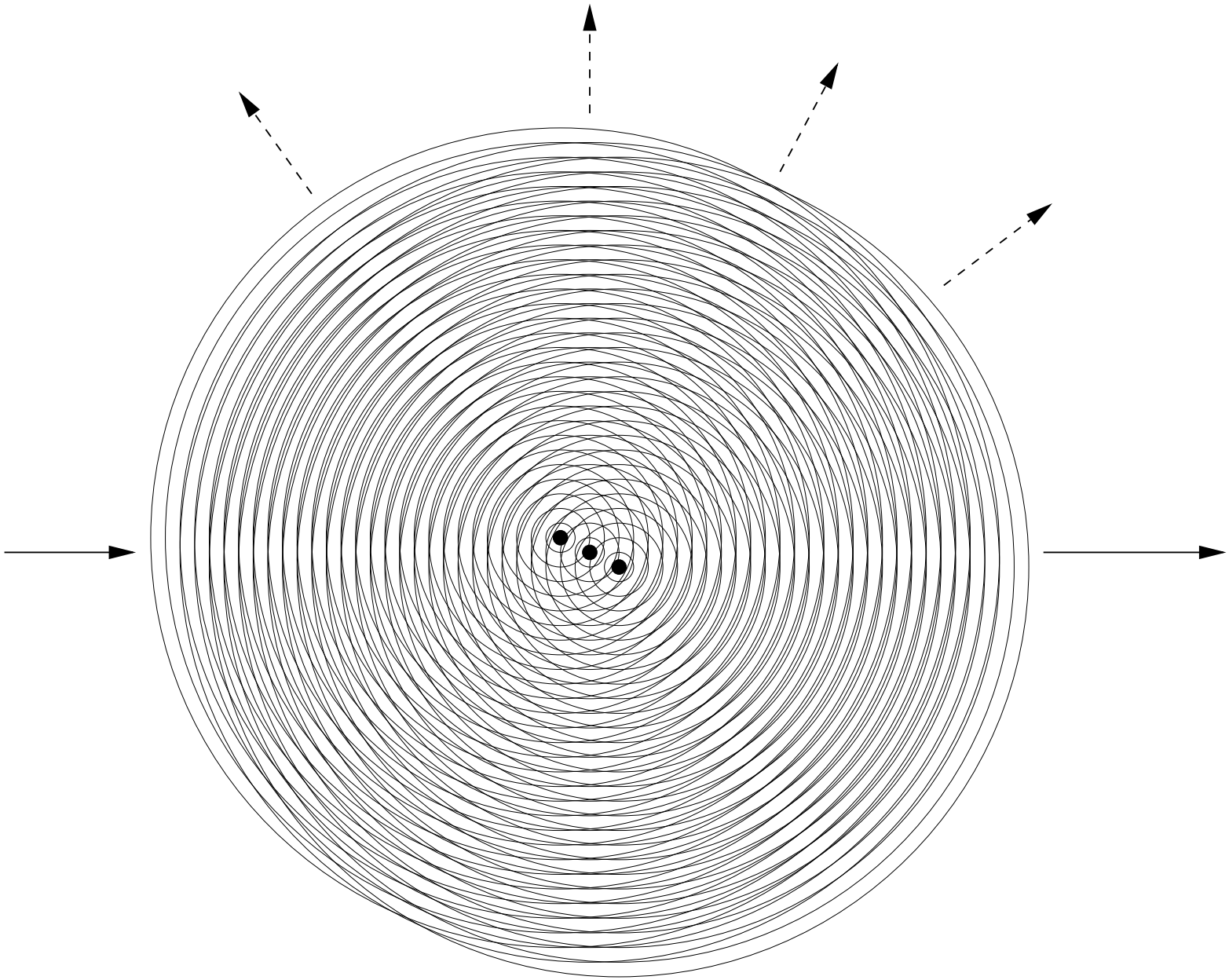


A plane-wave incident neutron beam is scattered by the point-like nuclei of an isotropic sample's atoms into spherical waves that interfere with each other at the detector, producing a diffraction pattern "$d\sigma/d\Omega$" as a function of the scattering angle 2θ, or more exactly as a function of the wave-vector transfer **q** with magnitude $q = (4\pi/\lambda)\ \sin(\theta)$.

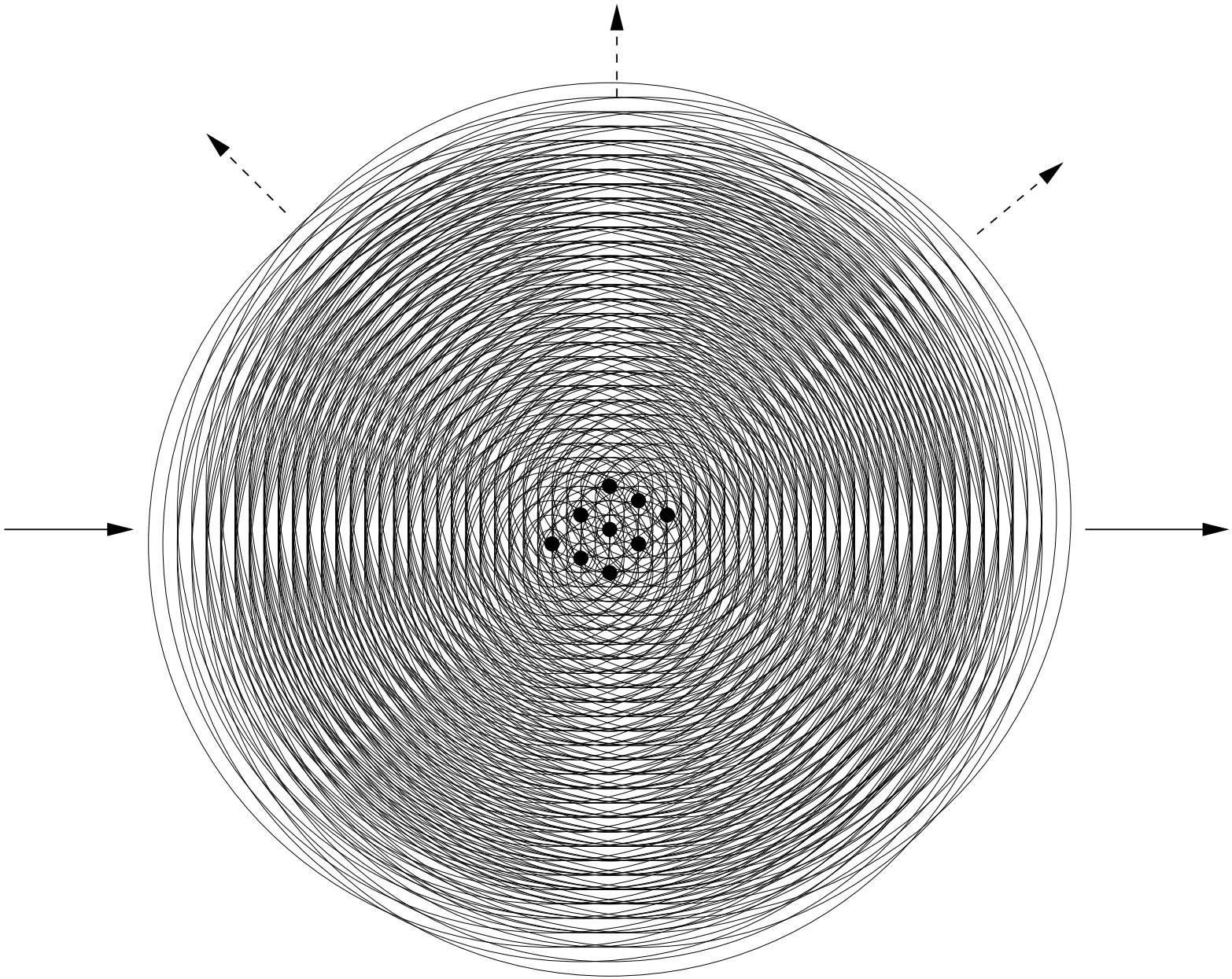
Interference from 2 diffracting atoms



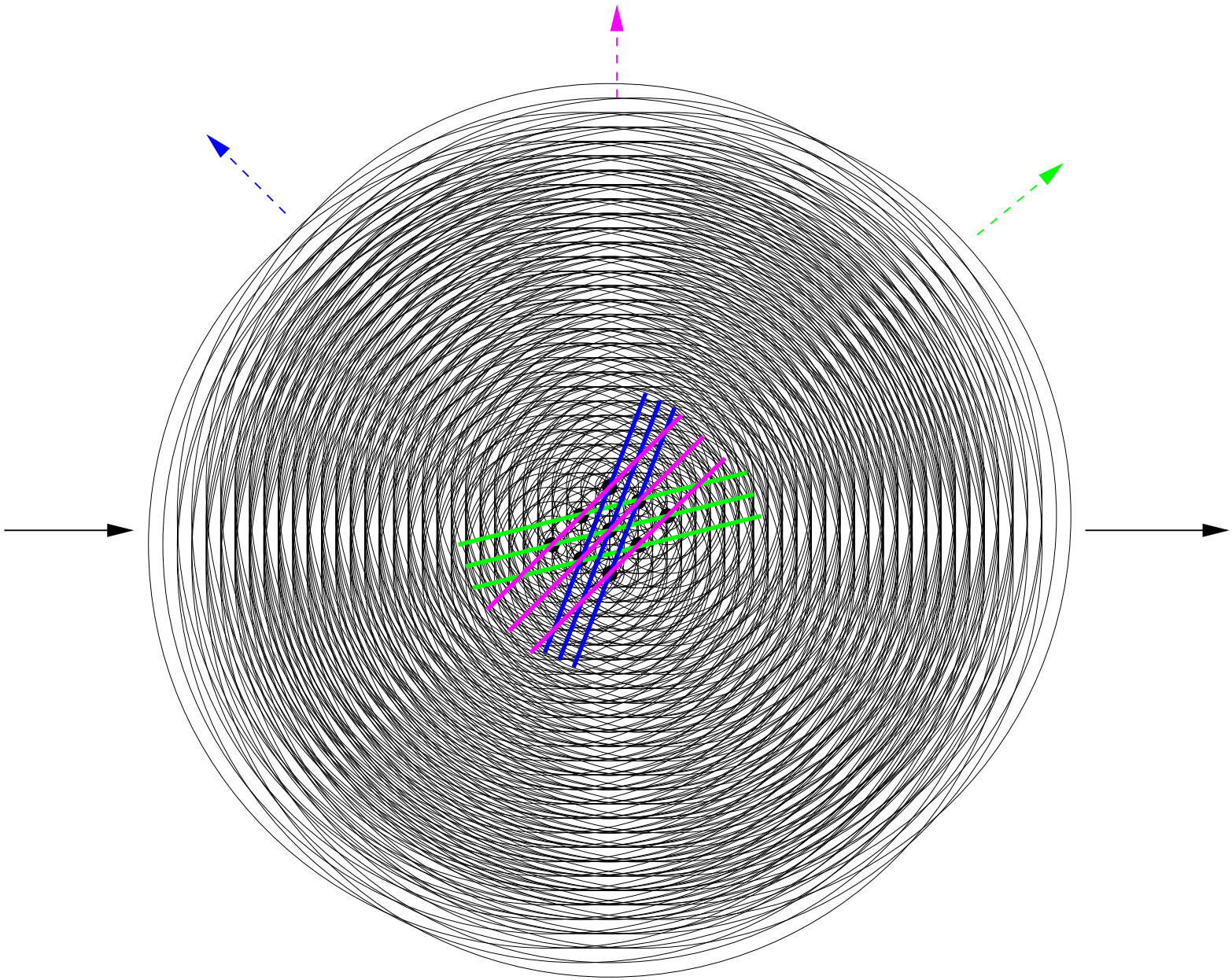
Interference from an ordered line of 3 atoms



Interference from an ordered array of 9 atoms

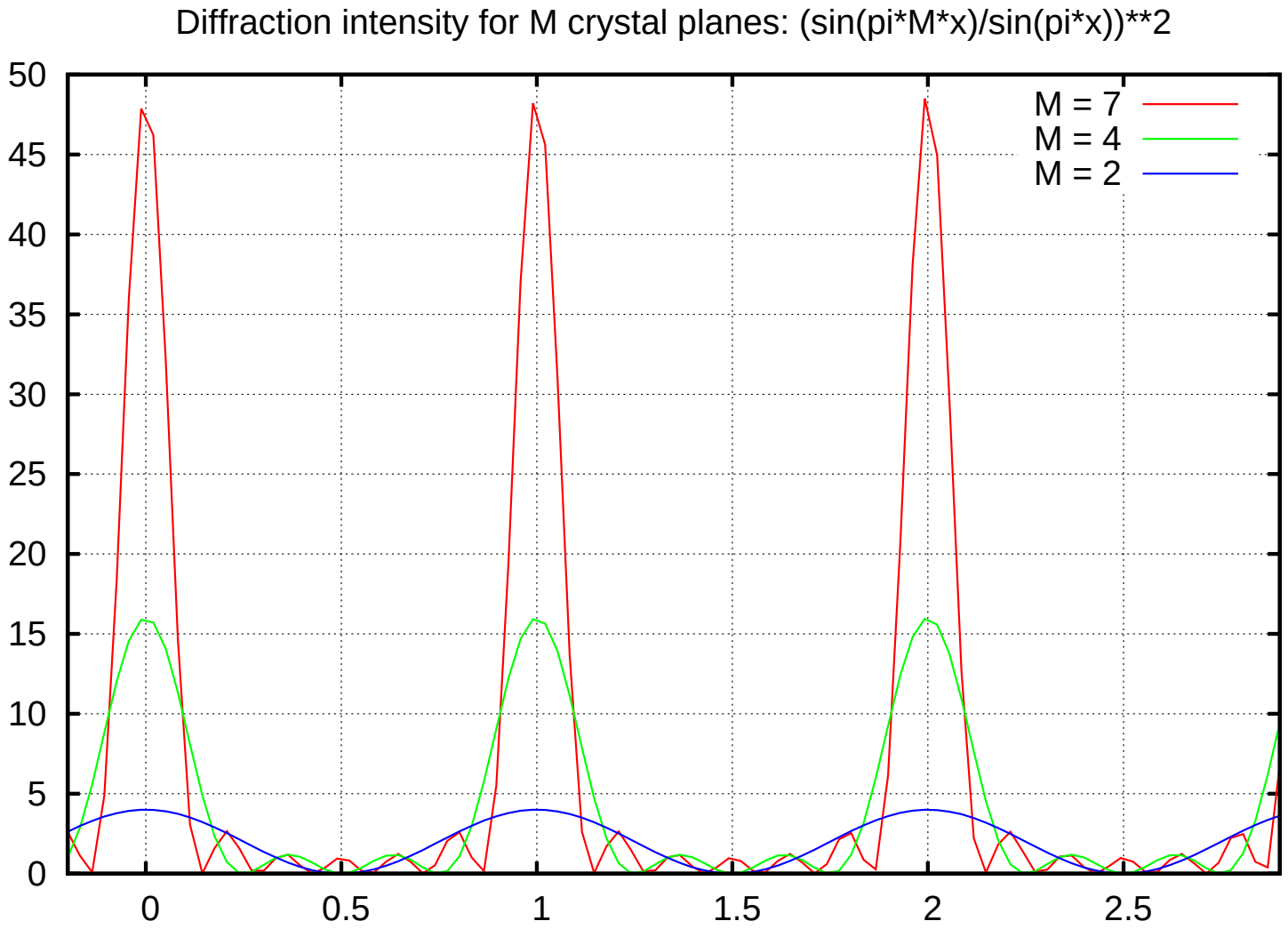


Diffraction intensity as reflected from Bragg planes

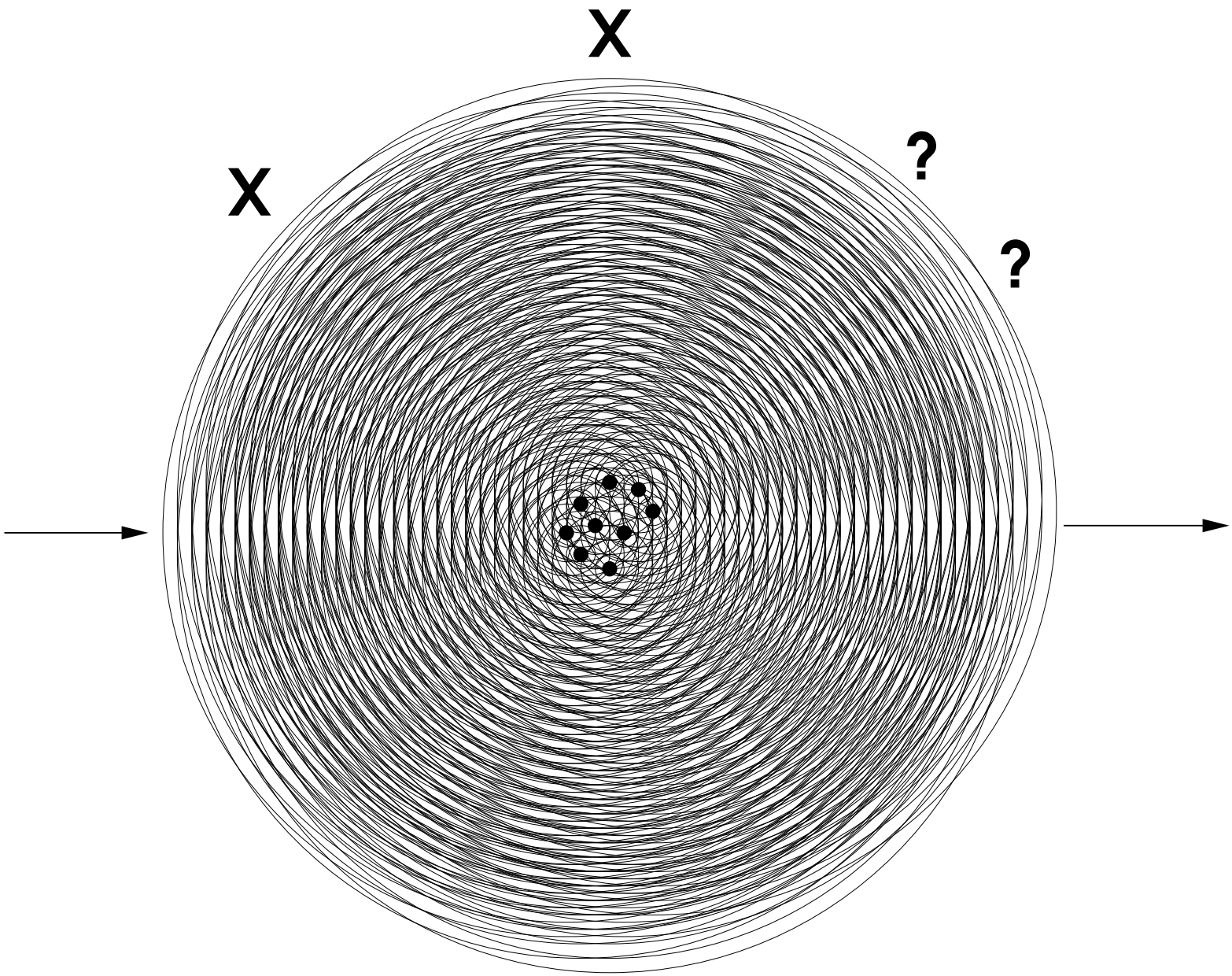


Laue function for diffraction from *M* atomic planes

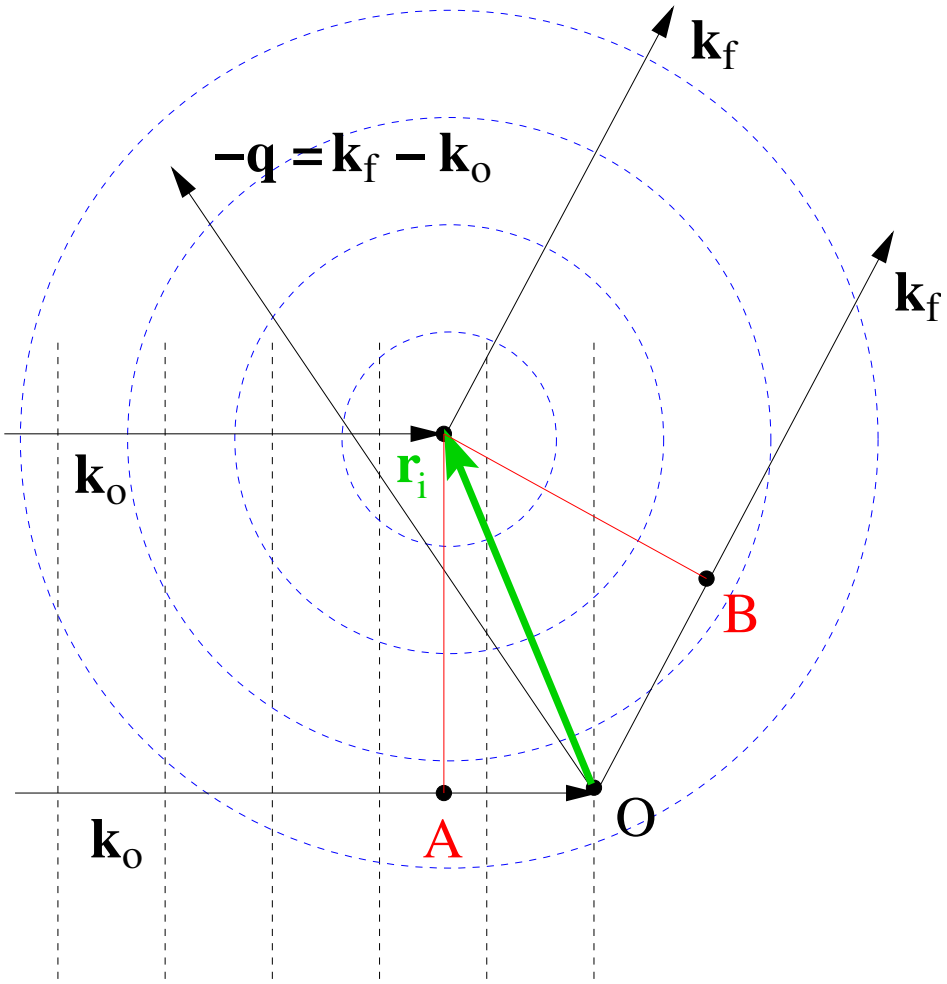
The diffraction peaks get sharper in angle as the number *M* of parallel diffracting crystal planes increases (*i.e.*, as ζ increases):



Diffuse intensity from a disordered array of 9 atoms



Phase of a neutron wave scattering through **q** at $\mathbf{r}_i$



Consider relative plane wave amplitudes at $t = 0$:

incident beam: $e^{i\mathbf{k}_o \cdot \mathbf{r}}$

at detector: $(b_i / r_{\text{det}}) e^{i\mathbf{k}_f \cdot \mathbf{r}}$

The phase ϕ_i of the wave scattered at $\mathbf{r}_i$ with respect to the wave scattered at the origin lags by a phase $|AO|k_o + |OB|k_f$. Thus:

$$\begin{aligned}\phi_i &= -(-\mathbf{k}_o \cdot \mathbf{r}_i + \mathbf{k}_f \cdot \mathbf{r}_i) \\ &= (\mathbf{k}_o - \mathbf{k}_f) \cdot \mathbf{r}_i \\ &= \mathbf{q} \cdot \mathbf{r}_i\end{aligned}$$

is the phase *difference* from diffraction through **q** at $\mathbf{r}_i$.

Whence the total diffraction amplitude *per solid angle* at the detector:

$$A_{\text{det}}(\mathbf{q}) = \sum_i^N b_i \, e^{i\mathbf{q}\cdot\mathbf{r}_i} \qquad b_i = \text{"scattering length"}, \text{ N atoms}$$

Classical versus QM waves

Classical: Amplitude squared = Intensity (*e.g.* power in watts)
QM: Amplitude squared = Probability (*e.g.* per solid angle)
$\Rightarrow$ QM waves consist of propagating *probability amplitudes*.

For an incident neutron flux Φ (n/s/cm^2) and a detector cell of solid angle $d\Omega$, the measured counting rate (n/s) diffracted by a sample is:

$$I(\mathbf{q}) \;=\; \Phi \, \frac{d\sigma}{d\Omega}(\mathbf{q}) \, d\Omega$$

where the differential scattering cross-section $d\sigma/d\Omega$, notably, is a function of **q** *only*, and must have units of cm^2 per steradian (str).
For a sample of cross-sectional area S with respect to the incident beam, ΦS is the number of neutrons per second striking the sample, and thus we can rewrite the detector counting rate as:

$$I(\mathbf{q}) \;=\; [\Phi S] \left[d\Omega \, \frac{d\sigma}{d\Omega}(\mathbf{q}) \, / S \right] \;=\; [\Phi S] \, P_{q,d\Omega}$$

where $P_{q,d\Omega}$ is the **probability** that a neutron striking the sample will scatter by **q** into a solid angle $d\Omega$. $\Rightarrow d\sigma/d\Omega = (P_{q,d\Omega}/d\Omega)\, S$ is a scattering probability per solid angle $\times$ the sample's cross-section S.

Expression for $d\sigma/d\Omega$

Since a probability is a number, and solid angles are also dimensionless (but not unitless!), then $d\sigma/d\Omega$ must have dimensions of L^2. In fact, it turns out that we simply square the scattered neutron wave amplitude:

$$|A_{\rm det}(\mathbf{q})|^2 \;=\; \frac{d\sigma}{d\Omega}(\mathbf{q}) \;=\; \left|\sum_i^N b_i\, e^{i\mathbf{q}\cdot\mathbf{r}_i}\right|^2 \;=\; \sum_{i,j}^N b_i b_j^*\, e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \;,$$

where $\mathbf{q} = \mathbf{k}_{\rm o} - \mathbf{k}_{\rm f}$ as before, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the relative position of atom i with respect to atom j, and * denotes the complex conjugate.

Since phase information is lost in an intensity measurement, we cannot deduce the absolute positions of the atoms directly from the diffraction pattern, but only the *relative positions*. Furthermore, even if we included the time dependence $(-i\omega_f t)$ of the diffraction amplitude at the detector, the detection probability is constant in time (caveat: MIEZE technique):

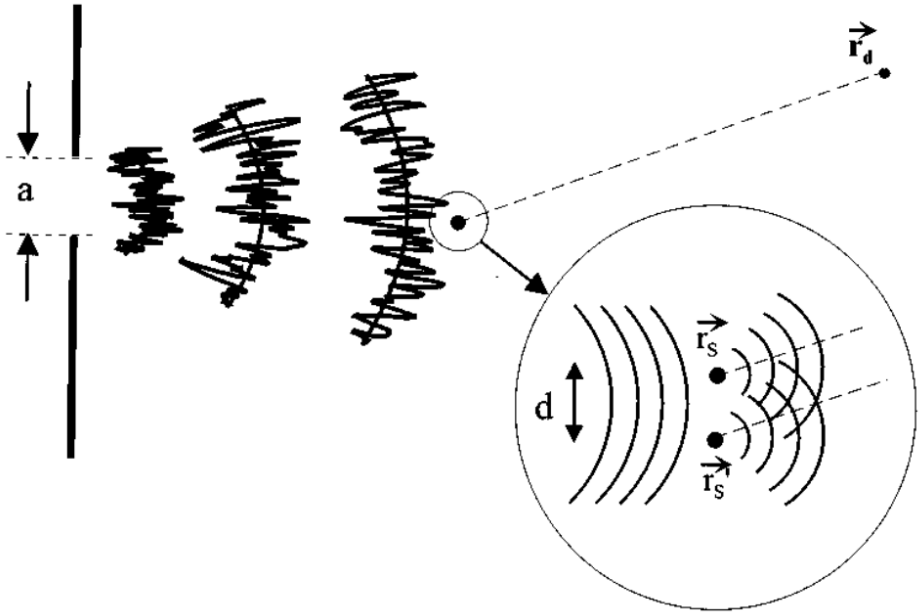
$$|A_{\rm det}(\mathbf{q},t)|^2 \;=\; \left|\sum_i^N b_i\, e^{i\mathbf{q}\cdot\mathbf{r}_i - i\omega_f t}\right|^2 \;=\; \sum_{i,j}^N b_i b_j^*\, e^{i\mathbf{q}\cdot\mathbf{r}_{ij}\; -i\omega_f t\; +i\omega_f t} \;,$$

where $\hbar\omega_f = E_f = (\hbar k_f)^2/2m$, and $\mathbf{q}\cdot\mathbf{r}_{ij}$ is the *relative* phase *difference* of the neutron waves diffracted via $\mathbf{q}$ by atom i with respect to atom j.

Length scales:
How big is a neutron wave?

All neutron sources are incoherent

There is no equivalent of a laser, ondulator or Xfel for neutrons. They are emitted incoherently, *i.e.* no phase relation between each other.

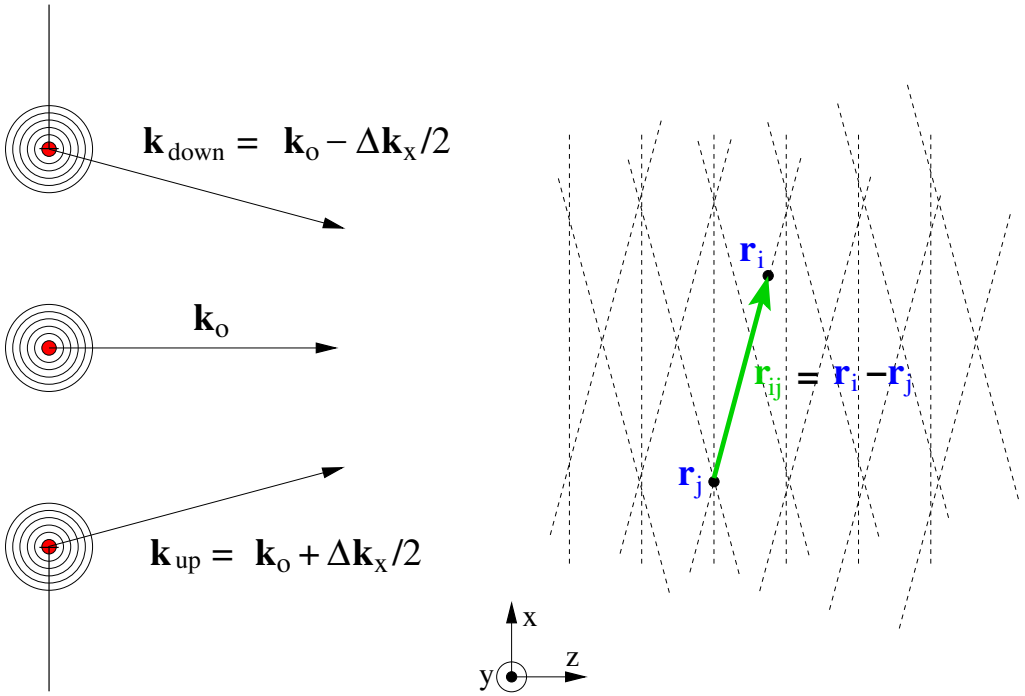


The surface of an entrance slit for a neutron beam can be considered as an array of point-like sources that emit neutron waves with uncorrelated phases, but whose amplitudes add up to produce a common wavefront.

The initial wavefront is very jaggedy. After propagating a very short distance $r \gtrsim a$, the wave's phase remains ∼constant (*i.e.* coherent) over a very small transverse length $d \sim r\lambda/a$ separating new point-like sources (shown at r_s and r'_s) that propagate the wave iteratively via a Huygen's construction, leading to a progressively smoother wavefront. A beam of neutron waves thus acquires transverse coherence simply via propagation. (Figure: *R. Gähler,* et al*, Phys. Rev. A* **58** *(1998) 280.*)

Transverse coherence length from a slit source

Consider 3 points of incoherent emission from a slit source. Let the maximal angular disperson in x be $\Delta k_x/k_o$. Each point source makes a *relative* phase $\phi_{ij} = \phi_i - \phi_j$ between atoms at $\mathbf{r}_i$ and $\mathbf{r}_j$ in the sample.



Relative phases ϕ_{ij}:

$$\phi_{ij,\mathrm{down}} = \mathbf{k}_{\mathrm{down}} \cdot \mathbf{r}_{ij} = 0$$
$$\phi_{ij,\mathrm{o}} = \mathbf{k}_{\mathrm{o}} \cdot \mathbf{r}_{ij} = 3\pi/2$$
$$\phi_{ij,\mathrm{up}} = \mathbf{k}_{\mathrm{up}} \cdot \mathbf{r}_{ij} = 3\pi$$

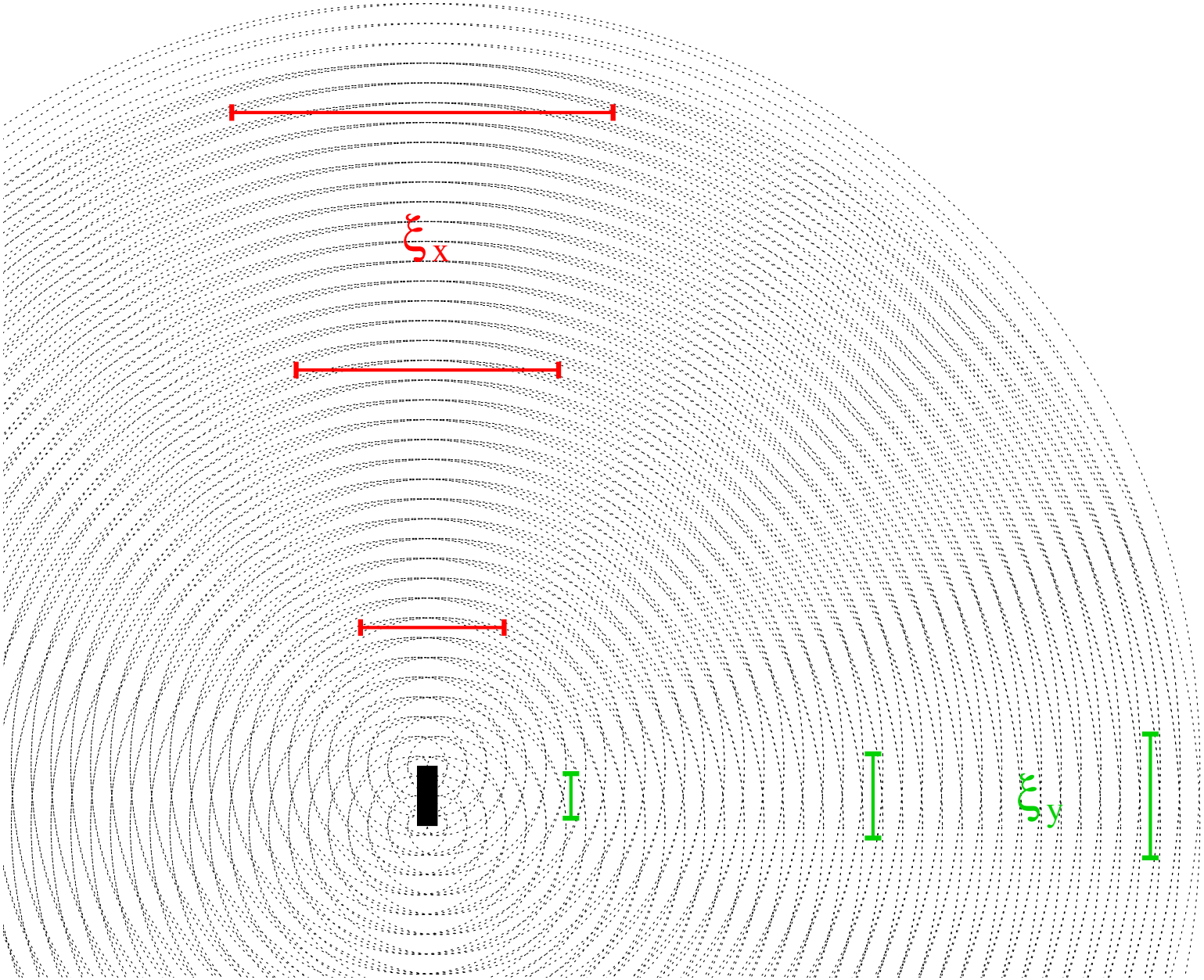
Maximal ϕ_{ij} variation:

$$\Delta\phi_{ij} = \phi_{ij,\mathrm{up}} - \phi_{ij,\mathrm{down}} = \Delta\mathbf{k}_x \cdot \mathbf{r}_{ij} = 3\pi$$

$\Rightarrow$ out of phase!

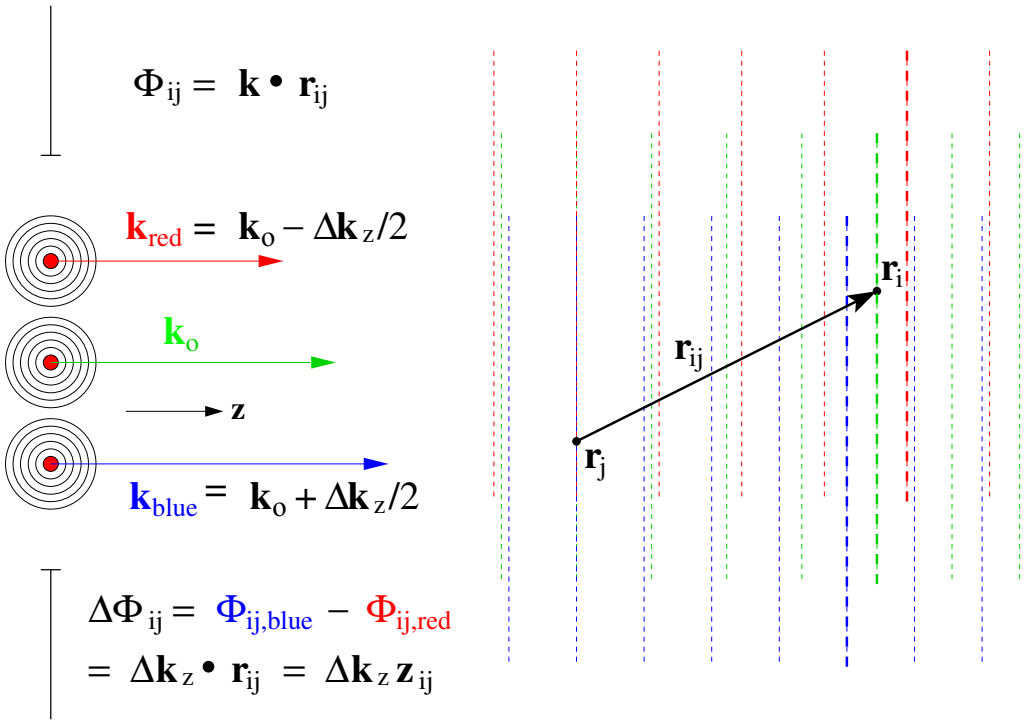
In order for atoms i and j to contribute roughly the same *relative* phase *difference* $\mathbf{q} \cdot \mathbf{r}_{ij}$ at a given $\mathbf{k}_f$ over the full range of incident wavevector dispersion $\Delta\mathbf{k}_x$ coming from the slit, their *relative phase spread* $\Delta\phi_{ij} = \Delta\mathbf{k}_x \cdot \mathbf{r}_{ij} = \Delta k_x x_{ij}$ must be $\lesssim 1$, *i.e.* the maximal separation x_{ij} of atoms i and j must be $\lesssim$ the transverse coherence length $\xi_x \sim 1/\Delta k_x$.

ξ_x and ξ_y from a $\lambda \times 3\lambda$ source size



Longitudinal coherence length from $\Delta\lambda/\lambda$

Consider 3 very closely spaced points of incoherent emission along z having a chromatic spread of $\Delta\lambda/\lambda = \Delta k_z/k_z$. Each point source produces a *relative* phase $\phi_{ij} = \phi_i - \phi_j$ between atoms at $\mathbf{r}_i$ and $\mathbf{r}_j$.



Relative phases ϕ_{ij}:

$\phi_{ij,red} = \mathbf{k}_{red} \cdot \mathbf{r}_{ij} = 7.3\pi$

$\phi_{ij,o} = \mathbf{k}_o \cdot \mathbf{r}_{ij} = 8\pi$

$\phi_{ij,blue} = \mathbf{k}_{blue} \cdot \mathbf{r}_{ij} = 8.8\pi$

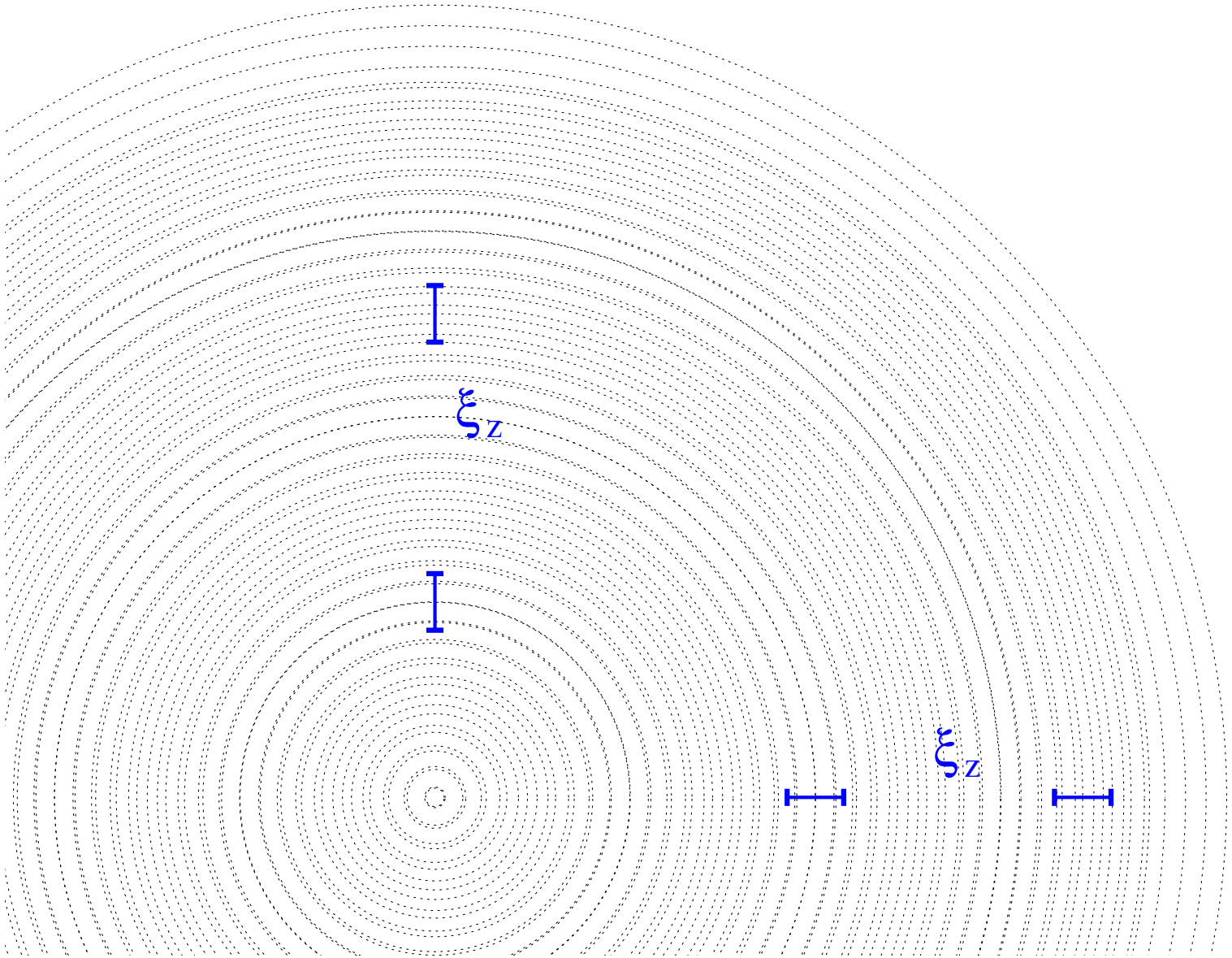
Maximal ϕ_{ij} variation:

$\Delta\phi_{ij} = \phi_{ij,blue} - \phi_{ij,red}$
$= \Delta\mathbf{k}_z \cdot \mathbf{r}_{ij} = 1.5\pi$

$\Rightarrow$ out of phase!

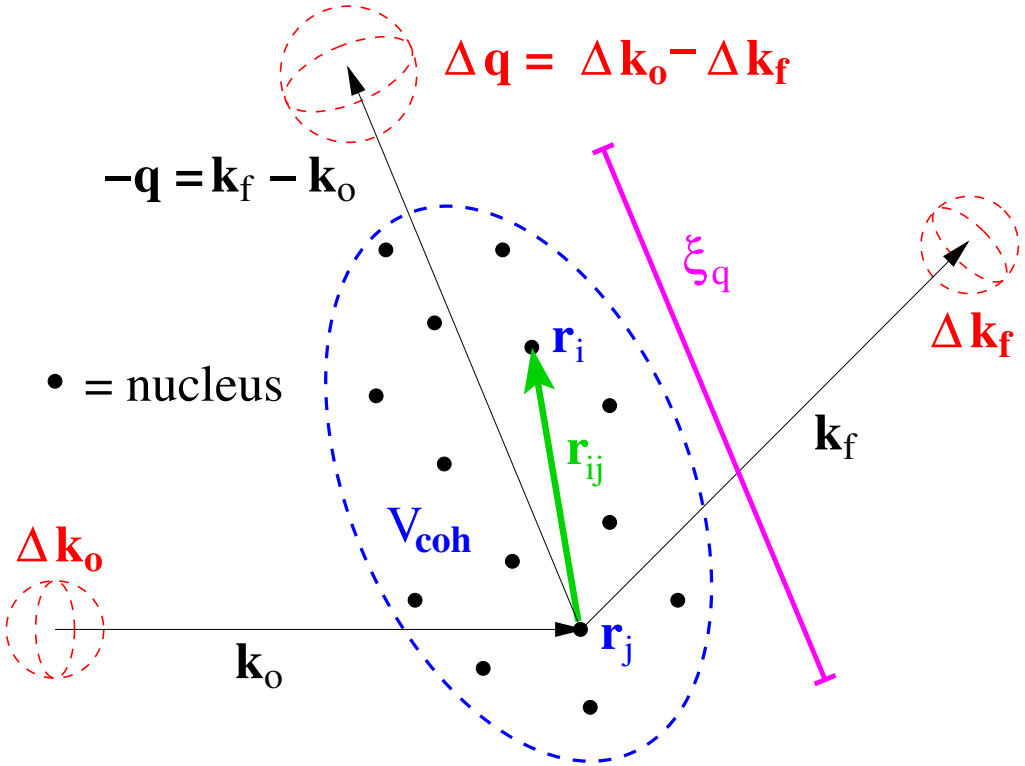
In order for atoms i and j to contribute roughly the same *relative* phase *difference* $\mathbf{q} \cdot \mathbf{r}_{ij}$ at a given $\mathbf{k}_f$ over the full range of incident wavevector $\Delta\mathbf{k}_z$ due to $\Delta\lambda/\lambda$, the *relative phase spread* $\Delta\phi_{ij} = \Delta\mathbf{k}_z \cdot \mathbf{r}_{ij} = \Delta k_z z_{ij}$ must be $\lesssim 1$, *i.e.* the maximal separation z_{ij} between atoms i and j must be $\lesssim$ the longitudinal coherence length $\xi_z \sim 1/\Delta k_z$. $(\tau_{coh} = \xi_z/v_g)$

ξ_z from a point source with $\Delta k_z/k_z = 10\%$



Coherence volume for $\Delta\mathbf{q} = \Delta\mathbf{k}_o - \Delta\mathbf{k}_f$

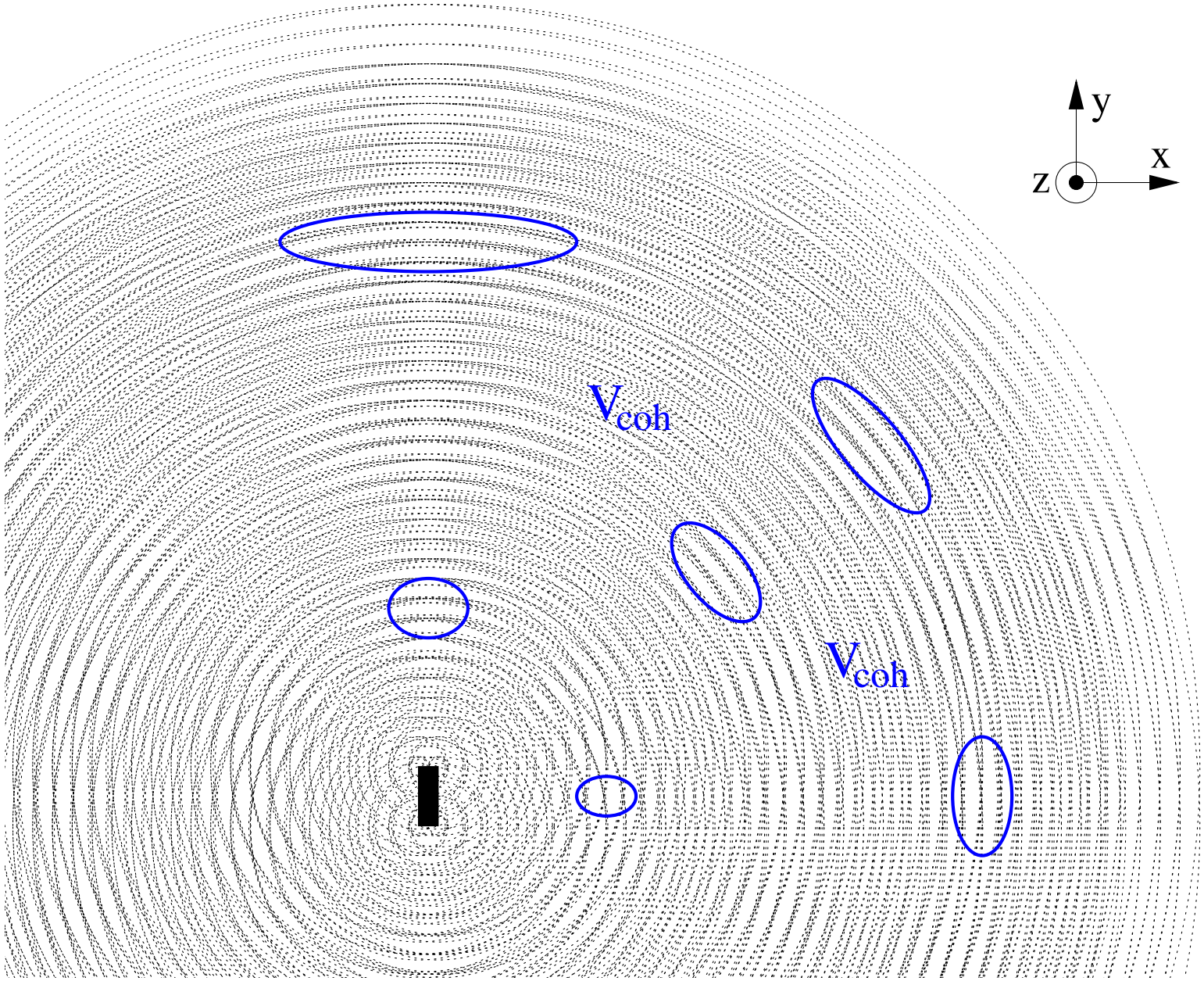
What we did for incident waves with $\Delta\mathbf{k}_o$ coming from a source, we also have to do for scattered waves post-selected by $\Delta\mathbf{k}_f$ (*i.e.* α_3 collimation and possibly an analyzer crystal) going towards the detector, simply by letting time run backwards, producing a total spread $\Delta\mathbf{q}$ in $\mathbf{q}$.



Since $\mathbf{k}_o$ is not $\parallel \mathbf{k}_f$, $\Delta\mathbf{q} = \Delta\mathbf{k}_o - \Delta\mathbf{k}_f$ will depend on q-space focussing aspects à la Caglioti, but in the end for a final measured q-resolution Δq of the diffractogram we have $\xi_q \sim 1/\Delta q$ as the coherence length $\parallel \mathbf{q}$.

The (q-dependent) coherence volume $V_{\rm coh} = \xi_x \xi_y \xi_z$ for $\xi_x \sim 1/\Delta q_x$, $\xi_y \sim 1/\Delta q_y$ and $\xi_z \sim 1/\Delta q_z$. The $\sim$ factor depends on whether "Δ" represents a standard deviation σ or a $\mathrm{FWHM} = 2\sqrt{\ln(4)}\,\sigma = 2.35\,\sigma$.

V_{coh} from a $\lambda \times 3\lambda$ source size with $\Delta k_z/k_z = 10\%$



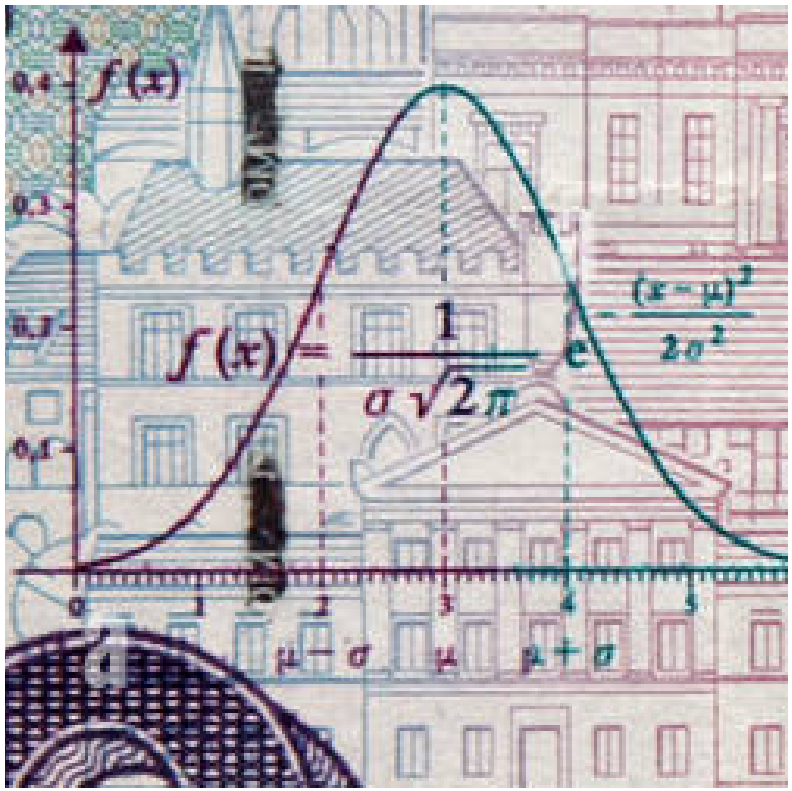
Gaussian functions and their normalization

Gaussian functions can be normalized to unit area or to unit amplitude:

$$G_{area}(x) = \frac{1}{\sigma_x \sqrt{2\pi}} \exp(-x^2/2\sigma_x^2) \qquad G_{ampl}(x) = \exp(-x^2/2\sigma_x^2)$$

$$\Rightarrow \int_{-\infty}^{+\infty} G_{area}(x)\, dx = 1 \qquad G_{ampl}(x=0) = 1$$

where: $\mathrm{var}(x) = \sigma_x^2 = <(x - <x>)^2> = <x^2> - <x>^2$



(1-D) Fourier Transforms: $x \leftrightarrow k$, $\omega \leftrightarrow t$

Application of the Fourier integral to a function in n dimensions leads to a factor of $(\sqrt{2\pi})^n$. Two successive applications therefore returns the original function multiplied by $(2\pi)^n$ which needs to be absorbed by a prefactor somewhere. Mathematicians prefer to share this factor equally between the FT and the inverse FT:

$$\mathrm{FT}[f(x)] = F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x)\, e^{-ikx}\, dx$$

$$\mathrm{FT}^{-1}[F(k)] = f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k)\, e^{+ikx}\, dx$$

Whereas physicists, for some reason, prefer the following convention:

$$\mathrm{FT}[f(x)] = F(k) = \int_{-\infty}^{+\infty} f(x)\, e^{-ikx}\, dx$$

$$\mathrm{FT}^{-1}[F(k)] = f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(k)\, e^{+ikx}\, dx$$

So, how do physicists know where to put the factor of $1/2\pi$?

(1-D) Fourier Transforms of Gaussian functions, etc

Consider the following two Gaussian functions in x-space and k-space:

$$G_{\rm area}(x) = \frac{1}{\sigma_x\sqrt{2\pi}}\,\exp(-x^2/2\sigma_x^2) \qquad G_{\rm ampl}(k) = \exp(-k^2/2\sigma_k^2)$$

The FT of a Gaussian is a Gaussian with $\sigma_x\sigma_k = 1$, and in addition, when we apply the physicist's convention for FT and inverse FT:

$$\mathrm{FT}[G_{\rm area}(x)] \;=\; \int_{-\infty}^{+\infty} G_{\rm area}(x)\; e^{-ikx}\; dx \;=\; G_{\rm ampl}(k)$$

$$\mathrm{FT}^{-1}[G_{\rm ampl}(k)] \;=\; \frac{1}{2\pi}\int_{-\infty}^{+\infty} G_{\rm ampl}(k)\; e^{+ikx}\; dx \;=\; G_{\rm area}(x)$$

$G_{\rm area}(x \text{ or } k)$ is useful as a convolution (*e.g.* resolution) function.
$G_{\rm ampl}(x \text{ or } k)$ is useful as a modulation function (*e.g.* D-W factor).

For $F(k) = \mathrm{FT}[f_{\rm real}(x)]$, then $F(-k) = F^*(k) \;\Rightarrow$ Friedel's Law.

$\mathrm{FT}[f_{\rm real,even}(x)]$ = cosine-transform = real-valued $F(k)$.
$\mathrm{FT}[f_{\rm real,odd}(x)]$ = sine-transform = imaginary-valued $F(k)$.

Another look at the expression for $d\sigma/d\Omega$

As a amplitude^2, the measured differential scattering cross-section

$$|A_{\rm det}(\mathbf{q})|^2 \;=\; \frac{d\sigma}{d\Omega}(\mathbf{q}) \;=\; \left|\sum_i^N b_i\, e^{i\mathbf{q}\cdot\mathbf{r}_i}\right|^2 \;=\; \sum_{i,j}^N b_i b_j^*\, e^{i\mathbf{q}\cdot\mathbf{r}_{ij}}$$

is sensitive to only the *relative* positions $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ of atoms in the sample. Let's define a scattering-length density function $b(\mathbf{r})$:

$$b(\mathbf{r}) = \sum_i^N b_i\, \delta(\mathbf{r}-\mathbf{r}_i) \quad \text{such that} \quad \int_{\rm r} b(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \;= \sum_i^N b_i\, e^{i\mathbf{q}\cdot\mathbf{r}_i}$$

which allows us to write for $\mathbf{R} = \mathbf{r} - \mathbf{r}'$:

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) \;=\; \left|\int_{\rm r} b(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}\right|^2 \;=\; \left[\int_{\rm r} b(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}\right]\cdot\left[\int_{\rm r'} b^*(\mathbf{r}')\, e^{-i\mathbf{q}\cdot\mathbf{r}'} d\mathbf{r}'\right]$$

$$= \int_{\rm r}\int_{\rm r'} b(\mathbf{r}) b^*(\mathbf{r}')\, e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} d\mathbf{r}\, d\mathbf{r}' \;=\; \int_{\rm R}\int_{\rm r'} b(\mathbf{R}+\mathbf{r}') b^*(\mathbf{r}')\, e^{i\mathbf{q}\cdot\mathbf{R}} d\mathbf{R}\, d\mathbf{r}'$$

$$= \int_{\rm R}\left[\int_{\rm r'} b(\mathbf{r}'+\mathbf{R}) b^*(\mathbf{r}')\, d\mathbf{r}'\right] e^{i\mathbf{q}\cdot\mathbf{R}} d\mathbf{R} \;=\; {\rm FT}[\, G_b(\mathbf{R})\,]$$

where $G_b(\mathbf{R}) = (b * b)(\mathbf{R}) = \int_{\rm r'} b(\mathbf{r}'+\mathbf{R}) b^*(\mathbf{r}')\, d\mathbf{r}' = \sum_{i,j}^N b_i b_j^*\, \delta(\mathbf{R}-\mathbf{r}_{ij})$

is the autocorrelation function of the scattering-length density $b(\mathbf{R})$.

For reference: The van Hove correlation functions

Ignoring factors of $b_j, 2\pi$ and other normalisation factors (N atoms):

Atomic position operators: $\mathbf{R}_j(t)$, $\mathbf{R}_k(t)$, $\mathbf{R}_j(0) = \mathbf{R}_j$, $\mathbf{R}_{jk} = \mathbf{R}_j - \mathbf{R}_k$.

Atomic density operators: $\rho(\mathbf{r},t) = \sum_j \delta\{\mathbf{r} - \mathbf{R}_j(t)\}$,
$\rho_{\mathbf{q}}(t) = \mathrm{FT}_{\mathbf{r}}[\rho(\mathbf{r},t)] = \sum_j \exp[-i\mathbf{q}\cdot\mathbf{R}_j(t)]$

The time-dependent pair-correlation function: $N \cdot G(\mathbf{r},t)$
$= \int_{\mathbf{r}'} \langle \rho(\mathbf{r}',0)\rho(\mathbf{r}'+\mathbf{r},t)\rangle \, d\mathbf{r}' = \sum_{j,k} \langle \delta\{\mathbf{r} - \mathbf{R}_j(t) + \mathbf{R}_k(0)\}\rangle$

The intermediate scattering function: $N \cdot I(\mathbf{q},t) = N \cdot \mathrm{FT}_{\mathbf{r}}[G(\mathbf{r},t)]$
$= \langle \rho_{\mathbf{q}}(0)\rho_{-\mathbf{q}}(t)\rangle = \sum_{j,k} \langle \exp[-i\mathbf{q}\cdot\mathbf{R}_j(0)] \exp[+i\mathbf{q}\cdot\mathbf{R}_k(t)]\rangle$

The dynamical structure factor: $S(\mathbf{q},\omega) = \mathrm{FT}_t[I(\mathbf{q},t)] = \mathrm{FT}_{\mathbf{r},t}[G(\mathbf{r},t)]$

The static pair-distribution function: $g(\mathbf{r}) = G(\mathbf{r},0) - \delta(\mathbf{r})$
$= (1/N) \cdot \sum_{j\neq k} \langle \delta\{\mathbf{r} - \mathbf{R}_{jk}\}\rangle = \mathrm{FT}_{\mathbf{q}}[S(\mathbf{q}) - 1] \sim \mathrm{PDF}(r)$

The static structure factor: $S(\mathbf{q}) = I(\mathbf{q},0)$ (*i.e.* instantaneous positions)
$= \int_{-\infty}^{+\infty} S(\mathbf{q},\omega)\, d\omega = (1/N) \cdot \sum_{j,k} \langle \exp[i\mathbf{q}\cdot\mathbf{R}_{jk}]\rangle = \mathrm{FT}_{\mathbf{r}}[g(\mathbf{r}) - 1]$

The Patterson function: $N \cdot G(\mathbf{r},\infty)$ (*i.e.* time-averaged positions)
$= \int_{\mathbf{r}'} \langle \rho(\mathbf{r}')\rangle\langle \rho(\mathbf{r}'+\mathbf{r})\rangle \, d\mathbf{r}' = N \cdot \mathrm{FT}_{\mathbf{q},\omega}[S(\mathbf{q},0)]$ (*i.e.* elastic)

where the averaging brackets $\langle \ldots \rangle$ represent a thermal average.

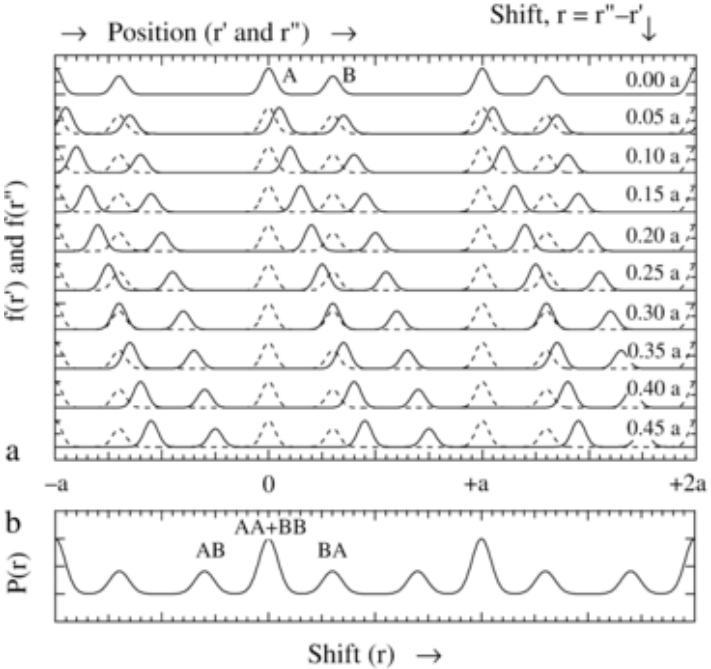
$G(\mathbf{r},t)$, $g(\mathbf{r})$, $S(\mathbf{q},\omega)$, $S(\mathbf{q})$ are real-valued, but $I(\mathbf{q},t)$ can be complex.

Autocorrelation and the Wiener-Khinchin theorem

We have seen that the measured differential scattering cross-section

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \mathrm{FT}_{\mathbf{r}}[\, G_b(\mathbf{r})\,], \; G_b(\mathbf{r}) = \int_{\mathrm{r}'} b(\mathbf{r}'+\mathbf{r}) b^*(\mathbf{r}')\, d\mathbf{r}' = \sum_{i,j}^{N} b_i b_j^*\, \delta(\mathbf{r}-\mathbf{r}_{ij})$$

is the FT of the spatial autocorrelation of the scattering-length density of the sample, where $G_b(\mathbf{r}) \rightarrow \mathrm{PDF}(r)$ is a Pair-Distribution Function. This is a special case of the *Wiener-Khinchin theorem* which states that the power spectrum of a structure or process is the FT of its autocorrelation function. Another example: the density of phonon states DOS(ω) is the FT of the atoms' velocity auto-correlation function in time.



For two atoms A and B in a 1-D periodic structure, the autocorrelation P(*r*) of their positions will show a strong peak when the displacement *r* equals the period, and secondary peaks when *r* equals $r_A - r_B$ or $r_B - r_A$, *i.e.* at all *relative* distances between atoms, such that P(*r*) becomes a symmetric and periodic function of the displacement *r*.

The Patterson function as prelude to PDF(r)

Patterson function as time avg: $N \cdot G(\mathbf{r},\infty) = \int_{r'} \langle \rho(\mathbf{r}') \rangle \langle \rho(\mathbf{r}'+\mathbf{r}) \rangle \, d\mathbf{r}'$

$$\left.\frac{d\sigma}{d\Omega}\right|_{coh}^{elastic}(\mathbf{q}) = \frac{\sigma_{coh}}{4\pi} \mathrm{FT}_{\mathbf{r}}[\, N \cdot G(\mathbf{r},\infty)\,] = \frac{\sigma_{coh}}{4\pi} \left| \int_{r} \langle \rho(\mathbf{r}) \rangle \, e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \right|^2$$

If the phases $\phi(hkl)$ of the structure factors $F(hkl)$ were known, one could calculate the scattering length density function $\rho(xyz)$:

$$\rho(xyz) = \frac{1}{V} \sum_{\substack{hkl \\ -\infty}}^{+\infty} |F(hkl)| \, . \, e^{-2\pi i[hx+ky+lz-\phi(hkl)]}$$

and thereby deduce the atomic positions x, y, z within the unit cell. By using instead the measured intensity $I(hkl) \propto |F(hkl)|^2$ in the Fourier series, we eliminate $\phi(hkl)$ and obtain the Patterson function $P(uvw)$ of all *interatomic distances* ($u = x_i - x_j$, $v = y_i - y_j$, $w = z_i - z_j$) rather than of all absolute atomic positions in the unit cell:

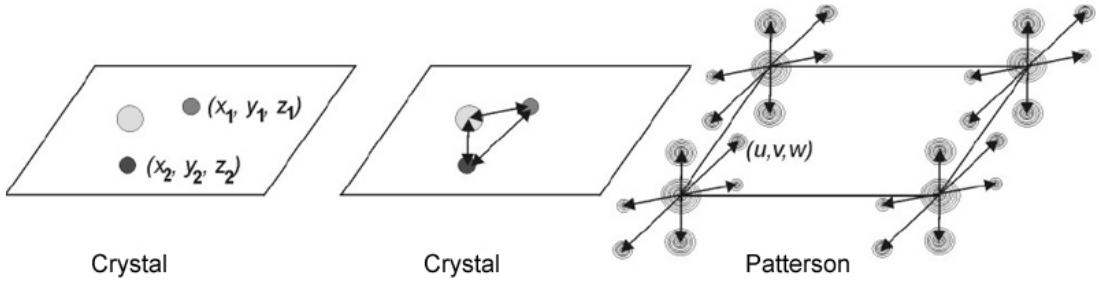
$$P(uvw) = \frac{1}{V} \sum_{\substack{hkl \\ -\infty}}^{+\infty} |F(hkl)|^2 \, . \cos 2\pi \, [hu + kv + lw]$$

A radial average of $P(uvw)$ produces a 1-D pair-distribution function $P(r)$ based solely on elastic Bragg peak intensities, thus representing the sample's structure as averaged over space and time.

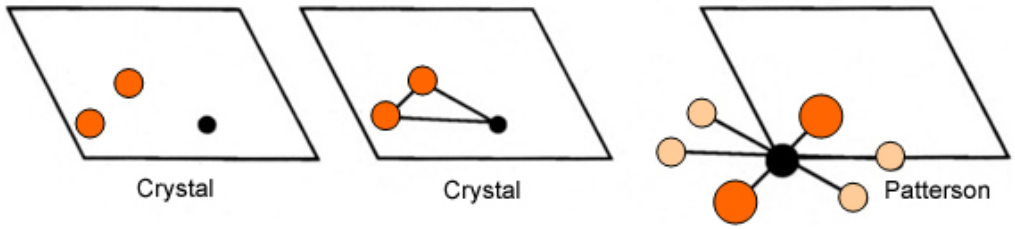
The Patterson function as prelude to PDF(r)

$$P(uvw) = G(\mathbf{r},\infty) = \mathrm{FT}_{\mathbf{q}}\left[\frac{4\pi}{N\sigma_{\mathrm{coh}}}\cdot\frac{d\sigma}{d\Omega}\Big|^{\mathrm{elastic}}_{\mathrm{coh}}(\mathbf{q})\right] \overset{\mathrm{Bragg}}{=} \mathrm{FT}_{\mathbf{q}}[\,|F(hkl)|^2\,]$$

Although $P(uvw)$ has the same unit cell as the crystal's, it contains a high density of peaks and is by definition centrosymmetric. In 2-D:



$P(uvw)$ is proportional to the product of the scattering lengths of the pair (or pairs!) of atoms separated by u, v, w, helping to determine their chemical identities. An "average atom" sits at $(uvw) = (000)$:



As $P(uvw)$ sees only *relative* distances, it has a center of inversion and all its symmetry operations have zero translation, leading to higher symmetry than the crystal lattice and only 24 Patterson space groups.

Gaussian wavepackets

A wavepacket $W(x,t)$ propagating along **x** can be formed by summing up plane waves whose amplitudes are a (narrow) Gaussian function of k. Ignoring normalisation factors of σ and $\sqrt{2\pi}$, we can write:

$$W(x,t) = \int_{-\infty}^{+\infty} A(k)\, e^{ikx - i\omega t}\, dk \qquad A(k) = \exp(-(k-k_o)^2/2\sigma_k^2)$$

where $A(k)$ effectively spreads or *convolves* by a width σ_k an otherwise $\delta(k-k_o)$ monochromatic distribution in k. The resulting wavepacket moves with group velocity $v_{\text{group}} = d\omega/dk$, and at $t = 0$ is given by:

$$W(x,0) = L(x)e^{ik_o x} \qquad L(x) = \exp(-(x-x_o)^2/2\sigma_x^2)$$

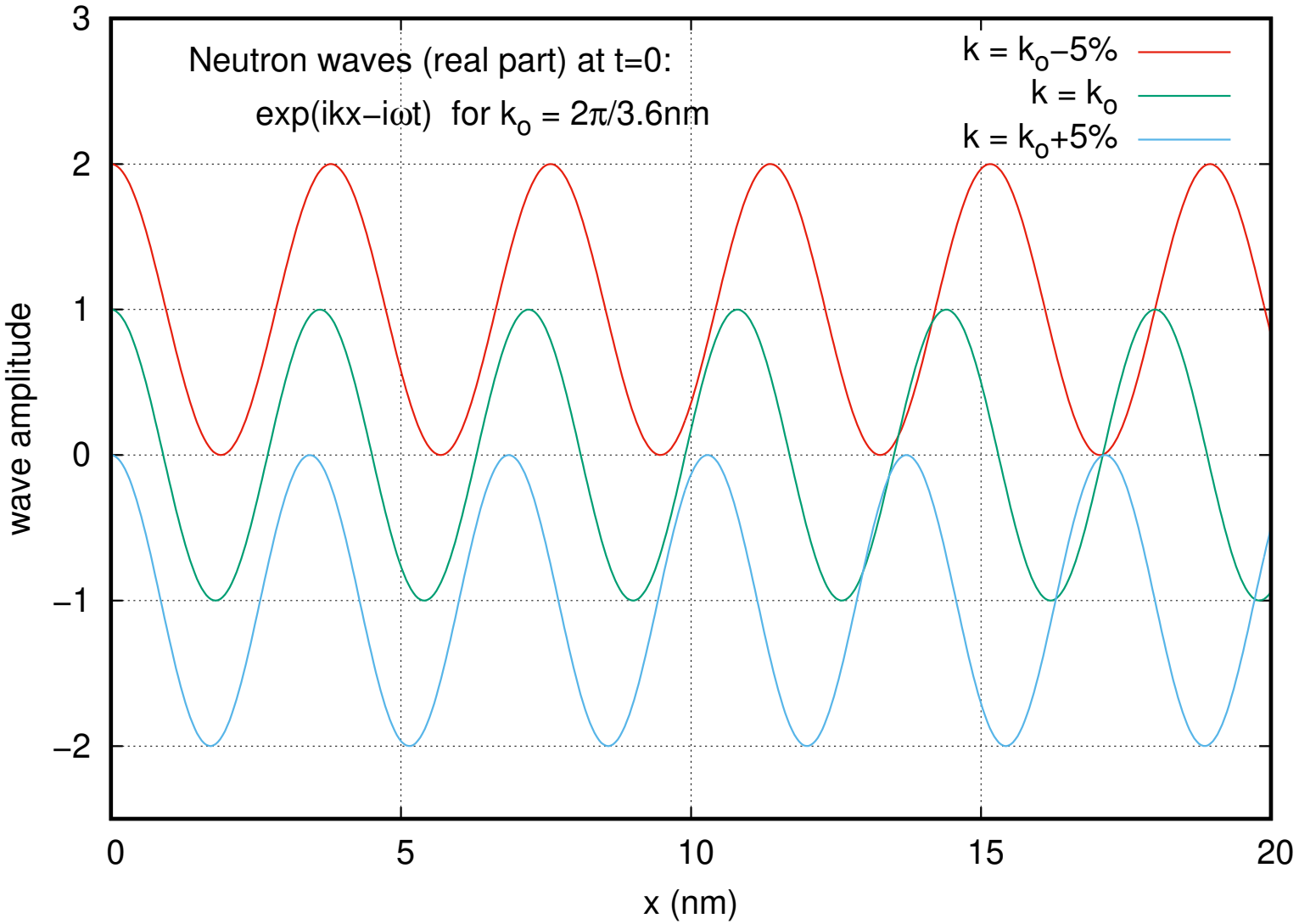
where the *modulating* envelope $L(x)$ is also Gaussian with $\sigma_x = 1/\sigma_k$ and represents the spatial localization of the wavepacket *amplitude* at $t = 0$. For wavepackets of probability amplitude, the *localisation of probability* in x- and k-space is given by $L^2(x)$ and $A^2(k)$, respectively, being Gaussian functions both narrowed by a factor of $\sqrt{2}$, such that:

$$\sigma_{x^2}\sigma_{k^2} = 1/2 \quad \Rightarrow \quad \sigma_{x^2}\sigma_{p^2} = \Delta x \Delta p = \hbar/2$$

in accordance with the Uncertainty Principle.

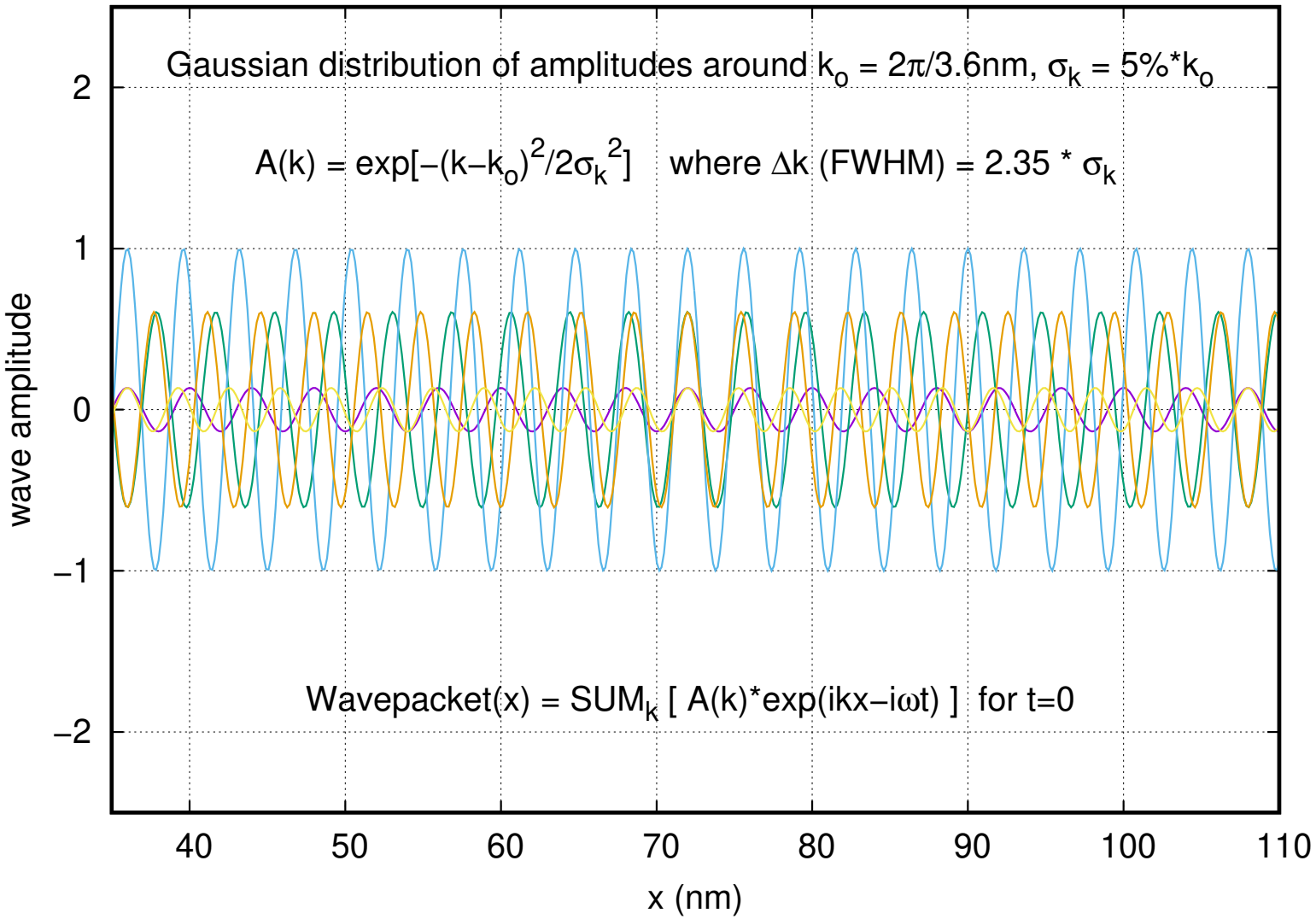
Building up a wavepacket in space

Consider only three waves having a +/- 5% spread in *k*. We see that they become completely dephased after only 4 or 5 periods.



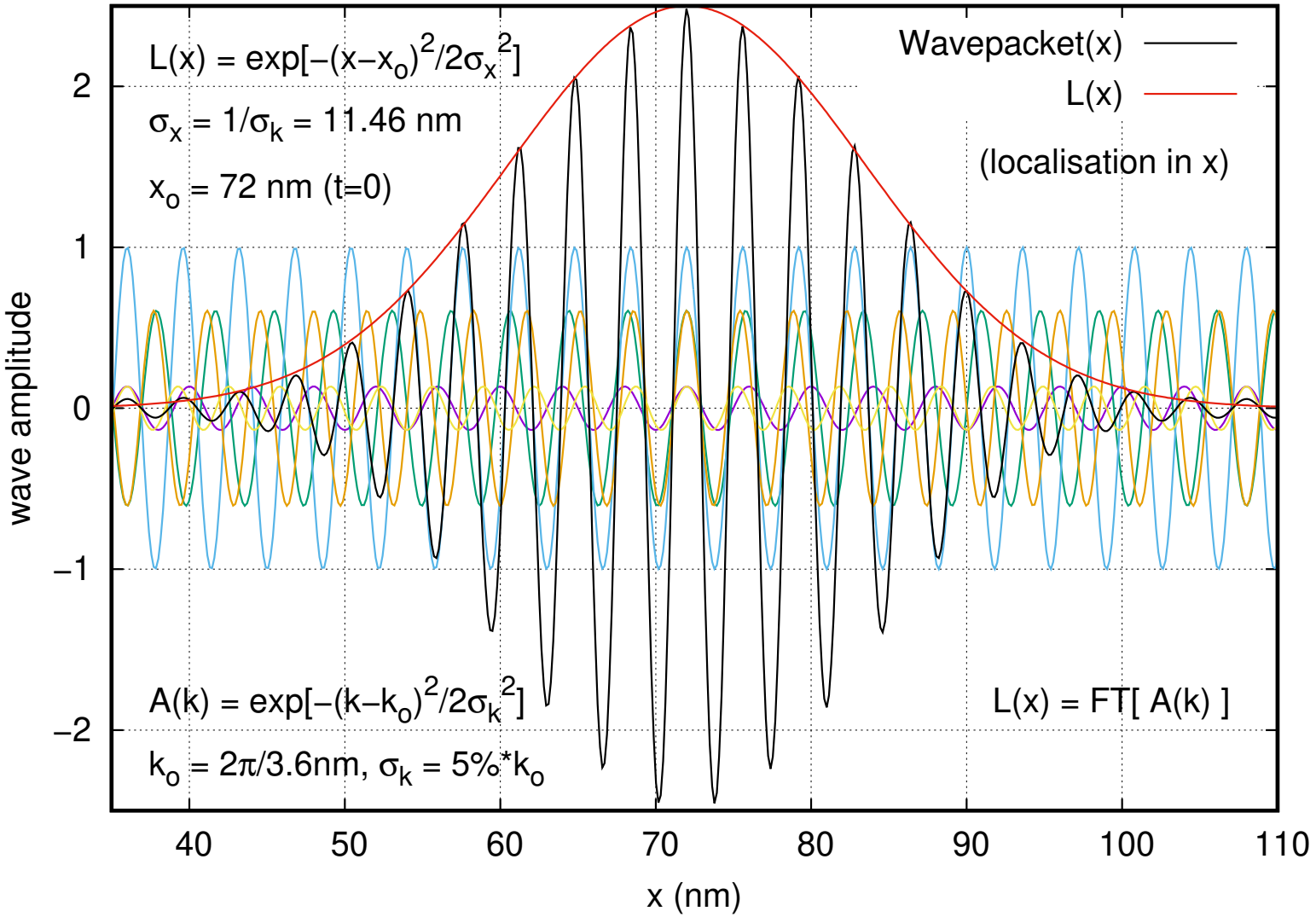
Building up a wavepacket in space

Now consider a discrete distribution of only 5 waves whose amplitudes are a Gaussian function of k with $\sigma_k = 0.05\ k_o$.



Building up a wavepacket in space

We see that adding up that Gaussian distribution of 5 waves leads to an impressively smooth localisation envelope having $\sigma_x = 1/\sigma_k$.



The Convolution Theorem (physicist's convention)

The *convolution* of two functions $f(q)$ and $g(q)$ is given by:

$$f(q) \otimes g(q) = (f \otimes g)(q) = \int_{-\infty}^{\infty} f(q')\, g(q - q')\, dq'$$

where q' averages over q-space (NB: $q - q' \rightarrow q + q'$ for correlation).

The *convolution theorem* states that the Fourier Transform (FT) of a convolution is the simply the product of the Fourier transforms:

$$\mathrm{FT}[f(q) \otimes g(q)] \;=\; \mathrm{FT}[f(q)]\,\mathrm{FT}[g(q)] \;=\; F(r)\, G(r)$$

so that a convolution in q-space gives a modulation in r-space, and vice-versa of course. Likewise the FT of a modulation

$$\mathrm{FT}[f(q)\, g(q)] \;=\; \mathrm{FT}[f(q)] \otimes \mathrm{FT}[g(q)] \;=\; F(r) \otimes G(r)$$

is a convolution of the Fourier transforms. For example, a q-resolution function for the measured diffraction intensity, leads to a r-space modulation of the PDF(r). And the D-W factor as modulation in q leads to a convolution (*i.e.* broadening) of the peaks in PDF(r).

Some useful rules of thumb for Fourier Transforms

The FT of a Gaussian with standard deviation σ_q is also a Gaussian but with standard deviation $\sigma_r = 1/\sigma_q$. And since:

$$\mathrm{HWHM}_q = \mathrm{FWHM}_q/2 = \sqrt{\ln(4)}\,\sigma_q = 1.18\,\sigma_q$$

then the FT of a Gaussian of width FWHM_q is a Gaussian of width

$$\mathrm{FWHM}_r = 4\ln(4)/\mathrm{FWHM}_q = 5.55/\mathrm{FWHM}_q$$

and therefore *not* $2\pi/\mathrm{FWHM}_q$. A sharp resolution function of small FWHM_q for the diffraction data will therefore lead to a broad or gentle modulation of large FWHM_r for the $\mathrm{PDF}(r)$.

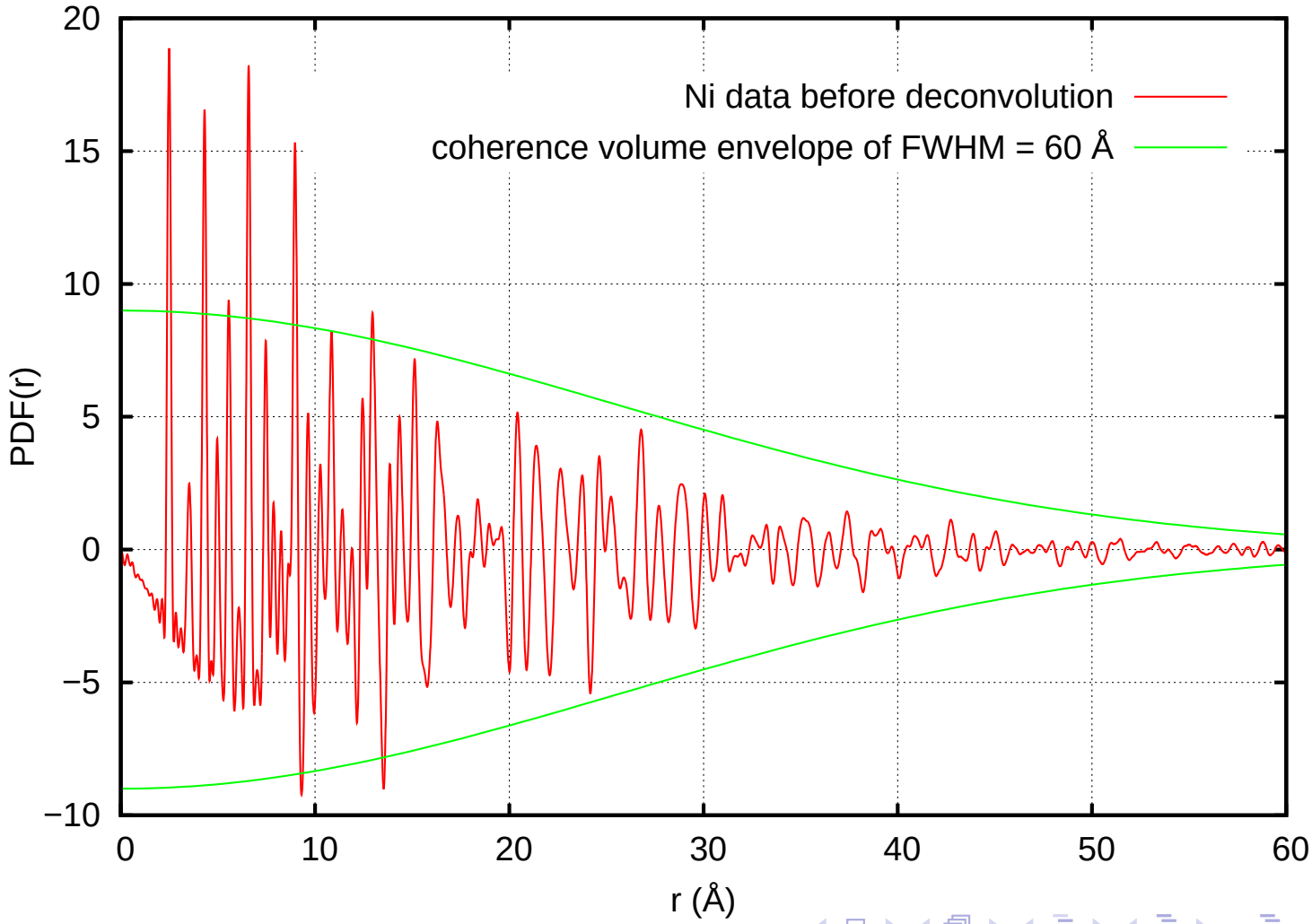
Note that for data of finite $q_{\max}$, the FT of the Heavyside step function is

$$sinc(r) = \sin(r)/r \quad \text{having} \quad \mathrm{FWHM}_r = 3.79/q_{\max}$$

so that the theoretical $\mathrm{PDF}(r)$ should be convolved with $sinc(r)$ before comparison to data. This is the source of the "low-*r* wiggles" in the FTs of diffraction data, which in fact exist around all sharp peaks in $\mathrm{PDF}(r)$.

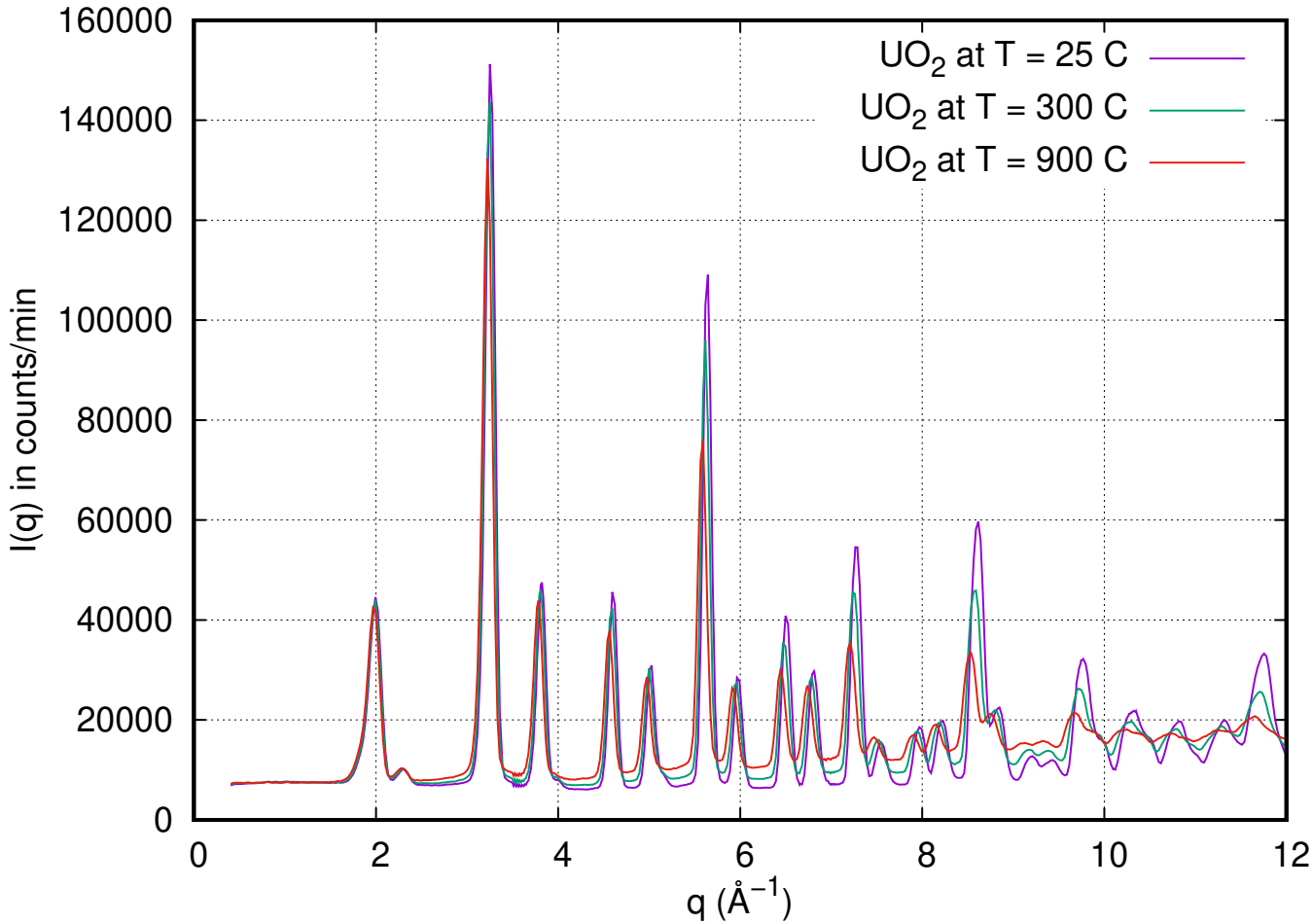
The measured PDF(*r*) for a nickel powder sample

Like the Patterson function, $\mathrm{PDF}(r) = \mathrm{FT}[d\sigma/d\Omega(q)]$ but including also diffuse and inelastic scattering. For an average q-resolution (D4@0.5Å) of: $\Delta q = \mathrm{FWHM}_q = 0.092$ Å^{-1}, the neutron coherence length is: $\xi_q = \mathrm{FWHM}_r = 5.55/\mathrm{FWHM}_q = 60$ Å, *i.e.* $\mathrm{HWHM}_r = 30$ Å.



Debye-Waller factor and Thermal Diffuse Scattering

Increased amplitudes of atomic vibration **u** at higher T lead to broader time-averaged "thermal clouds" of atomic positions that reduce Bragg peak intensities via the Debye-Waller factor: $\exp[-\langle(\mathbf{Q}_{hkl} \cdot \mathbf{u})^2\rangle]$:

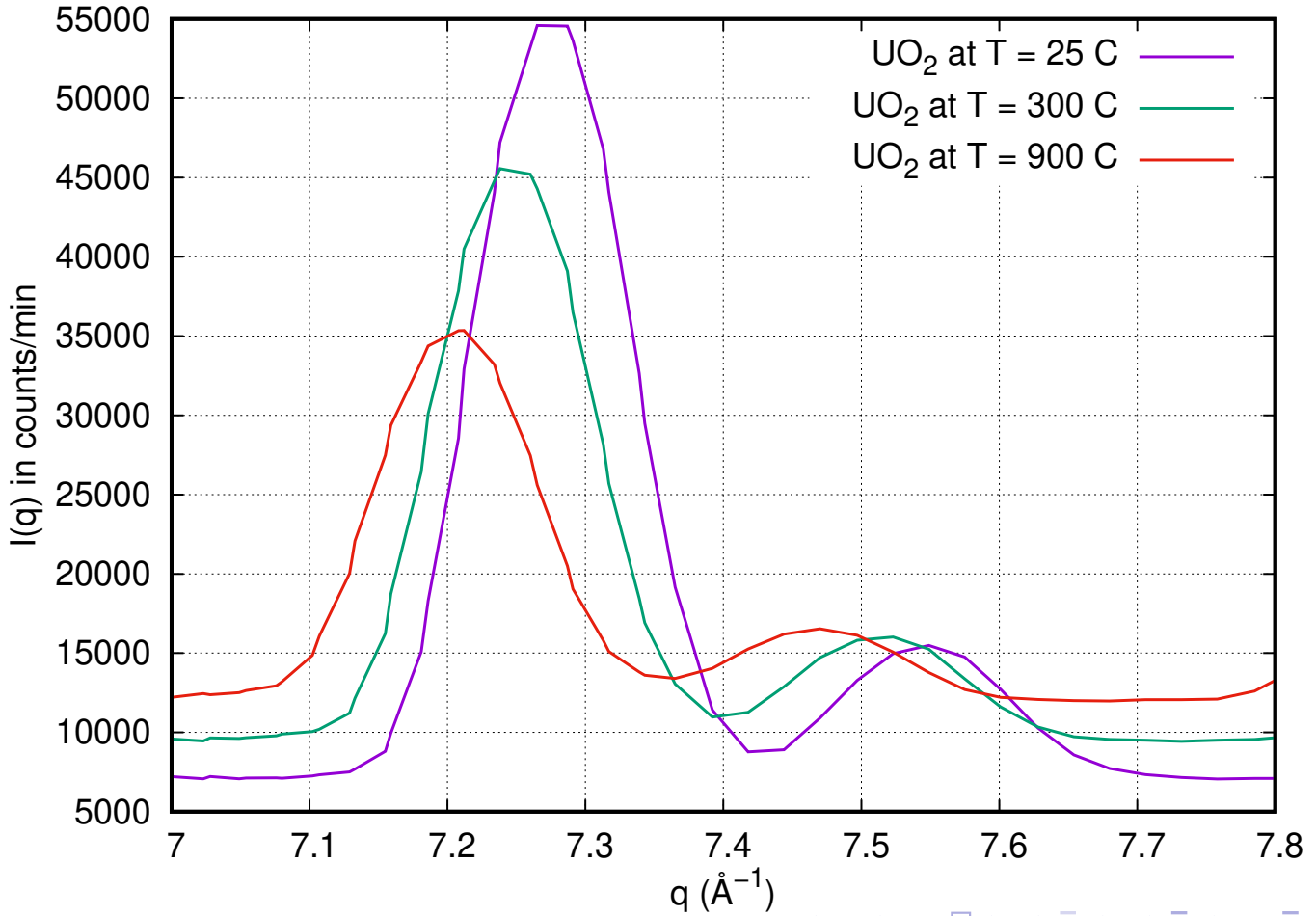


The lost intensity becomes Thermal Diffuse Scattering (TDS) at the base of the Bragg peaks.

The Debye-Waller factor in *q*-space

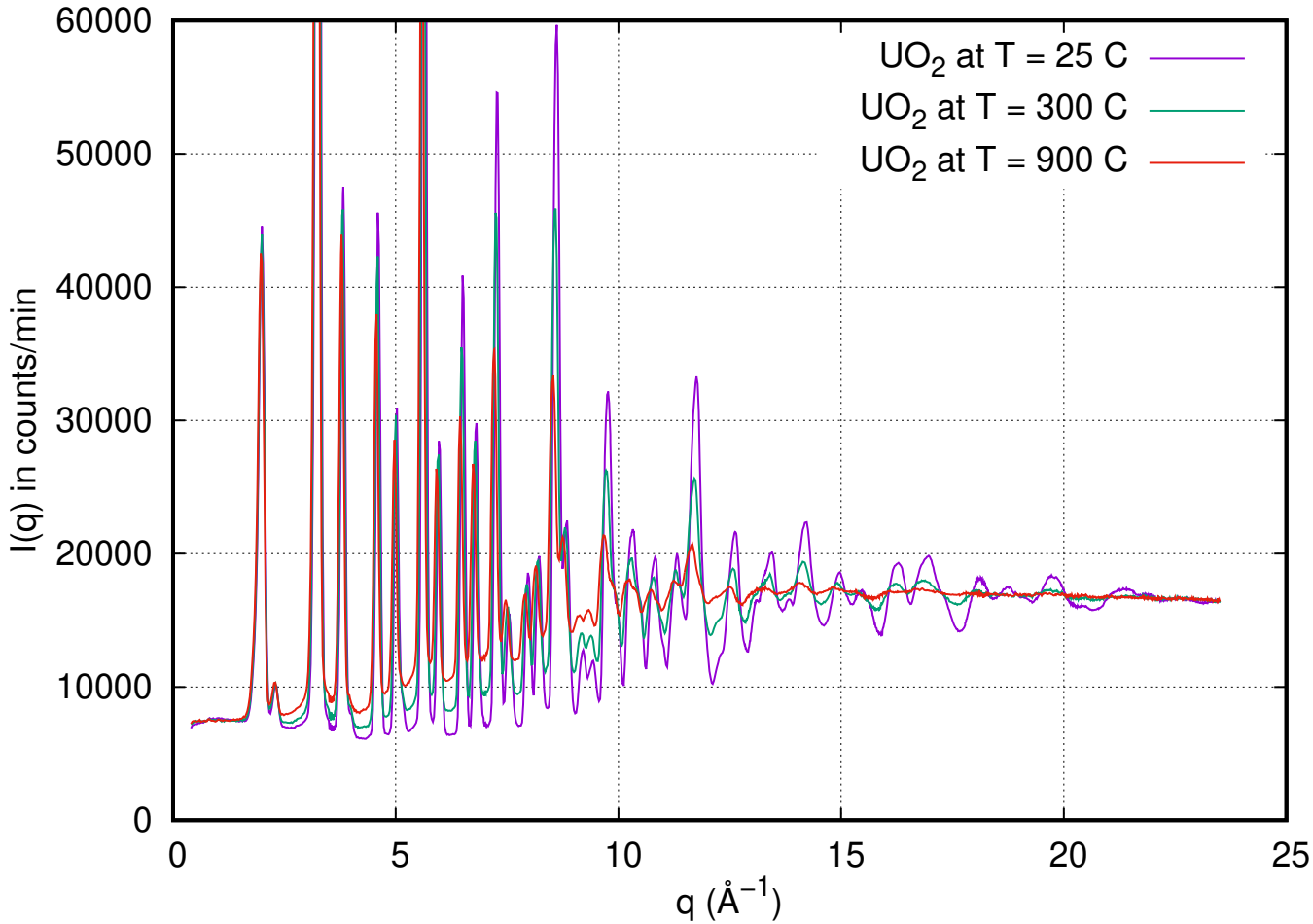
NB: For a cubic crystal: $\langle (\mathbf{Q}_{hkl} \cdot \mathbf{u})^2 \rangle = 2W = q^2 \langle u^2 \rangle / 3$.

The D-W factor is therefore a *q*-space modulation that reduces the amplitude of a Bragg peak *without affecting its width,* thus reducing its integrated intensity. The Bragg peak positions naturally shift to lower q as the lattice expands at higher temperature.



The Debye-Waller factor in *q*-space

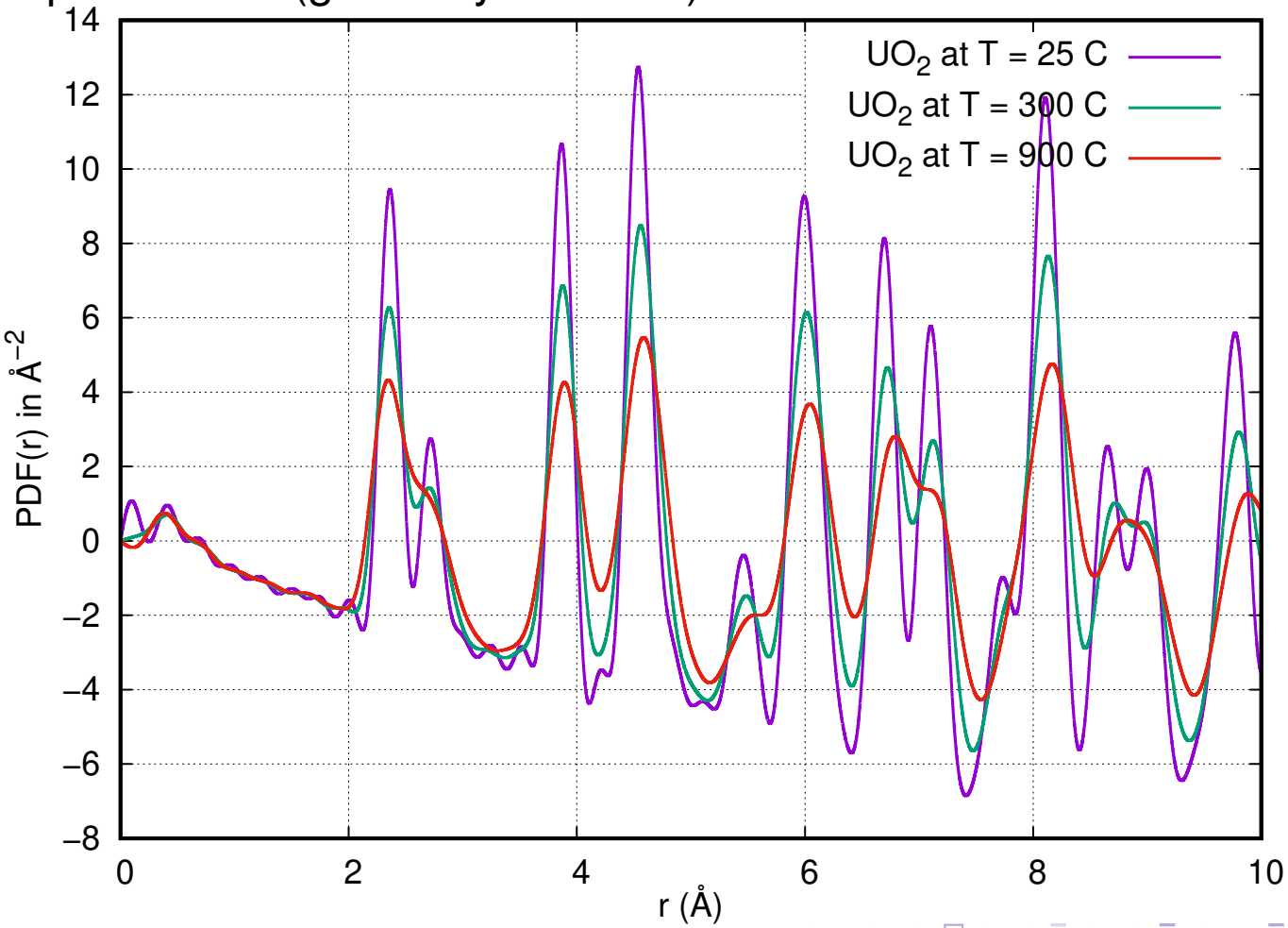
The D-W factor's (Gaussian-like) modulation of intensity in *q*-space, *i.e.* reduction of Bragg peak intensity especially at higher T, is particularly noticeable when diffraction data are taken up to high-q:



Such reduction in signal at "high harmonics" in q should, after Fourier transform, lead to broader features in r-space.

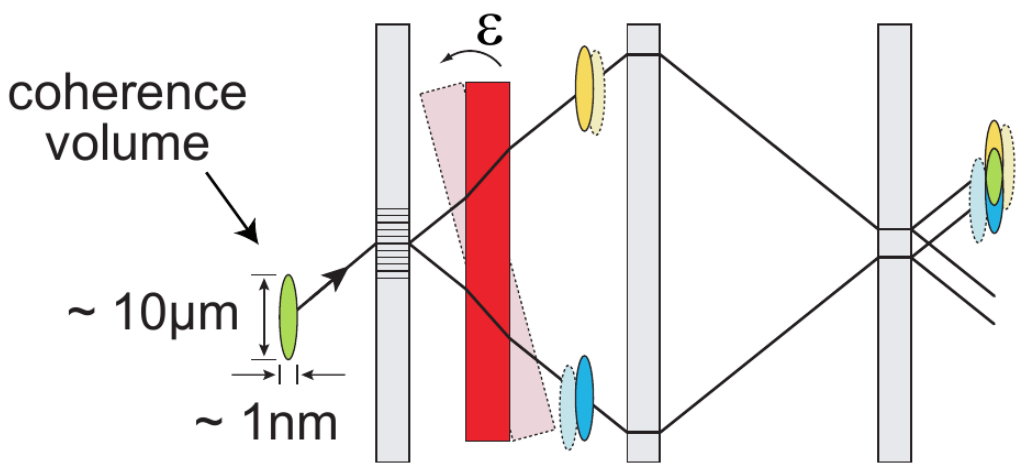
The Debye-Waller factor in *r*-space

The convolution theorem states that a modulation in *q*-space leads to a convolution in *r*-space (and vice-versa), such that the the D-W factor broadens the peaks in $\mathrm{PDF}(r)$ according to the vibration amplitudes of the corresponding atomic pairs, *while preserving the peak areas* which are proportional to (generally constant) coordination number:



V_{coh} effects in neutron interferometry

Ex: Sample-as-phase-shifter in the standard=dispersive configuration:



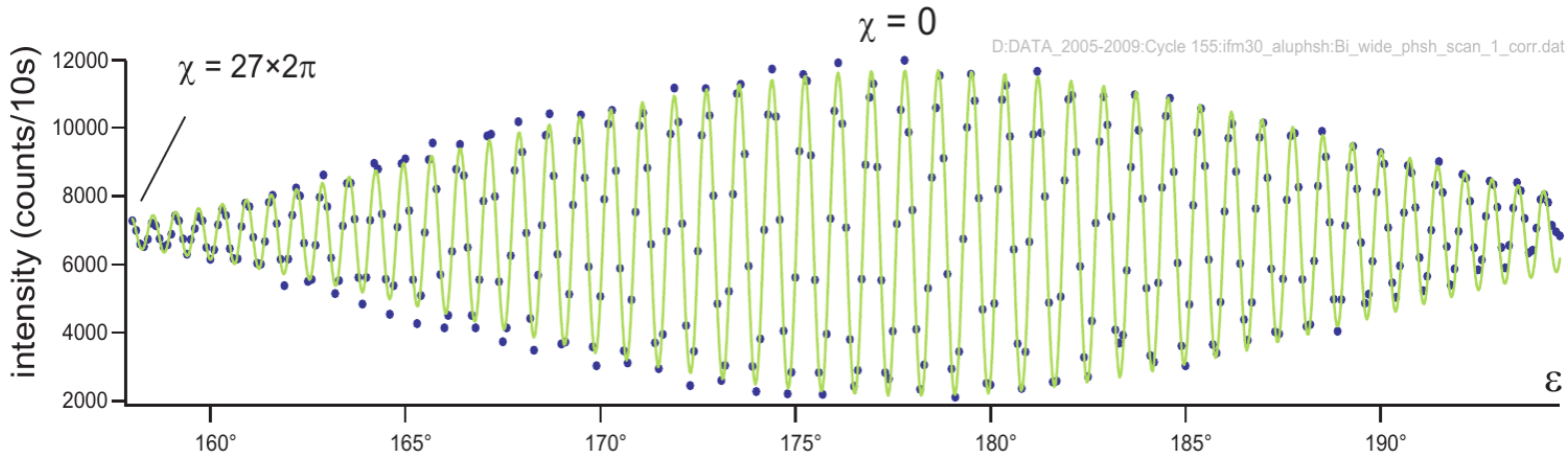
Sample's refactive index: $n = 1 - \lambda^2 N b_c / 2\pi \lesssim 1$ when the coherent scattering length $b_c > 0$. Within the sample of thickness D, $k_n = n k_o$ and the group velocity $v_n = \hbar k_n / m = n v_o$.

Consider an incident neutron wavepacket that is split at the first interferometer blade. For a central plane wave $\exp(i\mathbf{k}_o \cdot \mathbf{r} - i\omega_o t)$, continuity of phase at the interface requires that $\omega_n = \omega_o$ and that $k_{n,\|} = k_{o,\|}$, whereas both $k_\perp$ and $v_\perp$ change at the interface, leading to refraction and a transversal $(\uparrow)$ separation of the two wavepacket V_{coh}'s at the exit, even though they have have no longitudinal $(\rightarrow)$ separation, and both sample-induced phase shifts $D\Delta k_\perp$ remain equal. However, a rotation by ε will change *differently* the longitudinal (and transversal) projections of D along the two paths, such that the two V_{coh}'s may no longer superpose at the exit, regardless of their relative phase.

Measuring and calculating ξ_{long} in neutron IFM

Bragg reflection from the perfect Si crystal IFM blades assures that the FWHM $\xi_{trans} \sim 1/\Delta Q_{Bragg}$ is very long, here estimated as 10 μm. The effects of the incident beam's FWHM angular dispersion $\Delta k/k \sim S/L$, from slits of width $S = 20$ mm placed $L = 1.5$ m upstream of the sample, are therefore concentrated longitudinally, such that the FWHM $\xi_{long} = 2\ln(4)/\Delta k = 0.44\ \lambda\ L/S = 6.33$ nm, where $\lambda = 1.913$ Å.

$\Rightarrow$ Here are data for a bismuth sample as phase-shifter of thickness $D \sim 10$ mm, for the above configuration of the S18@ILL interferometer:



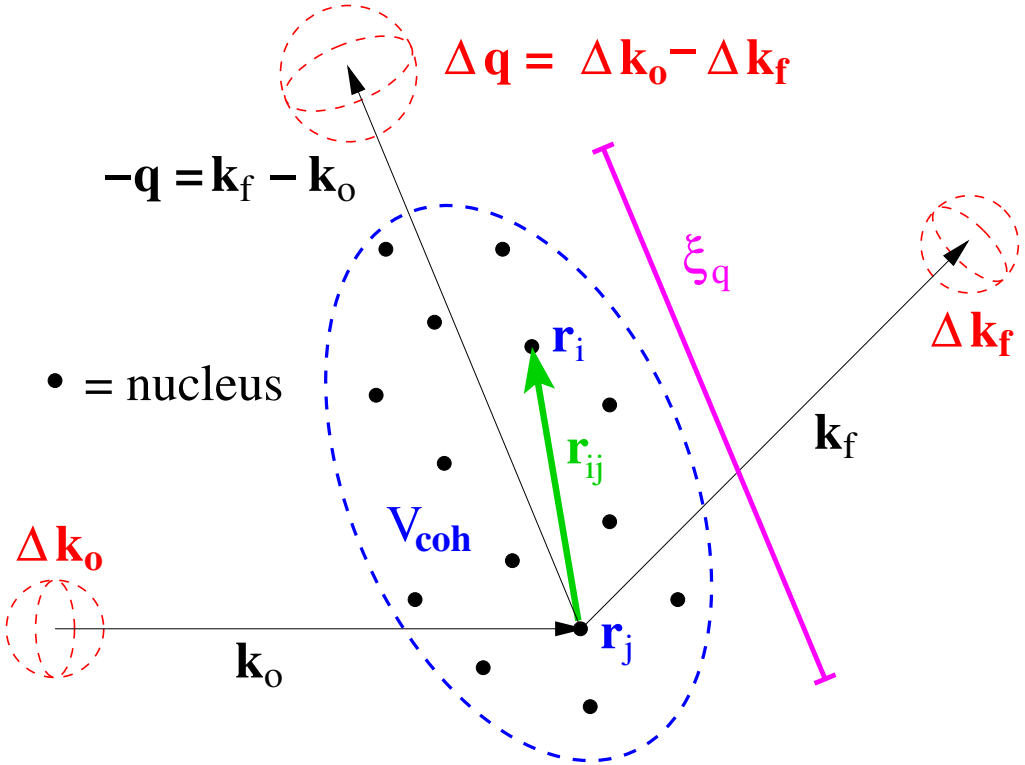
As each oscillation or "fringe" represents a distance λ, the measured FWHM $\xi_{long} = 32.5$ fringes $\times\ \lambda = 6.22$ nm, which agrees very well with theory. In terms of standard deviation: $\sigma_{long} = \xi_{long}/2.355 = 2.64$ nm.

(See: *H. Lemmel & A.G. Wagh, Phys. Rev. A* **829** *(2010) 033626.*)

Time scales: How quickly does a neutron wave scatter?

Replay: Coherence volume for $\Delta\mathbf{q} = \Delta\mathbf{k}_o - \Delta\mathbf{k}_f$

A q-resolution function of FWHM Δq *convolves* the diffraction intensity, meaning $\mathrm{PDF}(r) = \mathrm{FT}[d\sigma/d\Omega(q)]$ is *modulated* by a FWHM ξ_q where $\xi_q \Delta q = 4\sqrt{\ln(4)} = 5.55 \;\Rightarrow\; \xi_q = 5.55/\Delta q$ defines a coherence length or "visibility distance" of the sample's structure as measured along **q** and characterized by a structural correlation length.

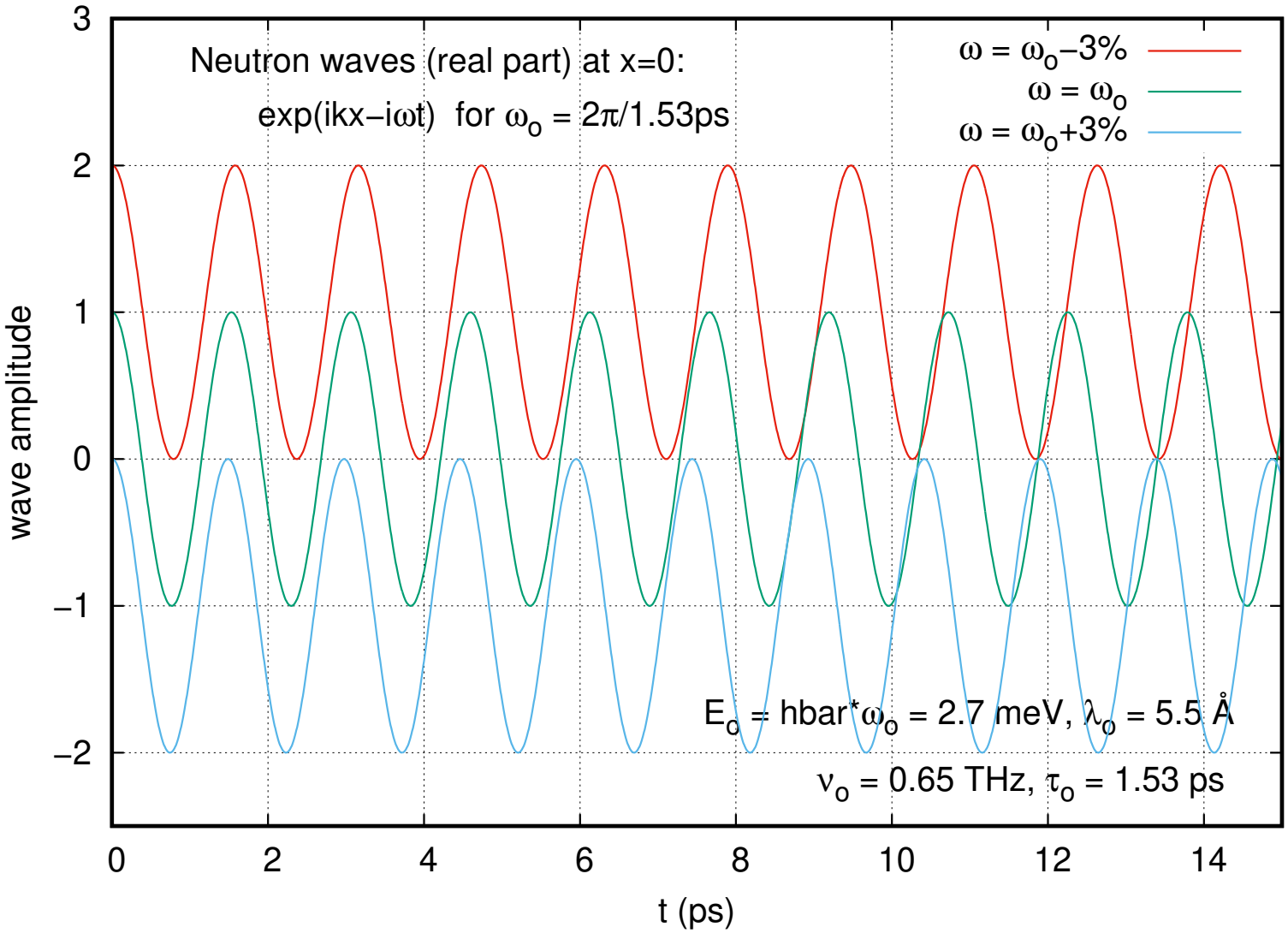


Since $\mathbf{k}_o$ is not $\parallel \mathbf{k}_f$, $\Delta\mathbf{q} = \Delta\mathbf{k}_o - \Delta\mathbf{k}_f$ will depend on q-space focussing aspects à la Caglioti, but in the end for a final measured q-resolution Δq of the diffractogram we have $\xi_q = 5.55/\Delta q$ as the coherence length $\parallel \mathbf{q}$.

But what about time dependence and the spread in $\omega_o = E_o/\hbar$?
$\Rightarrow$ Sum over all ω_o and ω_f for each neutron-scattering atom in V_{coh}.

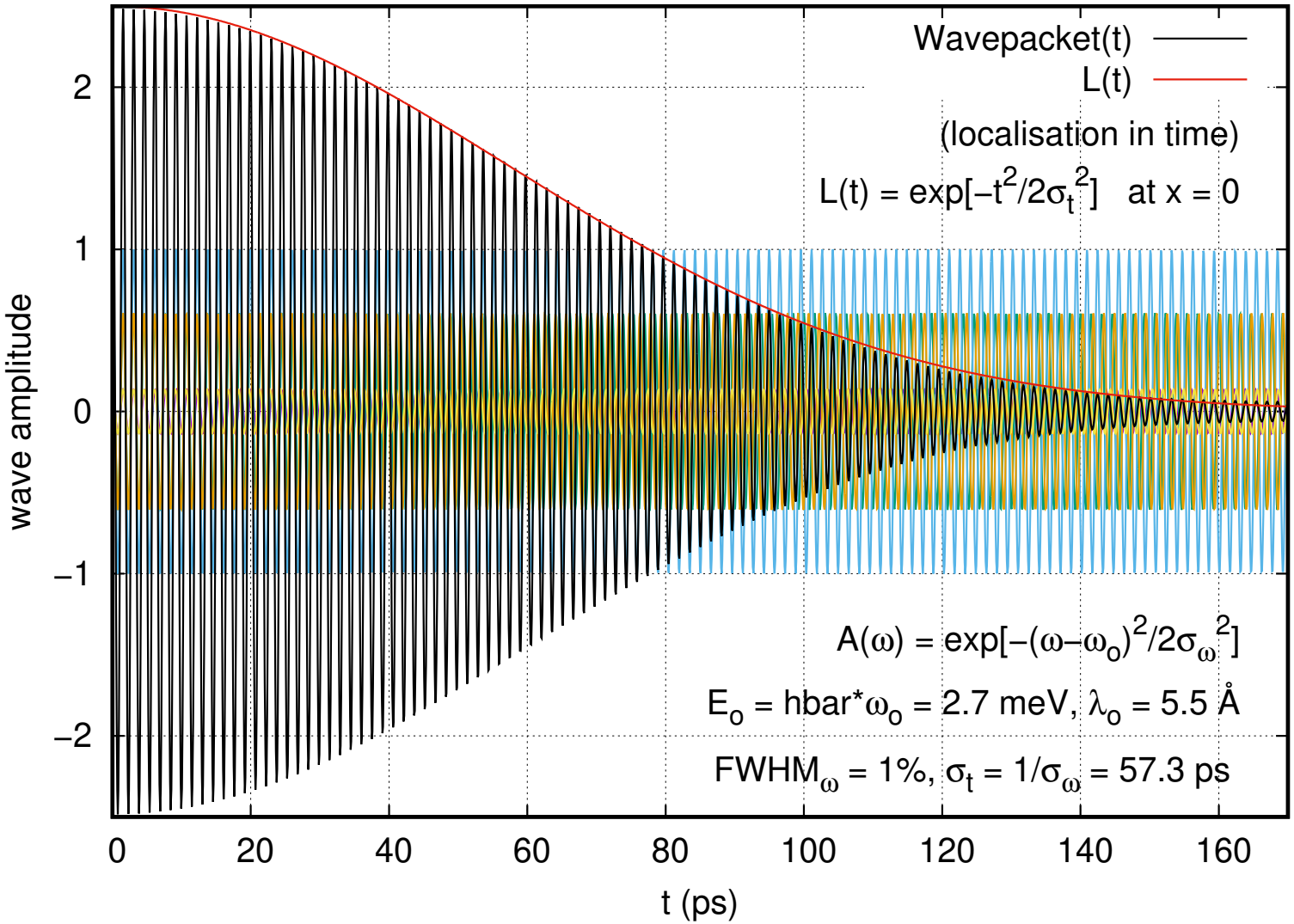
Building up a wavepacket in time

Consider only three waves having a +/- 3% spread in ω. We see that they become completely dephased after only 7 or 8 periods.



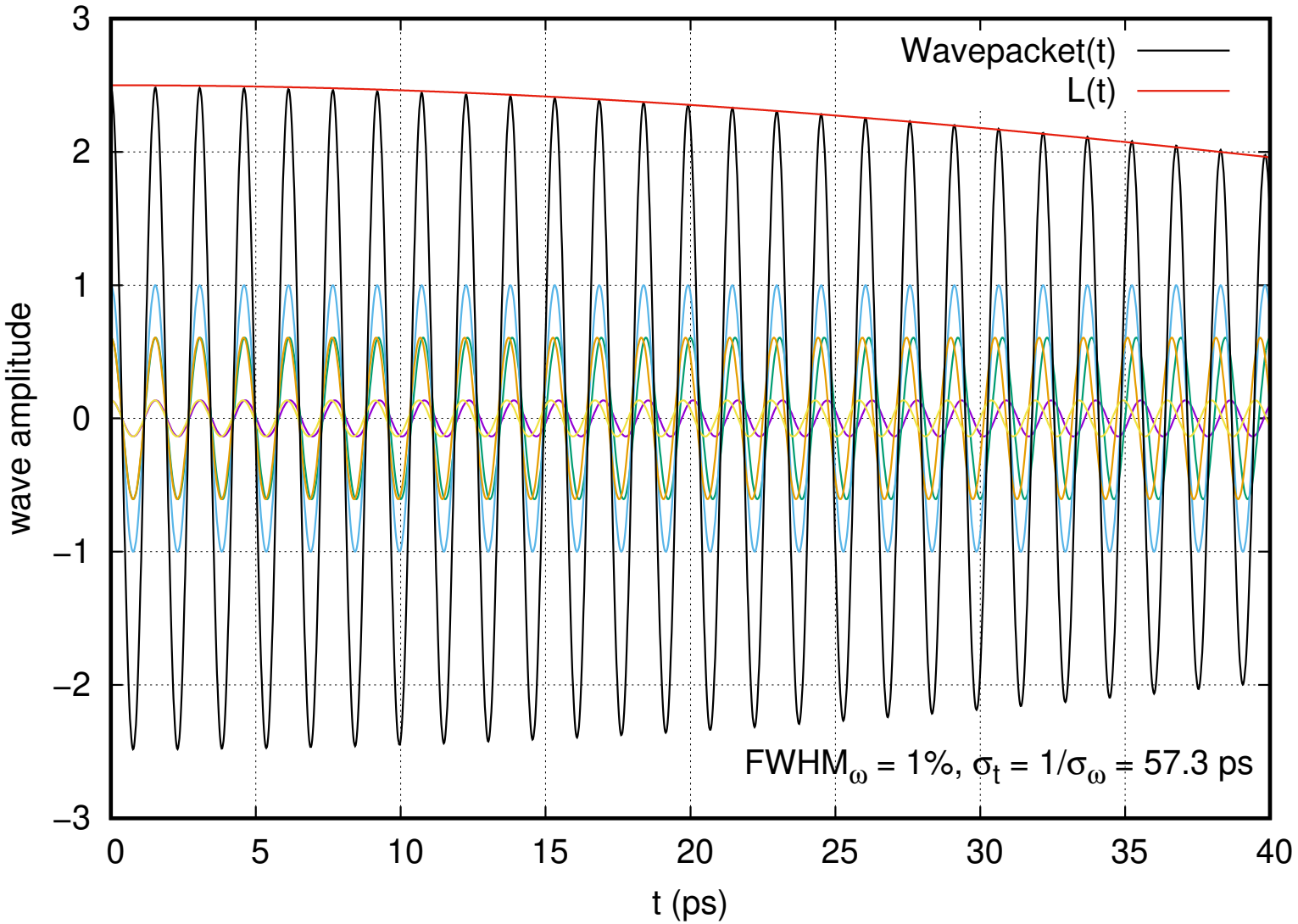
Building up a wavepacket in time

Now consider a discrete distribution of only 5 waves whose amplitudes are a Gaussian function of ω with $\mathrm{FWHM}_\omega = 0.01\ \omega_o = 2.35\ \sigma_\omega$.



Building up a wavepacket in time

We see that adding up that Gaussian distribution of 5 waves leads to a time localisation of $\sigma_t = 1/\sigma_\omega = 57.3$ ps for the neutron wave.



Adding up intensities over all V_{coh} and τ_{coh}

So far, we have written the differential scattering cross-section as:

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \left| \sum_i^N b_i \, e^{i\mathbf{q}\cdot\mathbf{r}_i} \right|^2 = \sum_{i,j}^N b_i b_j^* \, e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \quad \text{for } N \text{ sample atoms},$$

but now we understand that the phases $\phi = \mathbf{q} \cdot \mathbf{r}_{ij}$ will be washed out by the spread in $\Delta\mathbf{q} = \Delta\mathbf{k}_o - \Delta\mathbf{k}_f$ unless $\mathbf{r}_{ij}$ fits inside a V_{coh}. In addition, the phases $\phi = -\omega t$ (not shown) will be washed out by the spread $\sigma_\omega \sim \sigma_{\omega_o} + \sigma_{\omega_f}$ in $\omega = \omega_o - \omega_f$ after a time $\tau_{coh} = \sigma_t = 1/\sigma_\omega$. Within V_{coh} and during τ_{coh} however, the scattered neutron wavefunction will contribute its probability amplitude coherently to the detector where its square becomes a probability for detecting a neutron at a given $\mathbf{q}$ and with a counting rate proportional to $d\sigma/d\Omega(\mathbf{q})$ and the incident flux Φ. If the structure within V_{coh} has evolved during τ_{coh}, then the probability of detection at $\mathbf{q}$ will represent the V_{coh}-local structure as *time-averaged* over τ_{coh}. These probability (or intensity) contributions to $d\sigma/d\Omega(\mathbf{q})$ are then added up *incoherently* over all the V_{coh} in the sample's volume and over all the τ_{coh} during the duration of the data acquisition. But we prefer to keep the above expression for $d\sigma/d\Omega(\mathbf{q})$ as summed over all N atoms and simply smear it out a bit according to the q-resolution.

How elastic is a Bragg peak?

It all depends on how well the (inelastic) Thermal Diffuse Scattering (TDS) can be subtracted away from the base of the Bragg peaks before integrating their intensities, which in turn depends on monochromaticity ΔE_o as well as q-resolution. Powder averaging of Bragg peaks will sum over all E_o, and for 1% FWHM in $E_o = 25$ meV, we can use the Uncertainty Principle to estimate $\tau_{\rm coh} = \sigma_t = \hbar/2\sigma_{E_o} \sim 3$ ps.

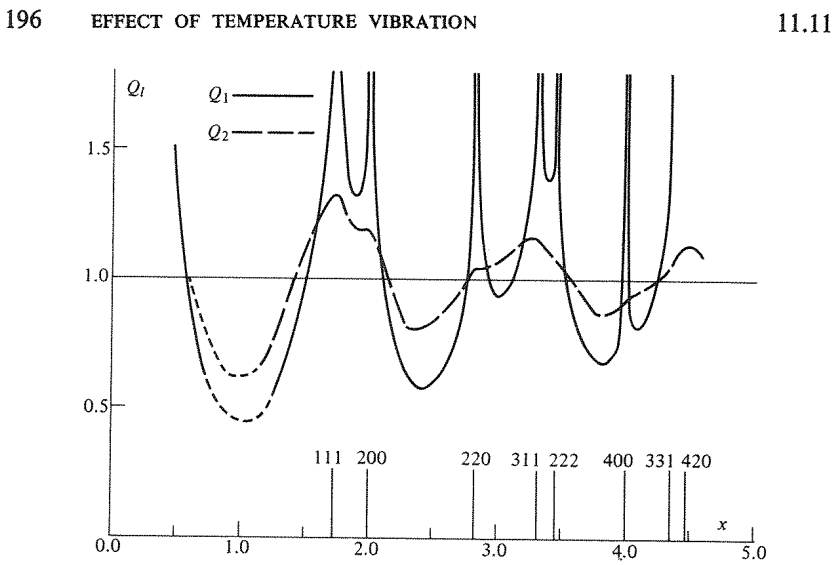


Fig. 11.17 The first-order and second-order TDS for the powder pattern of a FCC element, as a function of $x = (2a/\lambda)\sin\theta$. $Q_1 = I_1/I_e N f^2 e^{-2M} 2M$ and $Q_2 = I_2/I_e N f^2 e^{-2M}(2M)^2/2$. The first-order TDS peaks rather sharply at the positions of the various Bragg reflections.

Even for high-resolution x-ray powder diffraction, the sharp cusps of 1st and 2nd-order TDS can be difficult to fit+subract from the superposed Bragg peak intensities. Of course everything is easier at low-T where TDS is weaker, or for single crystal diffraction since the (hkl) peaks are much more separated in q-space.

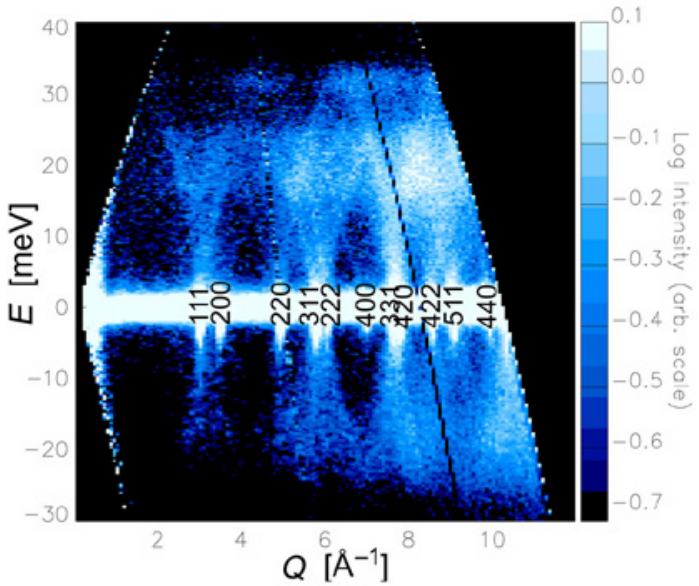
(Figure: *B.E. Warren, X-Ray Diffraction (1969) p196.*)

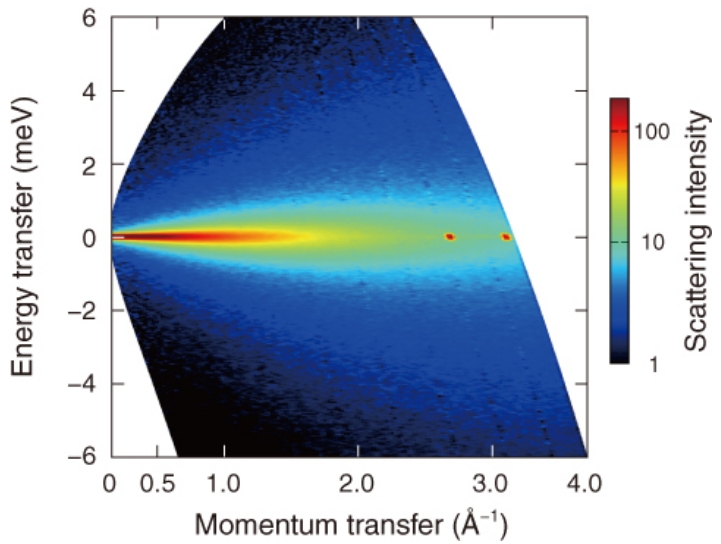
Total scattering vs Bragg intensities (time scales)

A diffraction pattern integrates over all sample-neutron E-transfers:

$$\left.\frac{d\sigma}{d\Omega}(\mathbf{q})\right|_{\text{meas}} = \int_{-\infty}^{E_o} d(\hbar\omega)\frac{\sigma}{4\pi}\frac{k_f}{k_o} N\, S(\mathbf{q},\omega)\ ,$$

$\Rightarrow \Delta E_f \sim \Delta E \sim E_o$ and $\tau_{coh} = \Delta t \sim \hbar/(2\Delta E) \sim 1$ fs for $\lambda = 0.5$ Å, thus representing a quasi-instantaneous "snapshot" of the sample's local structure, as ensemble-averaged over coherence volumes.

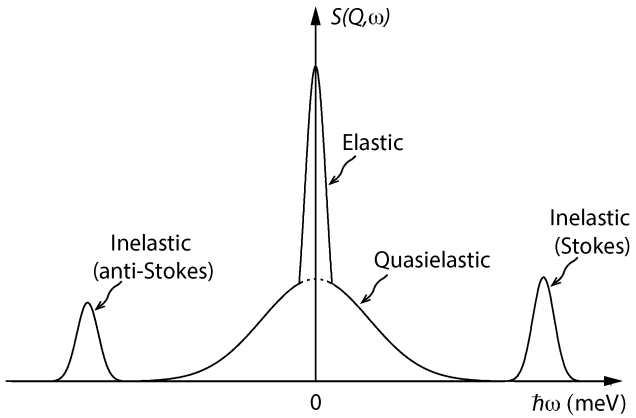


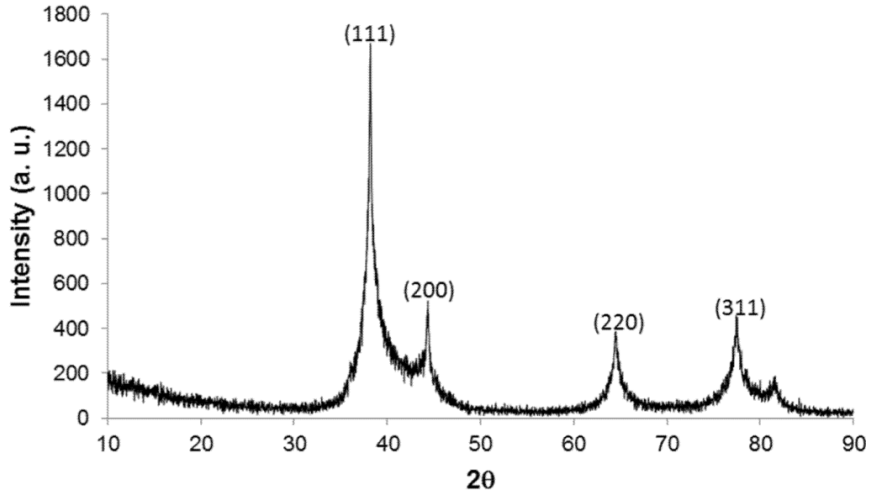


Rietveld refinement of *elastic* Bragg peaks disregards the inelastic scattering containing information about *dynamic* atomic correlations (*e.g.* phonons) and represents the sample's time-averaged structure.

Total scattering vs Bragg intensities (length scales)

In addition, the refinement of diffraction intensity only at Bragg-peak positions neglects the inter-peak diffuse intensity, which when elastic represents time-averaged or *static* local atomic correlations.





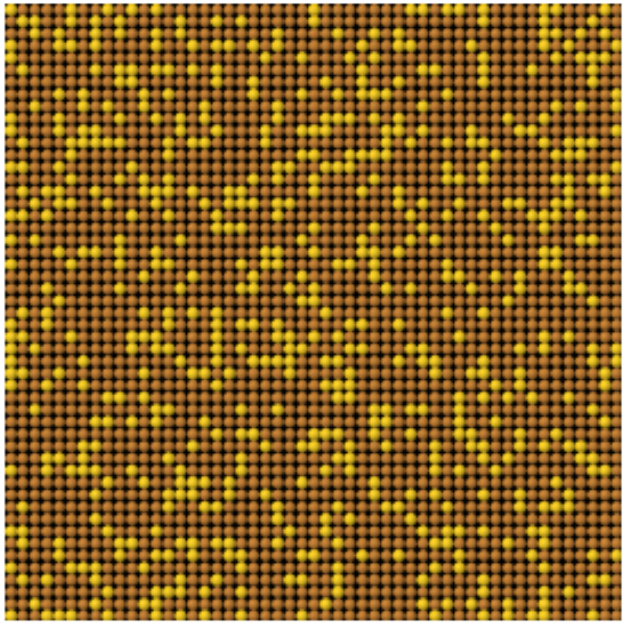
By neglecting the diffuse intensity between (and "under") Bragg peaks, Rietveld refinement additionally performs a spatial average over each neutron coherence volume, resulting in a time+space averaged picture of the sample's structure, which is very useful for crystallography.

By retaining all the original information in the differential cross-section $(d\sigma/d\Omega)(\mathbf{q})$ measured via diffraction, total-scattering represents an ensemble average of quasi-instantaneous snapshots of local structures (*i.e.* within each neutron coherence volume) throughout the sample.

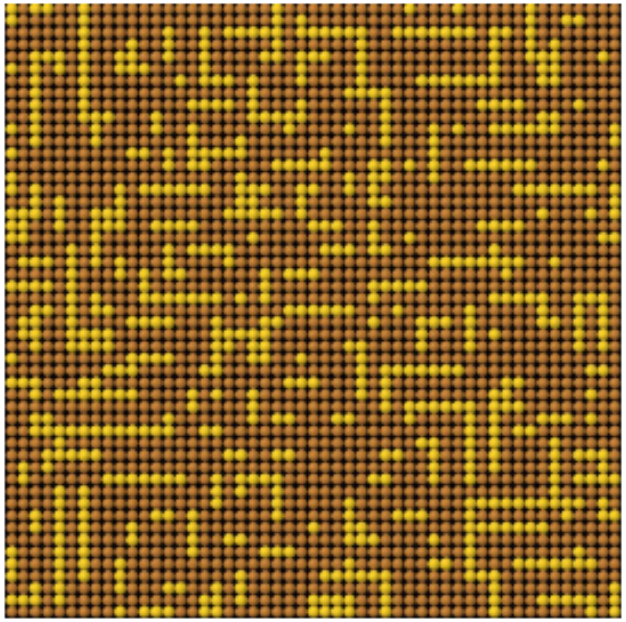
Substitution of A vs B atoms on a square lattice

Disordered Structures

Partial cross section of 200x200 unit cell model crystals
Composition 75% A 25% B



Random position of A B atoms

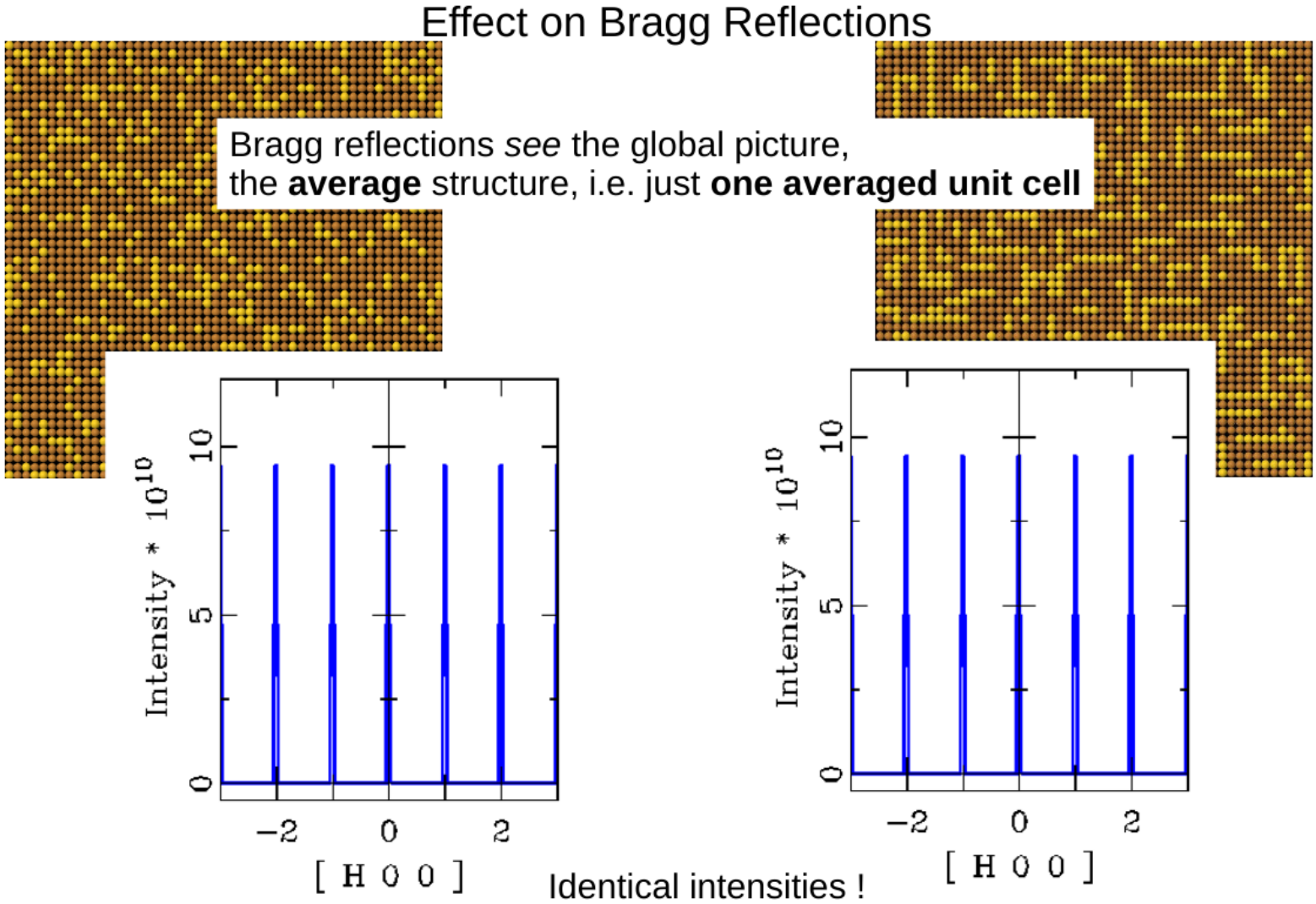


Non-random position of A B atoms

Properties of the two crystals will differ

(courtesy of R. Neder).

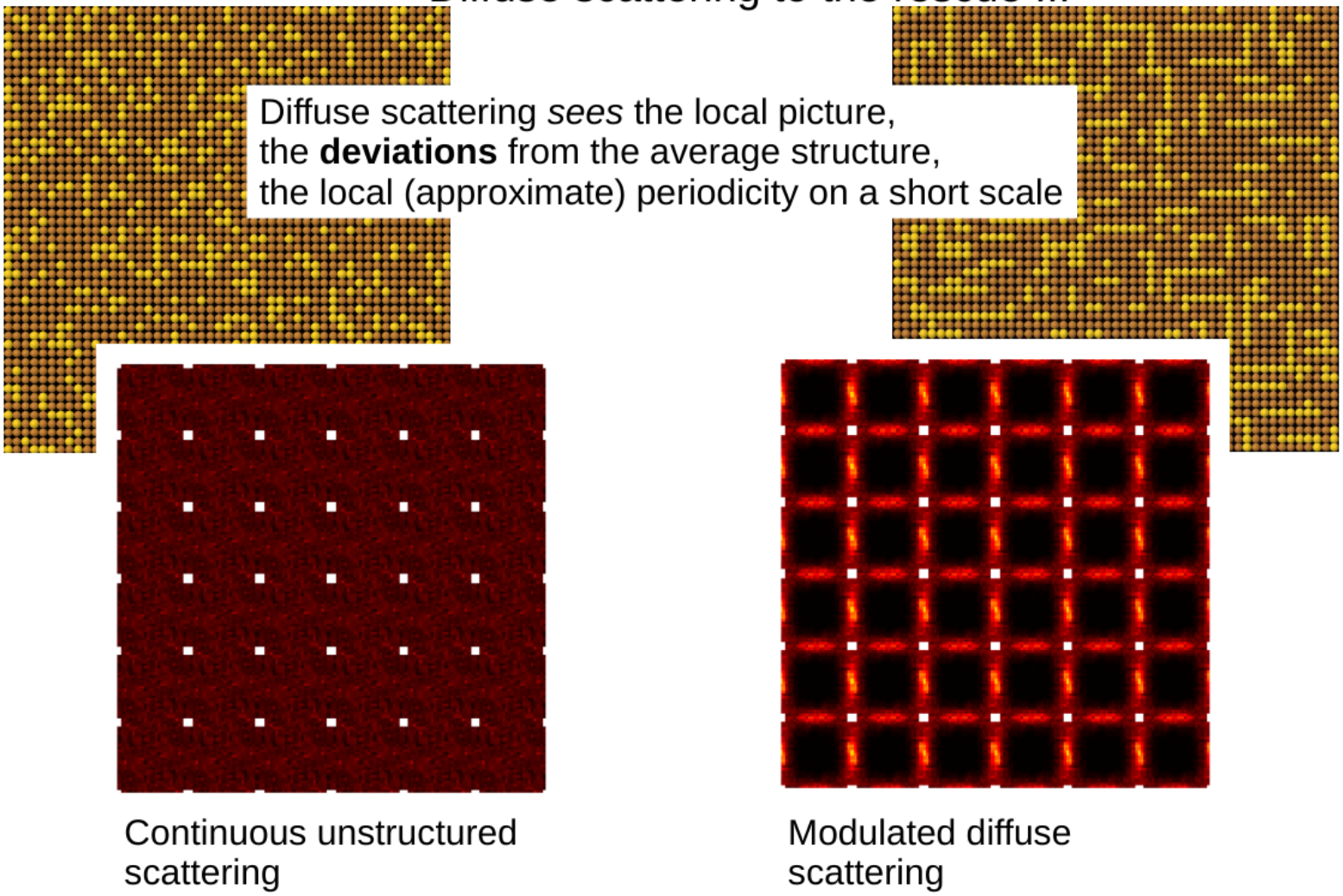
Bragg: sees an average atom at each lattice site



(courtesy of R. Neder).

Diffuse: sees all correlations between A & B atoms

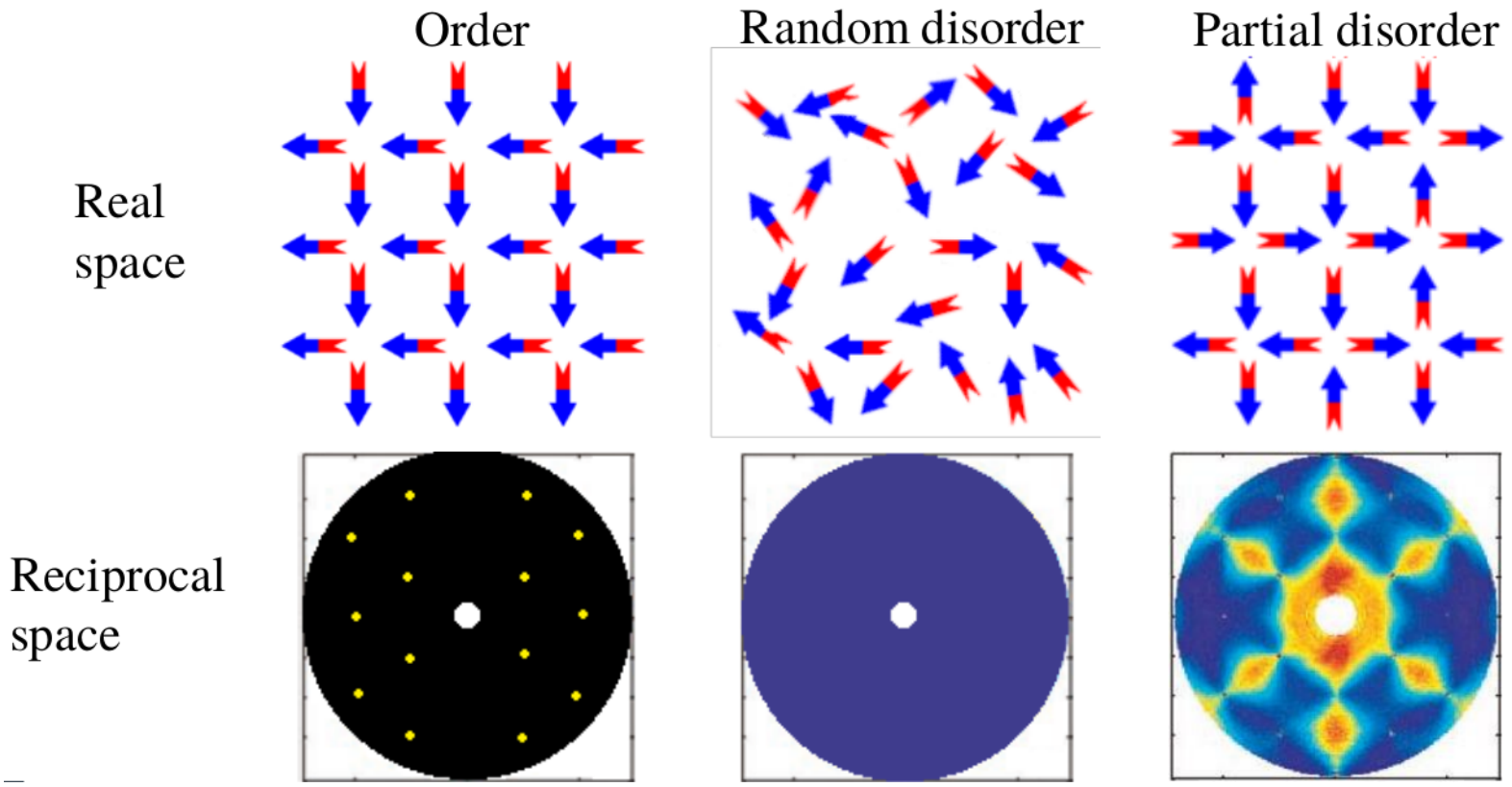
Diffuse scattering to the rescue ...



(courtesy of R. Neder).

Magnetic diffuse scattering & spin-spin correlations

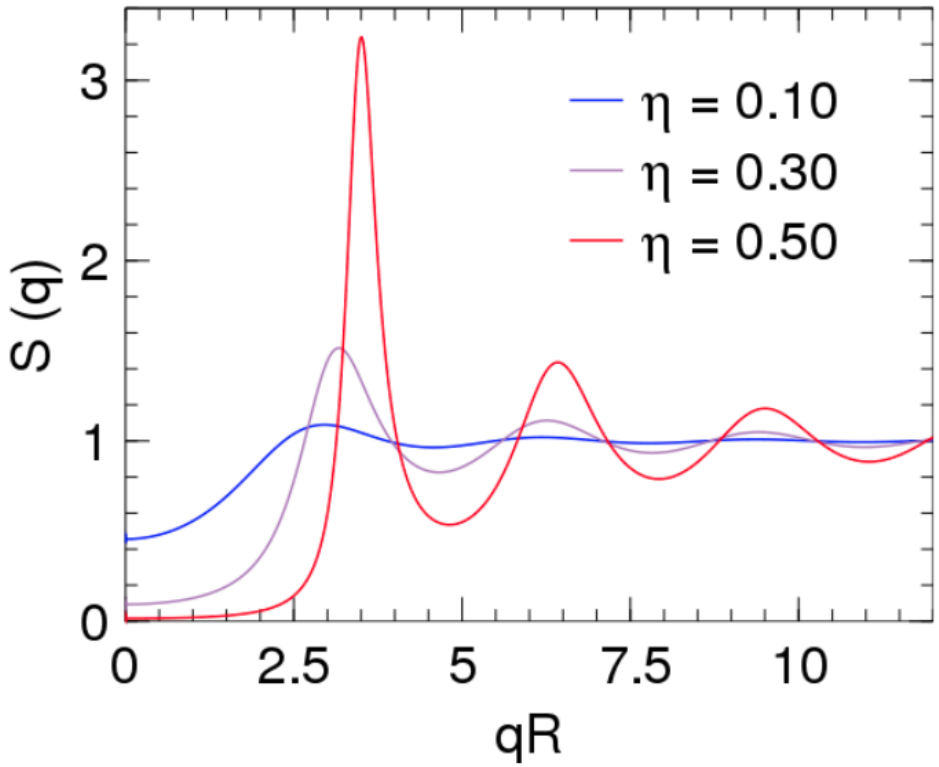
Zero orientational correlations between spins are achieved in a purely paramagnetic state, but partial orientational disorder can look a lot like orientational order at first glance in *r*-space, but not in *q*-space where diffuse scattering is very sensitive to deviations from perfect (dis)order:



(courtesy of T. Northam).

How disordered is "disordered" ?

A completely "disordered" system has no positional nor orientational correlations between scattering centers (atoms, molecules, magnetic spins), leading to an isotropic diffraction pattern $I(q)$. However, zero *positional* correlation can be hard to achieve, even in the case of the minimal constraints of the Percus-Yevick hard-sphere fluid potential:



$S(q) \propto I(q)$

R = hard-sphere radius

η = packing fraction

(courtesy of Wikipedia)

Even at low densities η, diffraction detects correlations, *i.e.* some structural "order", revealed by the shape of the diffuse scattering.

The static approximation for total scattering

When the incident energy E_o exceeds the maximum possible energy transfer $\hbar\omega_{max}$ between the scattered neutron and the excitations in the sample, and for $\varepsilon(E_f) = 1$, it is perfectly valid to use the *static approximation* to derive the *differential scattering cross-section* for diffraction as a function of $\mathbf{q}$ only (note that $q \ll k_o \Rightarrow k_f/k_o \sim 1$):

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \int_{-\infty}^{\omega_o \to \infty} d\omega \; N\frac{\sigma_s}{4\pi} \; S(\mathbf{q},\omega) \overset{\text{s.a.}}{=} \overline{\left\langle \left| \sum_i^N b_i \, e^{i\mathbf{q}\cdot\mathbf{r}_i} \right|^2 \right\rangle} = \left\langle \sum_{i,j}^N \overline{b_i b_j^*} \, e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \right\rangle ,$$

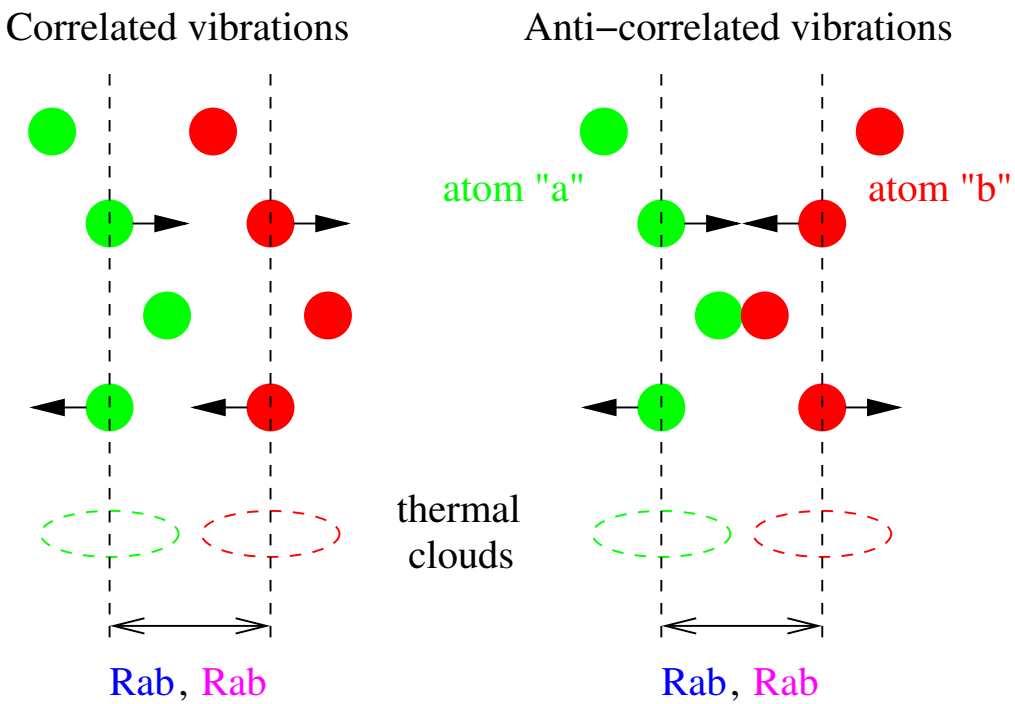
at $t = 0$, where b_i is the scattering length of the i^{th} atom at position $\mathbf{r}_i$, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The $\langle \ldots \rangle$ represent a thermal average and the horizontal bars an ensemble average over the different possible coherence volumes within the sample, each having a particular assignment of scattering lengths in the case of neutron diffraction.

$\Rightarrow (d\sigma/d\Omega)(\mathbf{q})$ measures an *ensemble average* of quasi-instantaneous snapshots of local structures (*i.e.* within the neutron coherence volume) throughout the sample volume over the duration of the data acquistion.

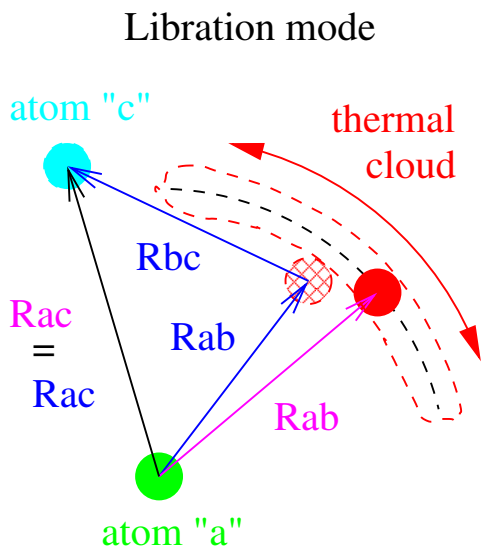
The extracted elastic integrated Bragg peak intensities provide however only a time+space averaged picture of the structure.

Vibration modes seen by Rietveld vs PDF-analysis

Whereas Rietveld refinement gives time-averaged distances between atomic pairs, PDF-analysis of total scattering sees an ensemble average of quasi-instantaneous atomic positions and relative distances:



Rietveld−refined Rab = PDF−analysed Rab
for both correlated and anti−correlated vibrations, but Rietveld's time−averaged thermal clouds cannot distinguish between the two cases. PDF(r) will however show a broader peak for the a−b atomic pair in the anti−correlated case.



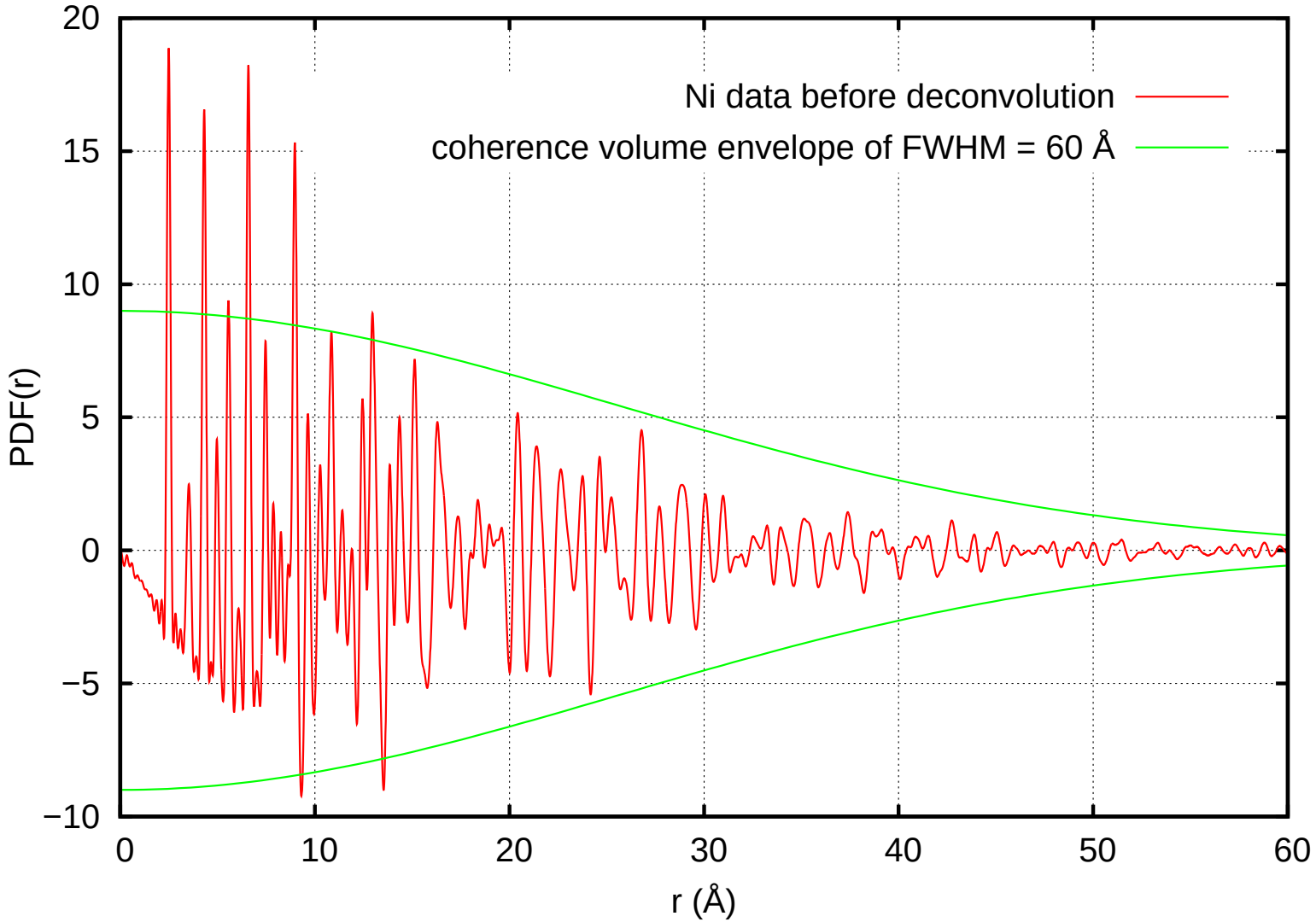
The time−averaged position of atom b is the barycenter of its banana−shaped thermal cloud, which is closer to atom a than any instantaneous position:

Rab (too short) < Rab (correct)

PDF(r) will show a sharp peak for the a−b and a−c atomic pairs but a very broad peak for b−c.

Effect of correlated atomic vibrations at low-*r*

At short interatomic distances the peaks in $\mathrm{PDF}(r)$ are sharper and taller (conserving area $\propto$ coordination number) as compared to the neutron coherence volume's $\mathrm{FWHM} \sim 60$ Å for the D4c diffractometer:



τ_{coh} in pulsed/chopped TOF-INS, indirect geometry

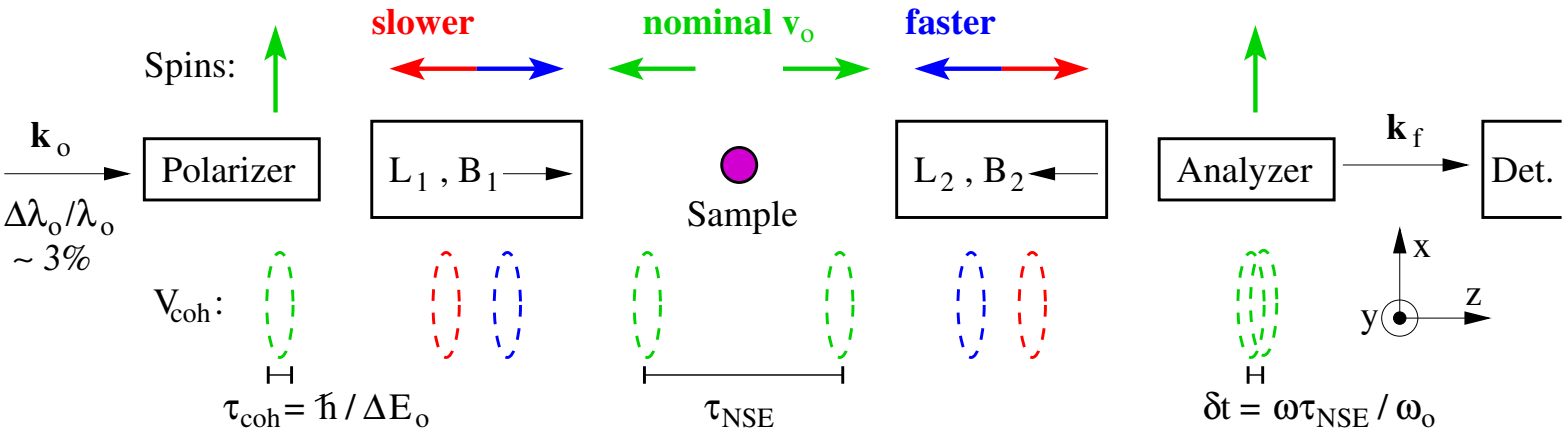
Consider a chopper or pulsed moderator that emits a "white" beam of neutron waves during $-T/2 < t < +T/2$ that are received at two times $t_1 \gtrsim t_o$, with $\delta = t_1 - t_o$, by the sample placed a distance L_o away.
For nominal emission at $t = 0$ and reception at t_o, the neutron wave's group velocity $v_o = L_o/t_o$ and kinetic energy $E_o = \hbar\omega_o = mv_o^2/2$.
Emission at $\pm T/2$ and reception at t_o by the sample then leads to:

$$v_\pm = \frac{L_o}{t_o \pm T/2} \approx v_o(1 \mp \frac{T}{2t_o}), \quad \omega_\pm \approx \omega_o(1 \mp \frac{T}{t_o}) \text{ for } \omega_o = \frac{mL_o^2}{2\hbar t_o^2}$$

Waves emitted at distinct dt within $\pm T/2$ have $\omega_- < \omega_{dt} < \omega_+$, as well as uncorrelated phase offsets ϕ_{dt} that cancel out for the phase *difference* seen by the sample at t_o vs t_1: $\Delta\phi_{dt} = \omega_{dt}(t_1 - t_o) = \omega_{dt}\delta$.
$\Rightarrow$ We want the spread in this phase difference over $\omega_- < \omega_{dt} < \omega_+$ to be maximally 1 rad $\Rightarrow$ $(\omega_+ - \omega_-)\delta_{max} = \Delta\omega\delta_{max} = \delta_{max} 2T\omega_o/t_o = 1$, thus defining $\tau_{coh} = \delta_{max} = t_o/(2T\omega_o) = \hbar/\Delta E_{res}$ for $\Delta E_{res} = \hbar\Delta\omega$, where considering only phases has lost the factor of 1/2 in the U.P.
NB: This τ_{coh} increases with t_o since the pulse appears increasingly instantaneous, just as we saw that ξ_x increases with increasing propagation distance from a slit as it appears increasingly point-like.
(Ref: *T. Keller,* et al, *Physica B* **234–236** *(1997) 1121.*)

Neutron spin-echo (QENS case): QM description

Schematic of a longitudinal, static-field neutron spin-echo experiment:



where as usual: $\mathbf{q} = \mathbf{k}_o - \mathbf{k}_f$ and $\hbar\omega = E_o - E_f$, and we'll assume $L_1 = L_2 = L$, $B_1 = B_2 = B$ for the quasi-elastic scattering (QENS) case.

After a 3% velocity selector, an incident neutron wavepacket is polarized vertically along *x*, which can be represented as the sum:

$$|\psi_o\rangle = |+\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle_z + |-\rangle_z) = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix}$$

of σ_z spin eigenstates which then non-adiabatically acquire different potential energies and hence via energy conservation also different kinetic energies in the B_1 field, due to the Zeeman energy splitting: $\hbar\omega_L = 2\hbar\omega_z = 2\mu_n B = \hbar\gamma_n B$, where γ_n is the neutron's gyromagnetic ratio, such that the neutron's magnetic moment $\mu_n = \gamma_n\hbar/2 = \gamma_n\hbar S$.

NSE: Phase differences between $|+\rangle_z$ and $|-\rangle_z$

An initial kinetic energy $E_o = mv_o^2/2$ with group velocity v_o leads to a nominal transit time $t_o = L/v_o$ through the first coil. Within B_1 however, these quantities change for states $|+\rangle_z$ and $|-\rangle_z$ to first order in v:

$$v_\pm \approx v_o \pm \frac{\hbar\omega_z}{mv_0} \;\Rightarrow\; t_\pm = \frac{L}{v_\pm} \approx \frac{L}{v_o} \mp \frac{\tau_{\rm NSE}}{2}, \;\text{ for }\; \tau_{\rm NSE} = \frac{2\hbar\omega_z L}{mv_o^3}$$

where $\tau_{\rm NSE}$ is thus the difference in arrival time of $|+\rangle_z$ and $|-\rangle_z$ at the sample position, and thus also the difference in starting time for their scattered waves of energy $\hbar\omega_f$, resulting in a net phase difference of $\Delta\phi_{\rm delay} = \omega_o\tau_{\rm NSE} - \omega_f\tau_{\rm NSE} = -\omega\tau_{\rm NSE}$ at any position after scattering.

Due to continuity of phase upon entering and exiting the potential of a coil, the oscillation frequency ω_o or ω_f (for each component of the wavepacket) cannot change, but nevertheless $|+\rangle_z$ and $|-\rangle_z$ accrue different relative phase differences within the 1st and 2nd coils:

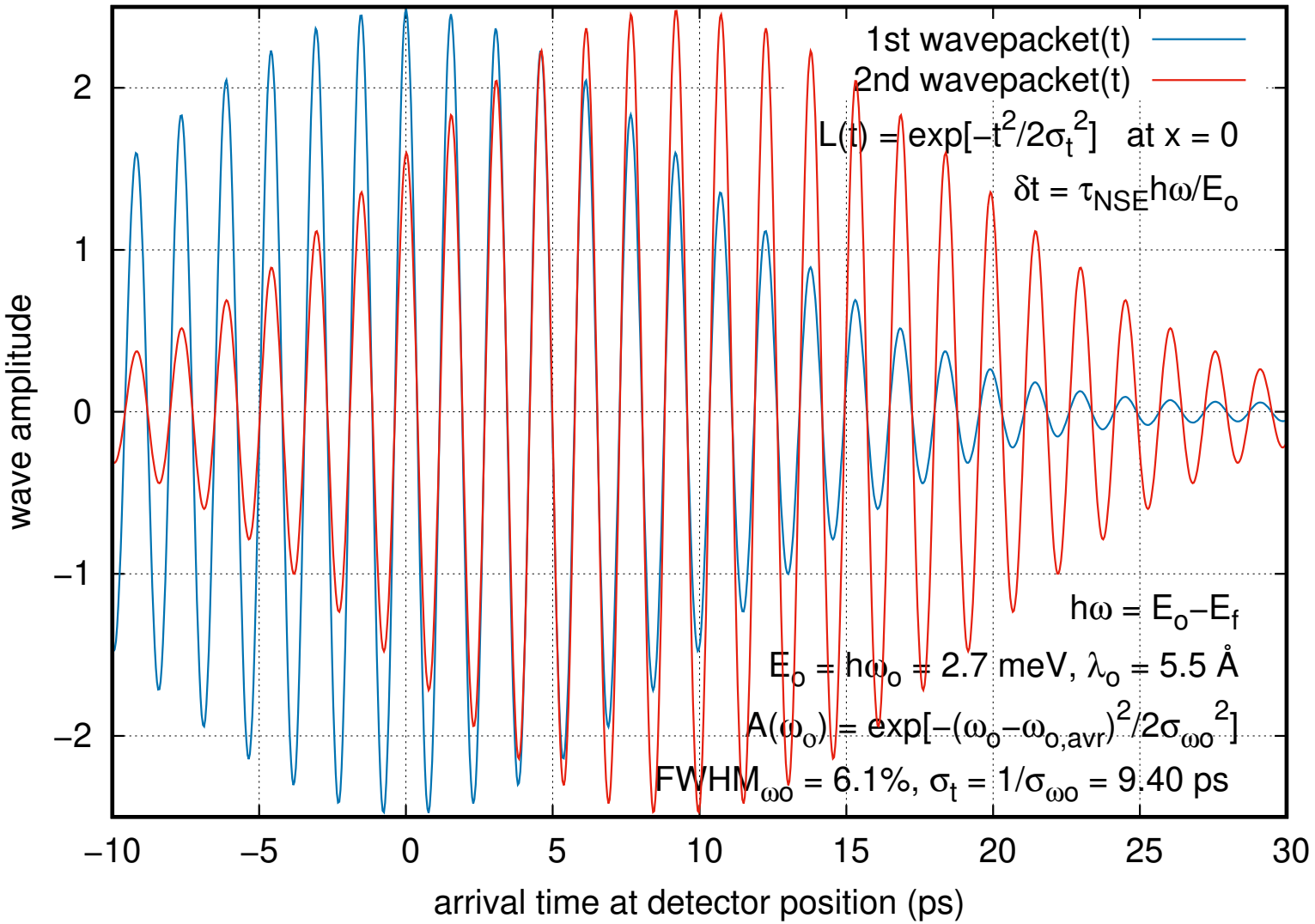
$$\phi_1^\pm = k_{o\pm}L \approx k_oL \pm \omega_z t_o \;\Rightarrow\; \delta\phi_1 = \phi_1^+ - \phi_1^- \approx 2\omega_z L/v_o$$
$$\phi_2^\pm = k_{f\mp}L \approx k_fL \mp \omega_z t_f \;\Rightarrow\; \delta\phi_2 = \phi_2^+ - \phi_2^- \approx -2\omega_z L/v_f$$

$$\Rightarrow\; \delta\phi_1 + \delta\phi_2 = 2\omega_z L\left(\frac{1}{v_o} - \frac{1}{v_f}\right) \approx \frac{2\omega_z L}{v_o^2}\Delta v \approx \frac{2\omega_z L}{mv_o^3}\Delta E = +\omega\tau_{\rm NSE}$$

Thus cancelling perfectly the $\Delta\phi_{\rm delay}$ at the detector position!

Arrival of both NSE wavepackets at the detector

The $|+\rangle_z$ and $|-\rangle_z$ wavepackets are in phase at the detector position, but their $V_{\rm coh}$ envelopes are time-shifted by *e.g.* $\delta t(\hbar\omega, B, L) = 9.2$ ps $\approx \sigma_t = \tau_{\rm coh} = 9.4$ ps. NB: $\Delta E_o/E_o = \Delta\omega_o/\omega_o = 2\Delta\lambda_o/\lambda_o = 6.1$ %.



NSE: QENS = wavepacket overlap at detector

The time delay δt between the two wavepackets at the detector results from the difference in nominal group velocities v_o vs v_f within the coils:

$$\delta t \;=\; \tau_{\rm NSE,o} - \tau_{\rm NSE,f} \;\approx\; \tau_{\rm NSE}\left(1 - \frac{v_o^3}{v_f^3}\right) \;=\; \tau_{\rm NSE}\left(1 - \frac{E_o^{3/2}}{E_f^{3/2}}\right)$$

$$\approx\; \tau_{\rm NSE}\left(1 - \left(1 - \frac{\Delta E}{E_f}\right)^{3/2}\right) \;\approx\; \tfrac{3}{2}\tau_{\rm NSE}\frac{\Delta E}{E_f} \;\approx\; \tfrac{3}{2}\tau_{\rm NSE}\frac{\hbar\omega}{E_o}$$

To assure sufficient time overlap of the $|+\rangle_z$ and $|-\rangle_z$ wavepackets at the detector, we require $\delta t(\omega) \lesssim \tau_{\rm coh}$ for all $\hbar\omega$ of interest:

$$\tfrac{3}{2}\tau_{\rm NSE}\frac{\hbar\omega}{E_o} \;\lesssim\; \frac{\hbar}{\Delta E_o} \;\Rightarrow\; \tfrac{3}{2}\tau_{\rm NSE}\frac{\Delta E_o}{E_o}\omega_{\rm max} \;=\; 3\tau_{\rm NSE}\frac{\Delta\lambda_o}{\lambda_o}\omega_{\rm max} \;\lesssim\; 1$$

otherwise one must adjust *e.g.* B_2L_2 so as to satisfy the resonance condition $\tau_{\rm NSE,o} = \tau_{\rm NSE,f}$ for some central value $\overline{v_f}$, depending on the $\hbar\overline{\omega} = \overline{E}_f - E_o = \frac{1}{2}m\overline{v_f}^2 - \frac{1}{2}mv_o^2$ of interest, and then go to the next $\overline{v_f}$:

$$\tau_{\rm NSE} = \left(\frac{2\hbar\omega_z L}{mv_o^3}\right) = \left(\frac{2\hbar\gamma_n B_1 L_1}{mv_o^3}\right) \Rightarrow \left(\frac{B_2L_2}{\overline{v_f}^3}\right) = \left(\frac{B_1L_1}{v_o^3}\right)$$

which allows to do large $\hbar\omega$ inelastic scattering with neutron spin-echo.

NSE/QENS: Scattered intensity of $|+\rangle_z$ and $|-\rangle_z$

Generally $\tau_{\rm coh} \ll \tau_{\rm NSE} \gtrsim 10$ ns, such that the scattering by atom $\mathbf{R}_j(t)$ of $|+\rangle_z$ at $t = 0$, and of $|-\rangle_z$ at $t = \tau_{\rm NSE}$, is quasi-instantaneous. Since all other phase factors cancel out in the QENS case, we can write the final neutron wavefunction's amplitude and its detected norm-square as:

$$|\psi_f\rangle = \frac{1}{\sqrt{2}} \sum_j^N \begin{bmatrix} e^{i\mathbf{q}\cdot\mathbf{R}_j(0)} \\ e^{i\mathbf{q}\cdot\mathbf{R}_j(t)} \end{bmatrix} \quad \text{and} \quad |\psi_f\rangle^\dagger = \frac{1}{\sqrt{2}} \sum_k^N \begin{bmatrix} e^{-i\mathbf{q}\cdot\mathbf{R}_k(0)} & e^{-i\mathbf{q}\cdot\mathbf{R}_k(t)} \end{bmatrix}$$

$$\Rightarrow A^2(\mathbf{q},t) = \langle\psi_f|\psi_f\rangle = \frac{1}{2}\sum_{j,k}^N \left\langle \begin{bmatrix} e^{-i\mathbf{q}\cdot\mathbf{R}_k(0)} & e^{-i\mathbf{q}\cdot\mathbf{R}_k(t)} \end{bmatrix} \begin{bmatrix} e^{i\mathbf{q}\cdot\mathbf{R}_j(0)} \\ e^{i\mathbf{q}\cdot\mathbf{R}_j(t)} \end{bmatrix} \right\rangle$$

$$= \frac{1}{2}\sum_{j,k}^N \left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_k(0)} e^{i\mathbf{q}\cdot\mathbf{R}_j(0)} + e^{-i\mathbf{q}\cdot\mathbf{R}_k(t)} e^{i\mathbf{q}\cdot\mathbf{R}_j(t)} \right\rangle = \sum_{j,k}^N \left\langle e^{i\mathbf{q}\cdot(\mathbf{R}_j - \mathbf{R}_k)} \right\rangle$$

$= N \cdot S(\mathbf{q})$, *i.e.* the static structure factor, which could be much more easily measured by a diffractometer. Here we have made use of: the atomic position operators $\mathbf{R}_j(t_1)$ and $\mathbf{R}_k(t_2)$ commute for $t_1 = t_2$ between atoms j and k, and the thermal average $< \ldots >$ includes a time average, such that equal-time correlations are the same at any t.

(Ref: *R. Gähler,* et al*, Physica B* **229** *(1996) 1–17.*)

NSE/QENS: Polarization analysis of $|+\rangle_z$ and $|-\rangle_z$

Instead, let's measure the vertical polarization of $|\psi_f\rangle$ along x just before the detector, since $|\psi_o\rangle$ was $|+\rangle_x$. NB: the time dependences of $|+\rangle_z$ and $|-\rangle_z$ produce a QM version of Larmor precession in the B fields. The expectation value of the polarization operator σ_x is:

$$\langle\psi_f|\sigma_x|\psi_f\rangle = \frac{1}{2}\sum_{j,k}^{N}\left\langle \begin{bmatrix} e^{-i\mathbf{q}\cdot\mathbf{R}_k(0)} & e^{-i\mathbf{q}\cdot\mathbf{R}_k(t)} \end{bmatrix} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} e^{i\mathbf{q}\cdot\mathbf{R}_j(0)} \\ e^{i\mathbf{q}\cdot\mathbf{R}_j(t)} \end{bmatrix} \right\rangle$$

$$= \frac{1}{2}\sum_{j,k}^{N}\left\langle \begin{bmatrix} e^{-i\mathbf{q}\cdot\mathbf{R}_k(0)} & e^{-i\mathbf{q}\cdot\mathbf{R}_k(t)} \end{bmatrix} \begin{bmatrix} e^{i\mathbf{q}\cdot\mathbf{R}_j(t)} \\ e^{i\mathbf{q}\cdot\mathbf{R}_j(0)} \end{bmatrix} \right\rangle \quad (\sigma_x \text{ has flipped } |\psi_f\rangle)$$

$$= \frac{1}{2}\sum_{j,k}^{N}\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_k(0)}e^{i\mathbf{q}\cdot\mathbf{R}_j(t)}\right\rangle + \frac{1}{2}\sum_{j,k}^{N}\left\langle e^{-i\mathbf{q}\cdot\mathbf{R}_k(t)}e^{i\mathbf{q}\cdot\mathbf{R}_j(0)}\right\rangle$$

$$= \frac{N}{2}I(\mathbf{q},t) + \frac{N}{2}I(\mathbf{q},-t) = \frac{N}{2}I(\mathbf{q},t) + \frac{N}{2}I^*(\mathbf{q},t) = N\cdot\Re[I(\mathbf{q},t)]$$

all for $t = \tau_{\rm NSE}$ since only then will $|+\rangle_z$ and $|-\rangle_z$ be in phase at the detector for all $\hbar\omega$, as we have seen. Hence, a final polarization $\langle\sigma_x\rangle$ measurement in NSE gives directly the real part of the otherwise complex intermediate scattering function $I(\mathbf{q},\tau_{\rm NSE})$. Again we used the homogeneity of time-correlation averages: $\langle\tau_{\rm NSE},0\rangle_t = \langle 0,-\tau_{\rm NSE}\rangle_t$.

(See also: *R. Golub,* et al*, Am. J. Phys.* **62** *(1994) 779.*)

Typical values of ξ, τ_{coh} for real experiments

Considering the ξ, τ_{coh} and Δ's to represent $\approx$ Gaussian FWHMs:

$$\xi_{x,\mathrm{SANS,IFM}} = \frac{2\ln(4)}{\Delta k_x} = 0.44\frac{\lambda L}{S}, \quad \xi_{q,\mathrm{diff}} = \frac{5.55}{\Delta q_{\mathrm{res}}}, \quad \xi_{z,\mathrm{mono}} = 0.44\frac{\lambda^2}{\Delta\lambda}$$

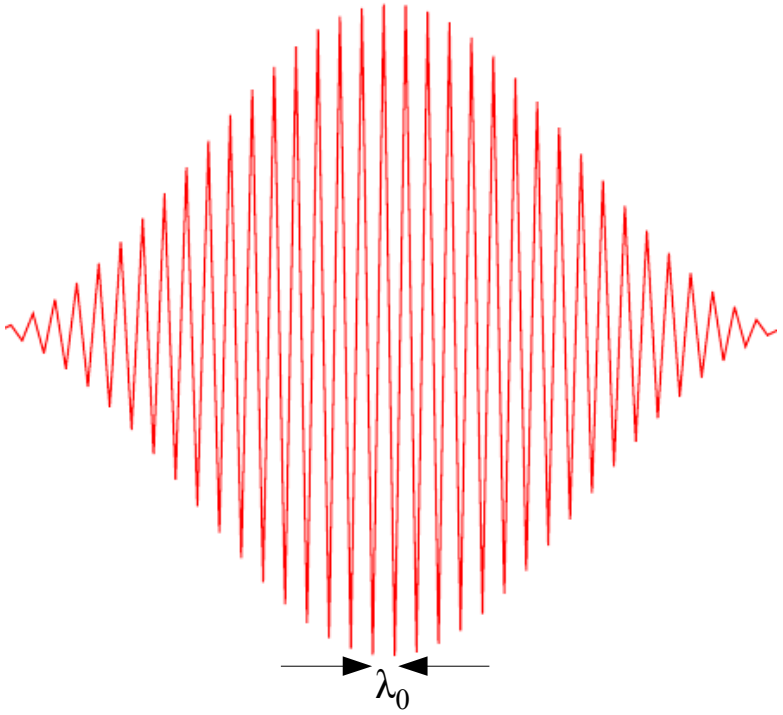
$$\tau_{\mathrm{TOF}} = \frac{t_o}{2\omega_o T} = \frac{\hbar t_o^3}{mL_o^2 T}, \quad \tau_{\mathrm{NSE}} = \frac{2\hbar\omega_z L}{mv_o^3} = \frac{2\mu_n BL}{mv_o^3}, \quad \tau_{\mathrm{mono}} = \frac{\xi_{z,\mathrm{mono}}}{v_o}$$

1) SANS: $\lambda = 10$ Å, $S = 1$ cm at $L = 20$ m $\Rightarrow$ $\xi_{x,\mathrm{SANS}} = 8800$ Å.
2) Diffraction: $\Delta q_{\mathrm{res}} = 0.03$ Å^{-1} on average $\Rightarrow$ $\xi_{q,\mathrm{diff}} = 185$ Å.
3) Monochromator: $\lambda = 1.82$ Å ($v_o = 2174$ m/s), $\Delta\lambda/\lambda = 1$ %
$\Rightarrow$ $\xi_{z,\mathrm{mono}} = 80$ Å, $\tau_{\mathrm{mono}} = 3.7$ ps.
4) Backscattering from perfect xtal Si: $\lambda = 6.28$ Å ($v_o = 630$ m/s),
$\Delta\lambda/\lambda = 5 \times 10^{-6} \Rightarrow$ $\xi_{z,\mathrm{mono}} = 55$ μm, $\tau_{\mathrm{mono}} = 88$ ns.
5) TOF instrument: $T = 10$ μs, $L_o = 5$ m, $\lambda = 5$ Å ($t_o = 6.3$ ms),
$\Rightarrow$ $\tau_{\mathrm{TOF}} = 63$ ps.
6) Velocity selector: $\lambda = 5$ Å ($v_o = 791$ m/s), $\Delta\lambda/\lambda = 10$ %
$\Rightarrow$ $\xi_{z,\mathrm{mono}} = 22$ Å, $\tau_{\mathrm{mono}} = 2.8$ ps.
7) NSE: $\lambda = 5$ Å ($v_o = 791$ m/s), $L = 2$ m, $B = 0.2$ T,
$\mu_n = -9.65 \times 10^{-27}$ J/T $\Rightarrow$ $\tau_{\mathrm{NSE}} = 9.3$ ns.

Localisation: When and Where is the neutron wave?

Try localising neutron wavepackets to V_{coh}

$\Psi(\mathbf{r},t)$ = probability amplitude for the propagating neutron's presence



$|\Psi(\mathbf{r},t)|^2$ = probability of finding the neutron at position $\mathbf{r}$ at time t

Propagation direction:

$\mathbf{k_0}$ = wavevector

$k_0 = |\mathbf{k_0}| = 2\pi/\lambda_0$

$E_0 = \hbar\omega_0 = \hbar^2 k_0^2 / 2m$

spread in wavelength:

$\Delta\lambda/\lambda = \Delta k/k \sim 1\ \%$

Consider a Gaussian neutron wavepacket of incident $\hbar\omega_0$ and $\mathbf{k}_o$ to be localized to its coherence volume $V_{coh} = \xi_x \xi_y \xi_z$ at $t = 0$, and which propagates with group velocity $v_g = d\omega/dk = \xi/\tau_{coh}$. In principle, different neutrons would then scatter from different V_{coh} somewhere in the sample, each V_{coh} comprising a few 100,000 atoms, thus averaging diffraction intensity over isotopes, spin-states and local structures.

Problem: Matter wavepackets are very dispersive!

All electromagnetic waves propagate with the same $c = d\omega/dk = \omega/k$. For matter waves however, $E = \hbar\omega = \hbar^2 k^2/2m$ is quadratic in k, such that the group velocity $v_g = d\omega/dk = \hbar k/m$. Therefore, the higher k components of a propagating neutron wavepacket will outpace the lower k components, leading to spatial spreading, *i.e.* delocalisation (but NOT to an increase in longitudinal coherence length).

For a Gaussian thermal neutron wavepacket initially localized to 100 Å, this envelope doubles in $\gtrsim 1$ ns, and after 2 m of propagation, the wavepacket is already ~ 2 cm long (laterally it spreads more slowly).

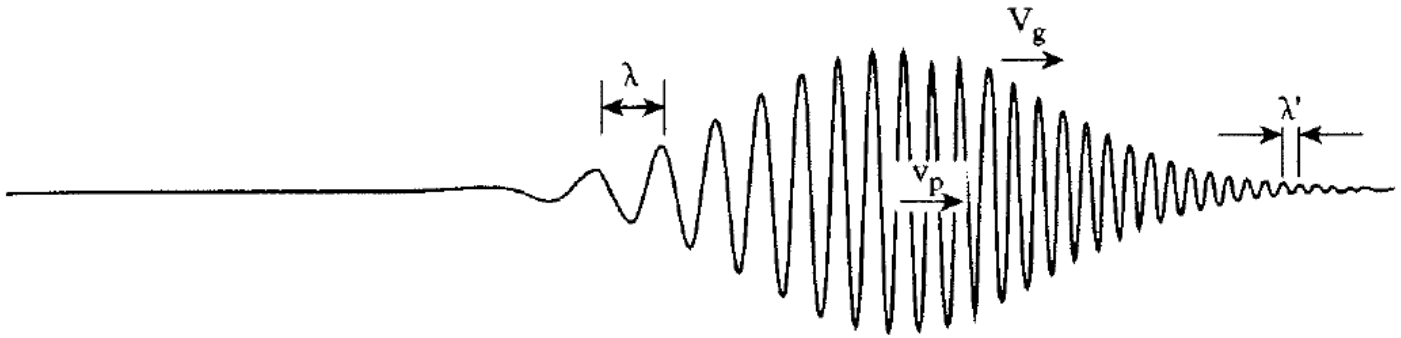
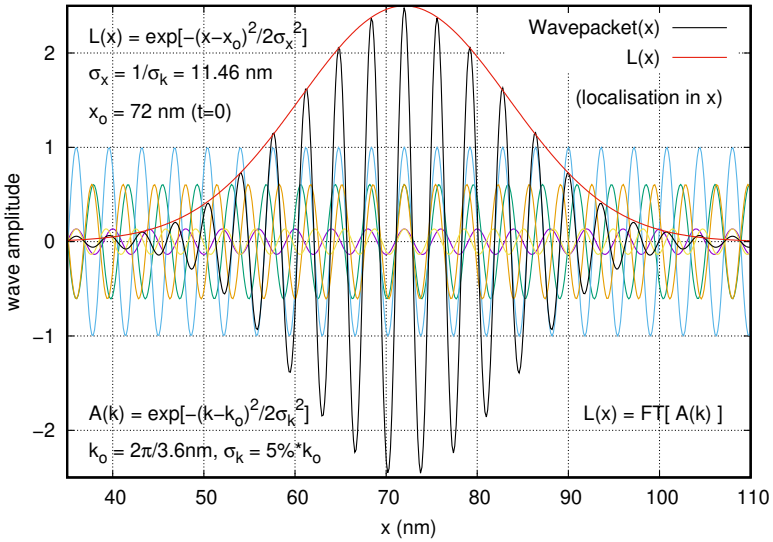


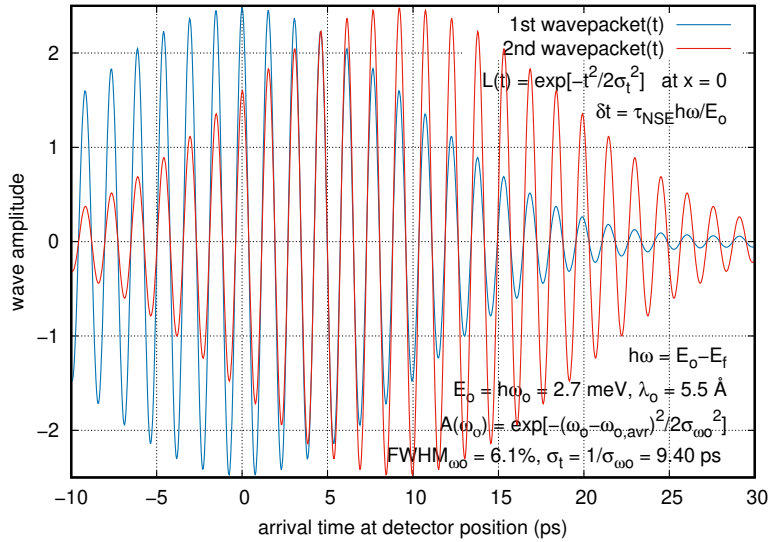
Figure 1.1 *Real part of a neutron wave packet traveling in the x-direction with group velocity v_g and phase velocity v_p. The imaginary part of the wave packet is complementary. The diagram is drawn for $\Delta k/k = 0.1$. Thanks to Robert Dimeo, NIST*

(Figure: *Rauch and Werner, Neutron Interferometry, 2nd Ed. (2015) p5.*)

Why is V_{coh} not already a localized wavepacket?

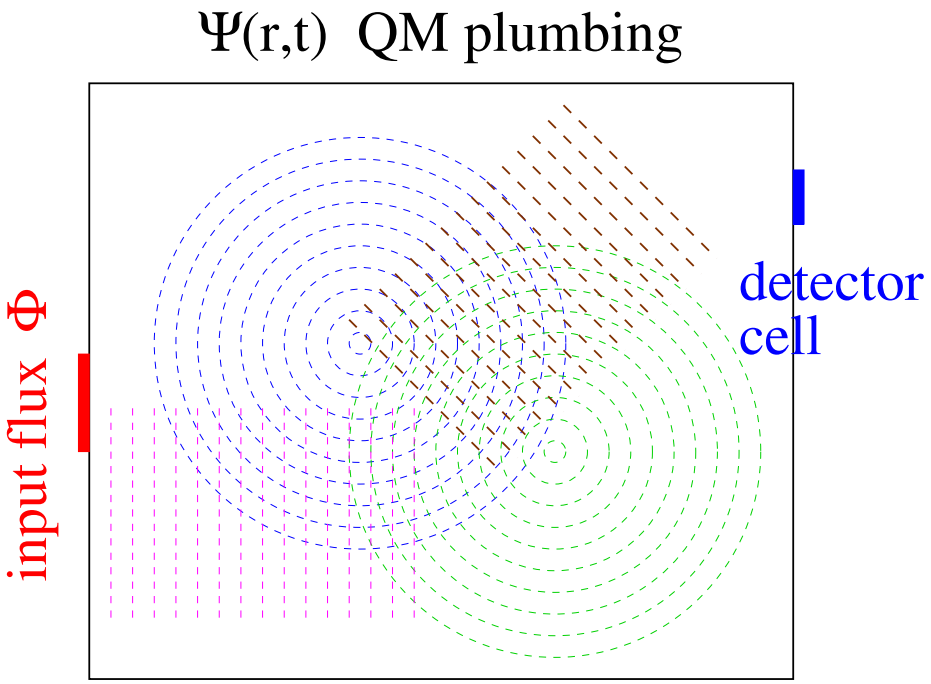
In localizing a wavepacket at a particular point in **r** or *t* we effectively assigned constant absolute phases ϕ_j^k and ϕ_j^ω, to the component plane waves *j* that are integrated up to form the wavepacket. A different choice of phases would have localized it to a different $(\mathbf{r}, t)$ point.





To relocalize the otherwise spreading wavepacket as it propagates, the phases ϕ_j^k, ϕ_j^ω need to be continually retuned. The coherence lengths and times, on the other hand, do not depend on these absolute phases, since we consider only the spread in the *phase differences for each plane wave* between 2 positions (ξ_{coh}) or between 2 times (τ_{coh}), such that the absolute phases cancel out completely. $\Rightarrow$ ξ_{coh} and τ_{coh} have no localization, but rather exist everywhere and always.

All neutrons have the same wavefunction $\Psi(\mathbf{r}, t)$



$\Psi(\mathbf{r}, t)$ as a probability amplitude is determined by applying Schrödinger's Eqn to the neutron optics and the sample's $G(\mathbf{r}, t)$. The flux Φ simply "populates" $\Psi(\mathbf{r}, t)$ with neutrons that contribute statistically to the same measured $d\sigma/d\Omega dE$.

We know Φ and we measure $d\sigma/d\Omega dE$ at the detector as a neutron counting rate, but the "trajectories" of the neutrons are *undetermined*. All detected neutrons have "inhabited" the same $\Psi(\mathbf{r}, t)$ wavefunction "plumbing" that results from summing probability amplitudes over all atoms, $\Delta\mathbf{k}$ and $\hbar\omega$ (leading to coherence volumes and times).

Each detected neutron at a given $\mathbf{k}_f$ and E_f is therefore statistically representative of the entire sample's $S(\mathbf{q}, \omega)$. In other words, all detected neutrons have "seen" the same "everything".

The CIA principle of Quantum Mechanics

Standard US policy asserts that CIA agents should be provided with sensitive information on a *need-to-know basis only*.

Nature assures that an element of information about a quantum system exists on a *need-to-exist basis only*, otherwise it remains *undetermined*.

The state of a QM system remains as undetermined as possible ("QM coherence") until it interacts irreversibly with a macroscopic environment ("QM decoherence"), *e.g.* via a measurement, which then determines the nature of its information content. (*e.g.* W. Zurek, *et al*).

The Uncertainty Principle conserves the total information content of a QM system, allowing redistribution among non-cummuting observables.

When a property of a QM system is undetermined, this does not mean that we simply do not know its value, but rather that its value does not exist (Copenhagen Interpretation). This important distinction can lead to real differences in predictions of experimental results (Bell Inequality).

In the case of an undetermined property of a QM system, we must sum over all possibilities for that property in order to predict the outcome of experiments (*e.g.* Feynman's $\sum_{\text{all paths}}$ formulation of QM).

The interpretation of Quantum Mechanics (Ex.)

A diffraction measurement of $d\sigma/d\Omega$ does not probe the trajectories of the neutrons, and therefore this information does not need to exist, and thus remains *undetermined*. Caveat: Weak interactions with air molecules, etc, can decohere particle wavefunctions, potentially leading to some localisation information.

In neutron diffraction, the sum over all possible energy transfers $\hbar\omega$ for detected neutrons leads to a very short coherence time, but the postselection by an analyser crystal placed before the detector results in a much longer coherence time, since a gain in E_f information leads to a loss of time information via the Uncertainty Principle.

A neutron in a spin-left (along y) state contains no information about its spin along z, which is therefore completely undetermined, since this information does not need to exist. A measurement of S_z by the environment/apparatus then produces a purely random result as the new spin state, and the spin-left information no longer exists.

The interpretation of Quantum Mechanics (Ex.)

The information of a double-slit interference pattern is converted (*e.g.* partially or completely) to which-path information when measurements are performed to localize the quantum particle, or simply when one path is more absorbing than the other. Again, the Uncertainty Principle assures that total information content is conserved.

An electron in an atomic orbital eigenstate has a definite energy E, but its position at a given time is completely undetermined. All information is concentrated into an exact value of E. If however the energy state has a finite lifetime τ, then this (weak) time information reduces slightly the E information content via the Uncertainty Principle, such that a spectral line broadens as $\Delta E \sim \hbar/\tau$.

In an Einstein-Podolsky-Rosen (EPR) experiment, the total spin information content of the two-particle (entangled) state is simply that the spins are antiparallel, but the spin axis itself remains undetermined until a measurement is made, *i.e.* until information is exchanged with the environment.

Summary: Coherence and Correlation

Structure depends on time and length scales

An amorphous material has short-range order, but no long-range order, implying a small *structural correlation length* ζ_{str}.

Even in a "perfect crystal" with long-range *average* order, the atoms are moving thermally, such that the "structure" depends on both time and space. The atomic displacements (*e.g.* for a phonon) are thus characterised not only by a ζ_{str}, but also by a *structural correlation time* τ_{str} aka lifetime or relaxation time.

A fluid (liquid, gas) can have a very short $\tau_{str} \lesssim 1$ ps.

The structure of a system/material must therefore be defined with respect to given length and time scales, and also specify whether any averaging over time, space or ensembles is considered.

A structural measurement probes the structure of a system over a certain range in space and with a certain time resolution, and scattering methods along with their analyses may also involve statistical averaging over time, space, or ensembles.

Coherence volume = spatial range of measurement

By applying simple geometry to the addition of neutron wave amplitudes as scattered by nuclei in a sample with a **q**-spread of $\Delta\mathbf{q} = \Delta\mathbf{k}_o - \Delta\mathbf{k}_f$, one can define a coherence volume $V_{\rm coh} = \xi_x \xi_y \xi_z$ within which neutron wave amplitudes can be added up roughly in phase.

ATTN: A naive application of the Uncertainty Principle $\delta x \cdot \delta p_x = \hbar/2$ (likewise for *y* and *z*) to Gaussian neutron wavepackets seemingly permits to interpret δx as the "undetermined-ness" of a neutron's position in the sample, thus localizing it to a volume $\delta x\ \delta y\ \delta z$ which could be identified with the coherence volume $V_{\rm coh}$, but this view is invalidated by the strong spatial dispersion of such matter wavepackets.

The coherence volume $V_{\rm coh}$ is effectively the reciprocal of the *q*-space instrumental resolution volume $\tilde{V}_{\Delta q} = \Delta q_x \Delta q_y \Delta q_z$ for which both upstream and downstream neutron optics need to be considered. The better the final *q*-space resolution that convolves the diffraction pattern, the greater the coherence volume as modulation envelope or "visibility volume" delimiting the range of structural measurement in the sample.

For a FWHM *q*-resolution of Δq in $d\sigma/d\Omega(q)$, the PDF(r) obtained by FT has an *r*-range of $\mathrm{FWHM}_r = \xi_q = 4\ln(4)/\Delta q = 5.55/\Delta q$.

Coherence time = time resolution of measurement

The atoms within $V_{\rm coh}$ witness a spread $\hbar\Delta\omega_o$ in the incident neutron wavefunction energy, as well as a (possibly much larger) spread $\hbar\Delta\omega_f$ in the scattered wavefunction energy arriving at the detector, leading to a total spread in neutron-sample E-transfer of $\hbar\Delta\omega \sim \hbar\Delta\omega_o + \hbar\Delta\omega_f$.

For $\omega = \omega_o - \omega_f$ per usual, the (inelastic) scattering phase difference $\phi = -\omega t$ will evolve differently in time for different ω components within the energy resolution $\sigma_\omega \sim \sigma_{\omega_o} + \sigma_{\omega_f}$, leading finally to a dephasing $\Delta\phi = \sigma_\omega t \gtrsim 1$ of ω components after a coherence time $\tau_{\rm coh} \sim 1/\sigma_\omega$.

During $\tau_{\rm coh}$ the time-dependent wavefunction amplitude is summed up (approximately) coherently, leading to the square of a time-averaged amplitude as the detection probability of neutrons by the detector. We can therefore also think of $\tau_{\rm coh}$ as the "duration" of the scattering event.

The better the energy resolution $\Delta E = \hbar\Delta\omega$ of $S(\mathbf{q},\omega)$ or $d\sigma/d\Omega(\mathbf{q})$ (or of an extracted part of it such as integrated Bragg peak intensities), the longer the coherence time $\tau_{\rm coh}$. In this case we may also apply the Uncertainty Principle: $\tau_{\rm coh} \sim \hbar/(2\Delta E) \sim 1$ fs for total-scattering with hot neutrons, and $\tau_{\rm coh} \sim 3$ ps for Rietveld refinement of Bragg peak intensities with thermal neutrons, compared to $\tau_{\rm phonon} \sim 0.3$ ps.

If time permits . . .

Atomic PDF-analysis: FT of a powder diffractogram

Disordered, nano-structured or reduced-dimensional crystals often lack sufficient long-range order to produce sharp diffraction peaks. It is then advantageous to sacrifice q-space resolution by using short wavelengths to provide a high $q_{\max}$ and thus better r-space resolution $\Delta r = 3.79/q_{\max}$ after Fourier Transform (FT) of the diffraction pattern taken as $d\sigma/d\Omega - \text{self\_scattering}$.
The resulting Pair-Distribution Function PDF(r) is the distribution of relative interatomic distances with respect to an average atom at the origin (*i.e.* an ensemble of quasi-instantaneous local structures $\neq$ the time+space averaged structure from Rietveld).
Instrumental q-space resolution Δq determines the neutron's coherence volume seen as an envelope that modulates and limits the spatial extent of the PDF(r) via $r_{\max} = (5.55/2)/\Delta q$.
NB: The PDF(r) is not the output of structural refinement, and is therefore a *model-independent* result that can of course then be used as input for structural modelling/simulation in r-space, thus concluding the technique of (atomic) "**PDF-analysis**".

Case of a monoatomic sample (only one Z)

In neutron scattering, a monoatomic sample can have a distribution of scattering lengths b_i, but there is no correlation between b_i and the structural environment of $\mathbf{r}_i$. The ensemble average over coherence volumes then leads to an expression (units of barns/str/atom) involving a **q**-dependent coherent term and an isotropic incoherent term:

$$\frac{1}{N}\left[\frac{d\sigma}{d\Omega}(\mathbf{q})\right] = \overline{b}^2 S(\mathbf{q}) + (\overline{b^2} - \overline{b}^2)$$

where the sample's average scattering length $\overline{b} = b_{\rm coh}$, the scattering cross-section $\sigma_s = 4\pi\overline{b^2}$, and $(\overline{b^2} - \overline{b}^2) = var(b)$ is simply the variance of scattering lengths throughout the sample. $\Rightarrow$ Incoherent scattering is merely the consequence of ensemble-averaging over the coherence volumes within the sample. The alternative expression:

$$\frac{1}{N}\left[\frac{d\sigma}{d\Omega}(\mathbf{q})\right] = \overline{b}^2 \left[S(\mathbf{q}) - 1\right] + \overline{b^2}$$

comprises a "distinct" term (interference between different atoms) and a "self" term (self-interference from individual atoms).

$\Rightarrow$ In x-ray diffraction (XRD), there is no isotopic incoherent scattering, but x-ray scattering lengths are q-dependent, *i.e.* there is a form factor.

Case of a monoatomic sample (cont'd)

The *static structure factor* (dimensionless) is then given by

$$S(\mathbf{q}) = \int_{-\infty}^{+\infty} d\omega \; S(\mathbf{q},\omega) \;\; = \;\; \frac{1}{N} \left\langle \sum_{i,j}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \right\rangle$$

and reduces to a real-valued sum of sinc() functions:

$$S(q) = \frac{1}{N} \left\langle \sum_{i,j}^{N} \frac{\sin(qr_{ij})}{(qr_{ij})} \right\rangle$$

in the case of conical Debye-Scherrer diffraction from an isotropic sample (*e.g.* powder, polycrystal, liquid, glass) for which

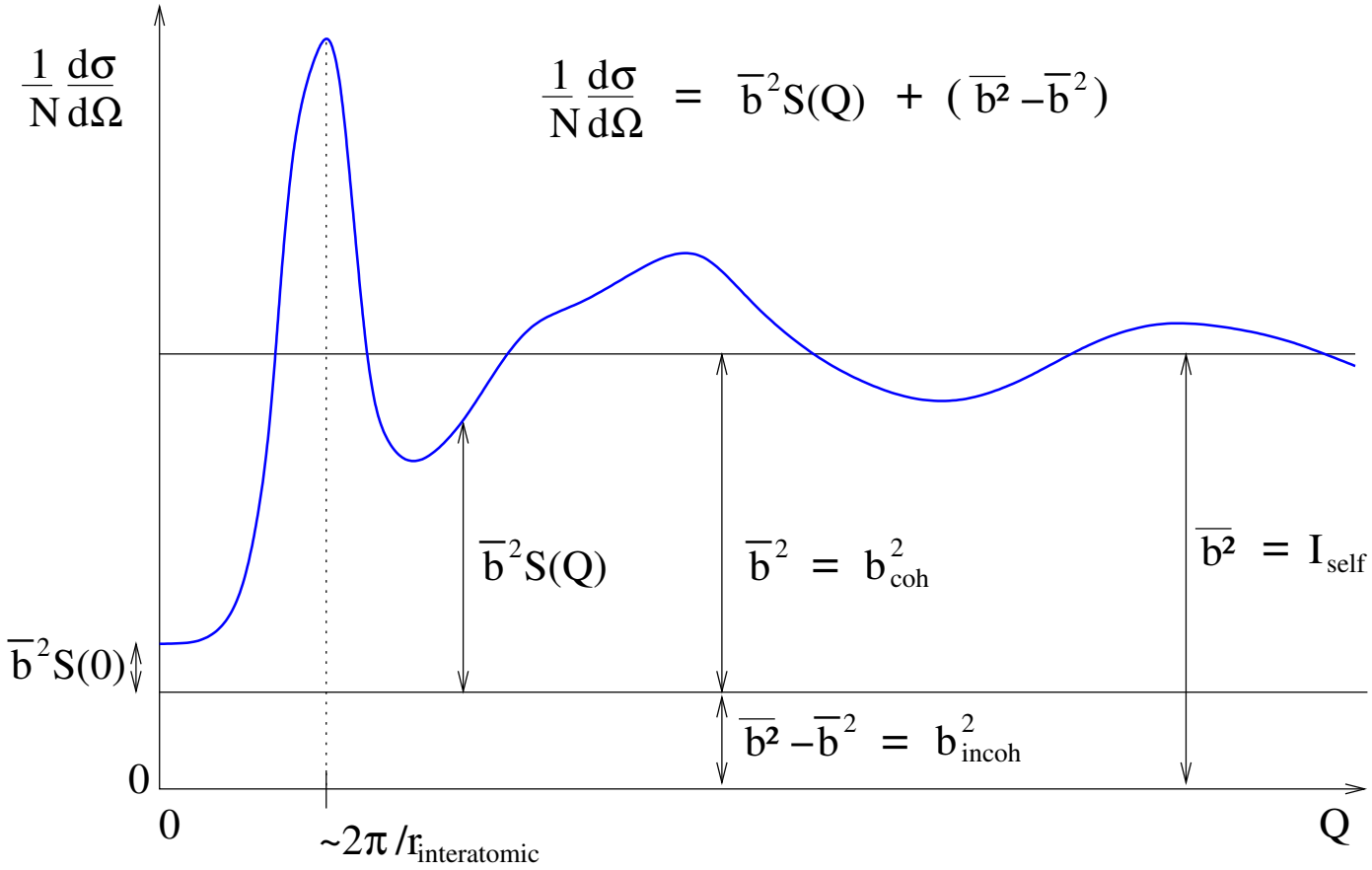
$$q = |\mathbf{q}| = (4\pi/\lambda) \; \sin(\theta)$$

and 2θ is the diffraction angle with respect to to the incident beam. Finally, for an incident flux Φ and a detector cell of solid angle $d\Omega$, the measured intensity (counts/s) from an isotropic sample is given by

$$I(q) = \Phi \; \frac{d\sigma}{d\Omega}(q) \; d\Omega$$

which, notably, is a function of q *only*.

$S(q)$ for a glass or liquid (isotropic, monoatomic)



Lack of long-range order, *i.e.* a short structural correlation length ζ_{str}, leads to broad peaks in the diffraction pattern for a glass/liquid, as opposed to sharp (resolution-limited) peaks for a crystalline powder of much greater ζ_{str}. In addition, $\tau_{coh} \sim 1$ fs $\ll \tau_{str} \sim 1$ ps = time scale of atomic displacement in a liquid, providing a "snapshot" of its structure.

Real-space functions (monoatomic case), PDF(r)

Fourier transform gives the *pair-distribution function* $g(r)$ which is proportional to the probability of finding an atom at a distance r from an average atom taken as the origin:

$$g(r) - 1 = \frac{1}{2\pi^2 r \rho_o} \int_0^\infty q\,[S(q) - 1] \sin(qr)\, dq$$

in addition to the density function $D(r)$ (also called $G(r)$) used for "PDF-analysis":

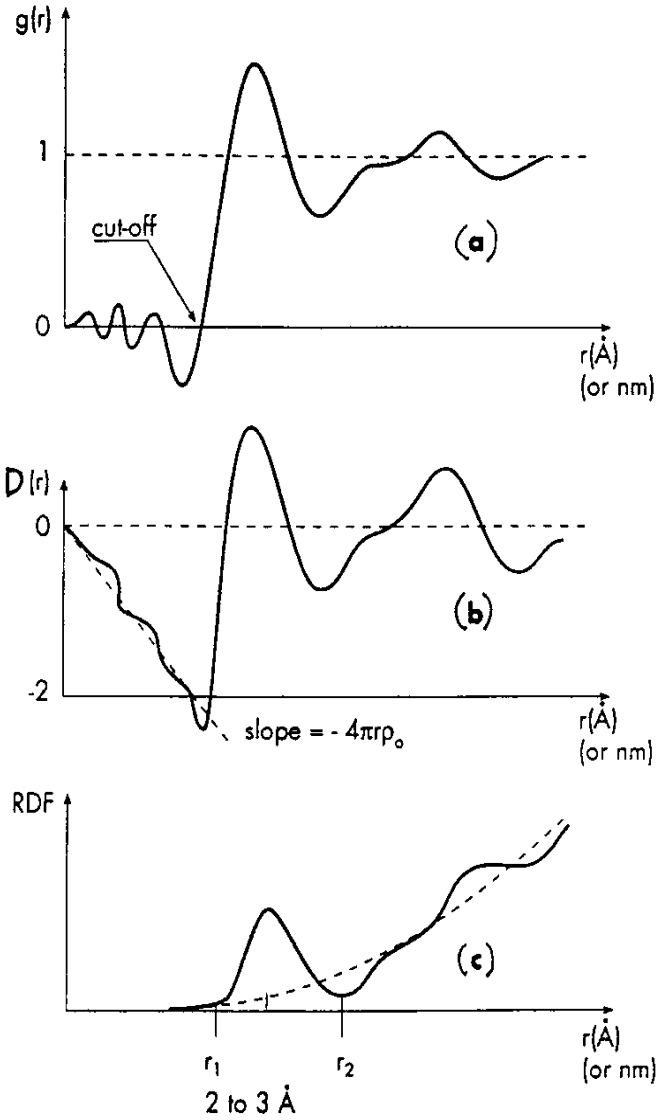
$$\mathrm{PDF}(r) = G(r) = D(r) = 4\pi r \rho_o\,[g(r) - 1]$$

$$= \frac{2}{\pi} \int_0^\infty q\,[S(q) - 1] \sin(qr)\, dq$$

as well as the radial distribution function:

$$\mathrm{RDF}(r) = 4\pi r^2 \rho_o\, g(r)$$

whose integration across peaks yields atomic coordination numbers.



Case of a polyatomic sample (several Z)

In a polyatomic system, the chemical affinities of n different atomic species Z_α necessarily leads to a correlation at atomic sites $\mathbf{r}_i$ between the structural environment and the average scattering length $\overline{b}_\alpha$. This correlation prevents a proper definition of a dimensionless $S(q)$, but the scattered intensity can still be expressed as the sum of a distinct term (the interference function $F(q)$) and a total self-scattering term:

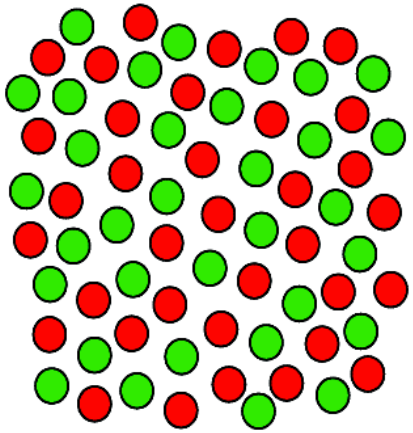
$$\frac{1}{N}\left[\frac{d\sigma}{d\Omega}(q)\right] = \sum_{\alpha,\beta}^{n} c_\alpha c_\beta \overline{b}_\alpha \overline{b}^*_\beta \left[S_{\alpha\beta}(q) - 1\right] + \sum_{\alpha}^{n} c_\alpha \overline{b^2}_\alpha \ ,$$

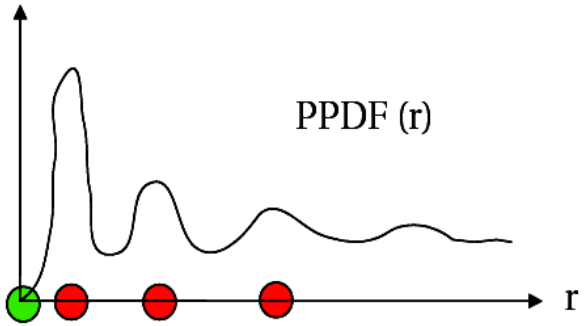
where c_α is the fraction or concentration of atomic species Z_α, and the *partial* structure factor (PSF) $S_{\alpha\beta}(q)$ is the Fourier transform of the *partial* pair-distribution function (PPDF) $g_{\alpha\beta}(r)$, which is in turn proportional to the probability of finding an atom of type Z_β at a distance r from an atom of type Z_α taken as the origin:

$$g_{\alpha\beta}(r) - 1 = \frac{1}{2\pi^2 r \rho_o} \int_0^\infty q \left[S_{\alpha\beta}(q) - 1\right] \sin(qr)\, dq \ .$$

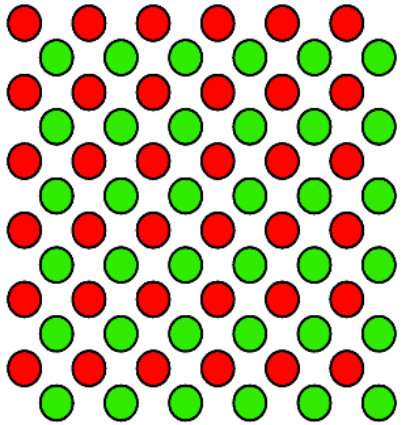
Atomic distributions in glass/liquid versus crystal

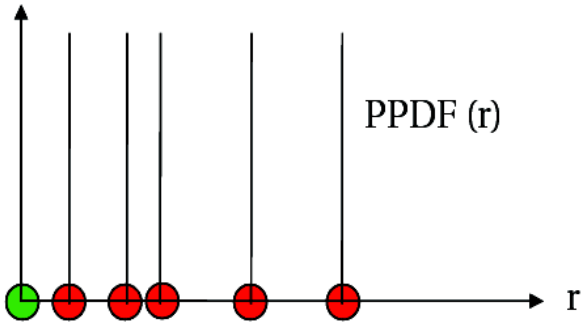
Liquid/Glass :





Crystal :





These *partial* PDFs or PPDFs (*e.g.* from NDIS) represent an ensemble average of quasi-instantaneous spatial correlations between red and green atoms: more specifically $g_{GR}(r)$ is proportional to the average probability of finding a Red atom at a distance r from a Green atom.

Coherence volume for an incident quantum

For each particle/wave emitted by an incoherent source of transverse FWHM size H by V, scattered by a sample at a distance L and then detected, purely geometric considerations impose a limit to the size of the scattering region within the sample over which a given quantum's scattered (from different atoms) amplitudes can be added coherently.

Assuming for convenience a Gaussian wavepacket for the incident quantum (*e.g.* x-ray or neutron), the Uncertainty Principle can be used to relate the standard deviations of its position and wavenumber:

$$\delta x_j \, \delta k_j \; = \; 1/2 \qquad \text{since} \qquad \delta x_j \, \delta p_j \; = \; \hbar/2$$

where the dimensions $j = h, v$ are transverse to the incident beam while $j = l$ is parallel (*i.e.* longitudinal). In terms of FWHM for the wavepacket:

$$\xi_j \, \Delta k_j \; = \; \frac{4 \ln(4)}{2} \qquad \Rightarrow \qquad \xi_j \; = \; \frac{5.55}{2 \, \Delta k_j}$$

where the mutually orthogonal *coherence lengths* ξ_j are the FWHM dimensions of the (roughly ellipsoidal) *coherence volume* $V_{\rm coh} = \xi_h \xi_v \xi_l$ from which the quantum scattered somewhere in the sample.

V_{coh} for an incident $\rightarrow$ scattered quantum

The Δk_j are given by the collimation FWHM's (small angle approx.) and by the monochromaticity (FWHM $\Delta\lambda$) of the incident beam:

$$\Delta k_{h,v} = \frac{2\pi}{\lambda}\frac{H,V}{L} \quad \text{and} \quad \Delta k_l = \frac{2\pi}{\lambda}\frac{\Delta\lambda}{\lambda}$$

and thus the 3 coherence lengths:

$$\xi_{h,v} = \lambda\frac{\ln(4)}{\pi}\frac{L}{H,V} = 0.44\,\lambda\frac{L}{H,V} \quad \text{and} \quad \xi_l = 0.44\,\lambda\frac{\lambda}{\Delta\lambda}$$

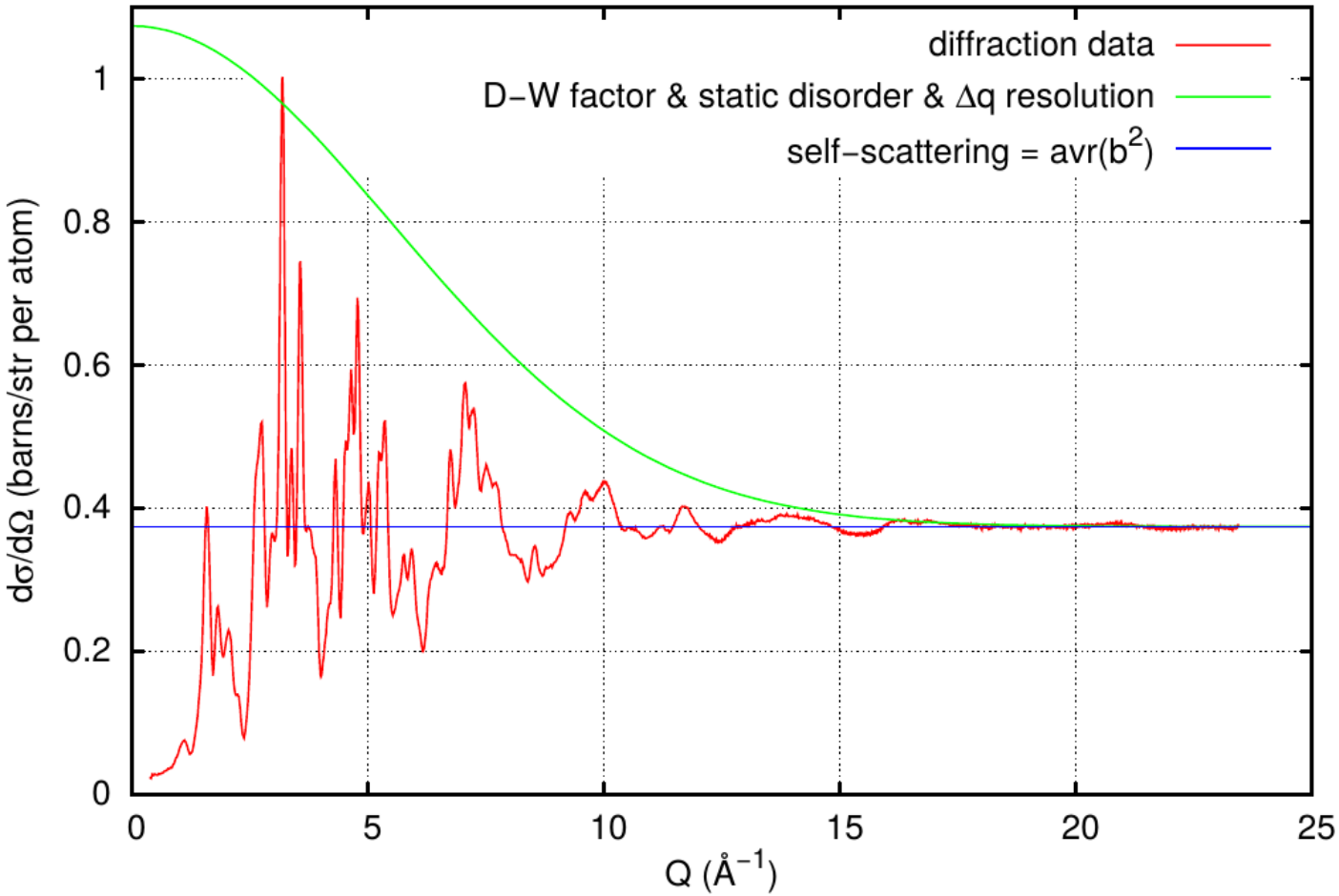
increase as the collimation and monochromaticity improve.

NB: In general, the sample-to-detector optics (*e.g.* α_3 collimation) also contribute to the instrumental resolution function of the diffraction pattern. In spite of occuring after the scattering event, such a *post-selection* of the scattered quanta leads to additional and complementary expressions in the above formulæ for ξ_j.

In the simplistic case of a constant-ish FWHM resolution of Δq for the final diffraction pattern, the FWHM coherence length in the diffraction plane of the scattering vector **q** is simply $\xi_q = 5.55/\Delta q$.

q-space versus *r*-space representations of data

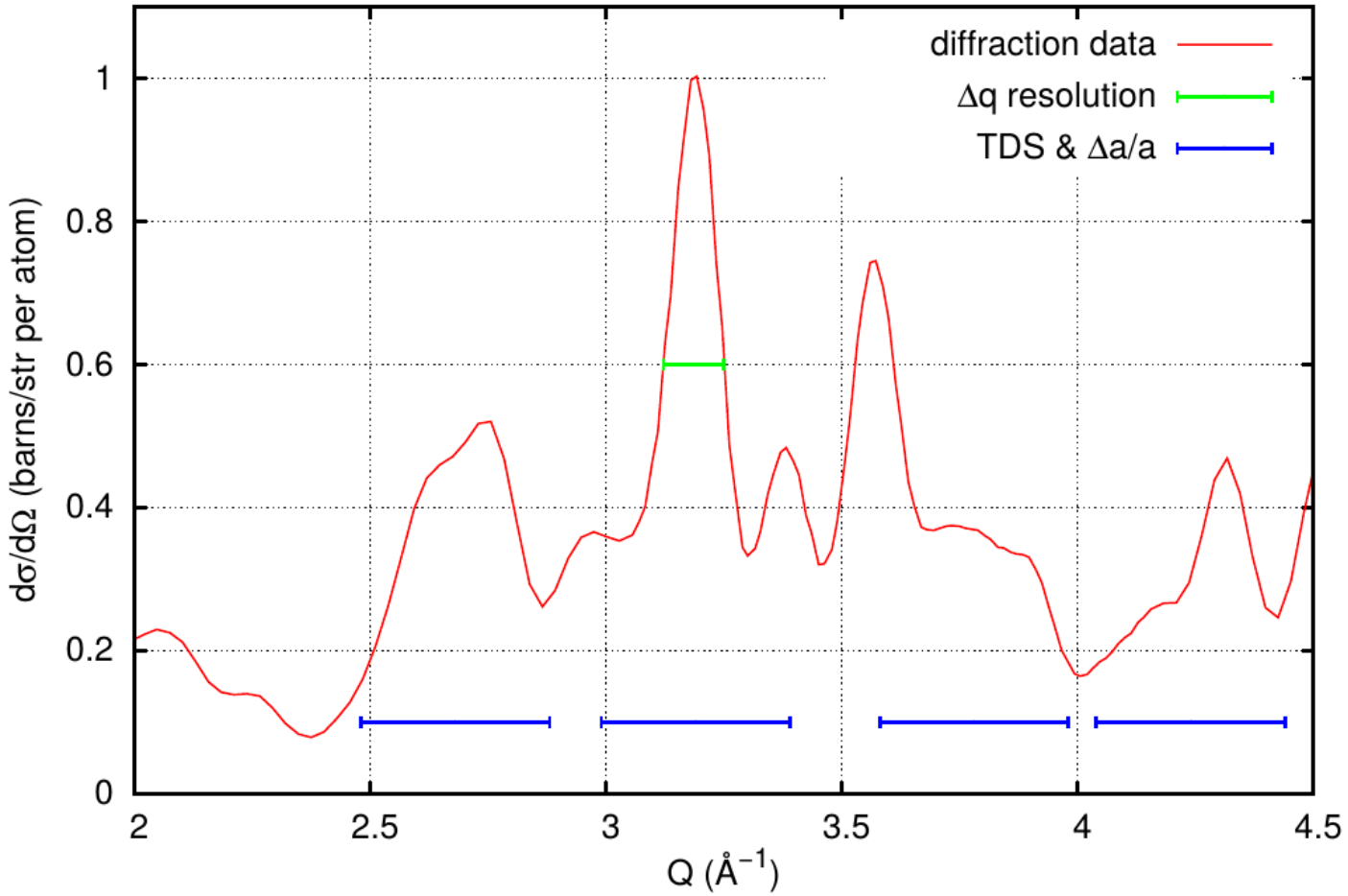
Diffraction data at high q_{max} show decreasing Bragg-peak intensities due to the Debye-Waller effect (thermal averaging of atomic positions), from static disorder, and also because of limited *q*-space resolution:



The diffraction intensity ultimately converges to the self-scattering limit $I_{self} = \overline{b^2}$ when q_{max} is high enough.

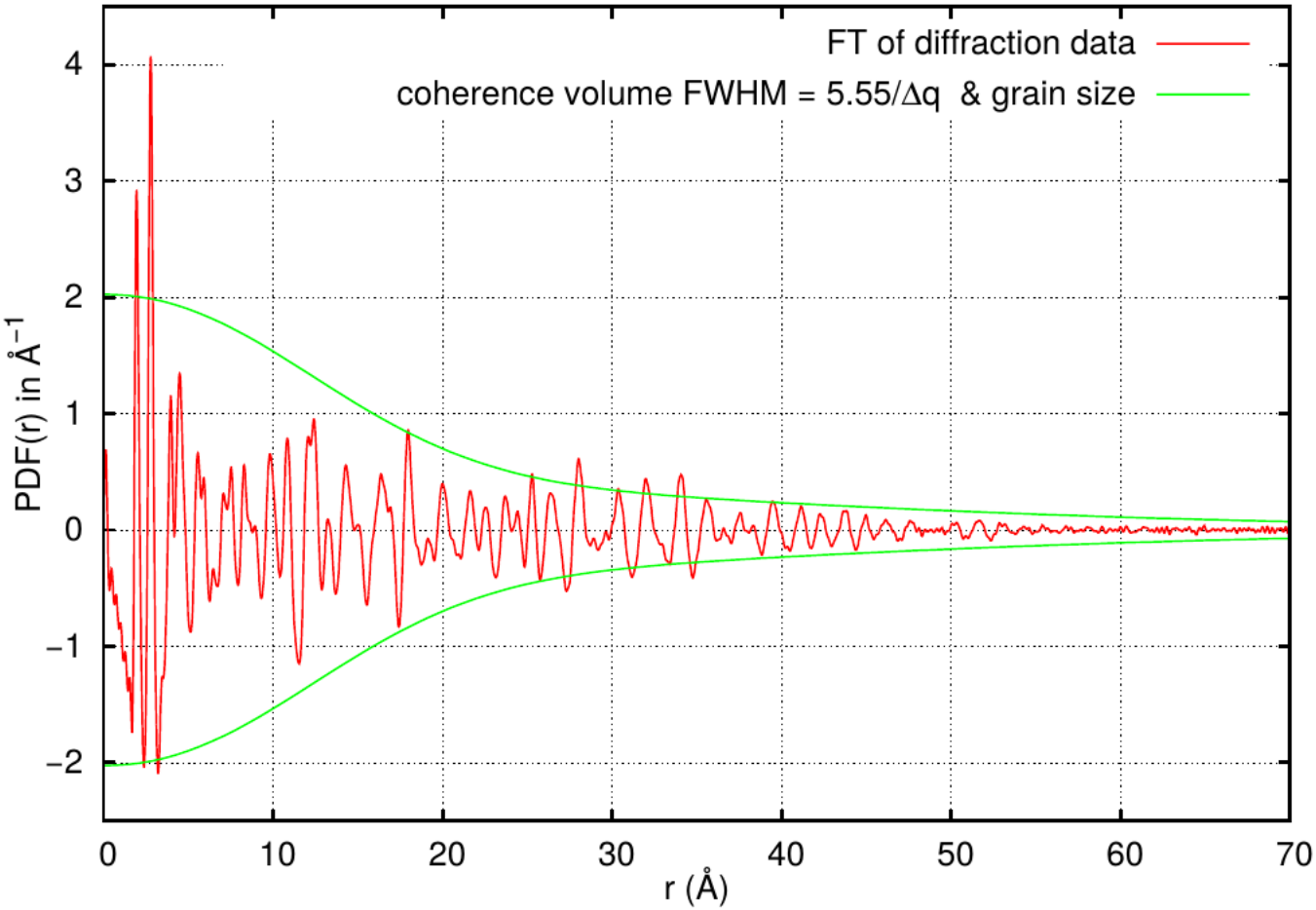
q-space versus *r*-space representations of data

The diffuse scattering "underneath" the Bragg peaks, subtracted away as "background" by Rietveld refinement, contains information about dynamic disorder (*e.g.* Thermal Diffuse Scattering = TDS) and static disorder (*e.g.* lattice-constant fluctuations $\Delta a/a$). The Bragg peak widths are generally limited by the instrumental resolution Δq:



q-space versus *r*-space representations of data

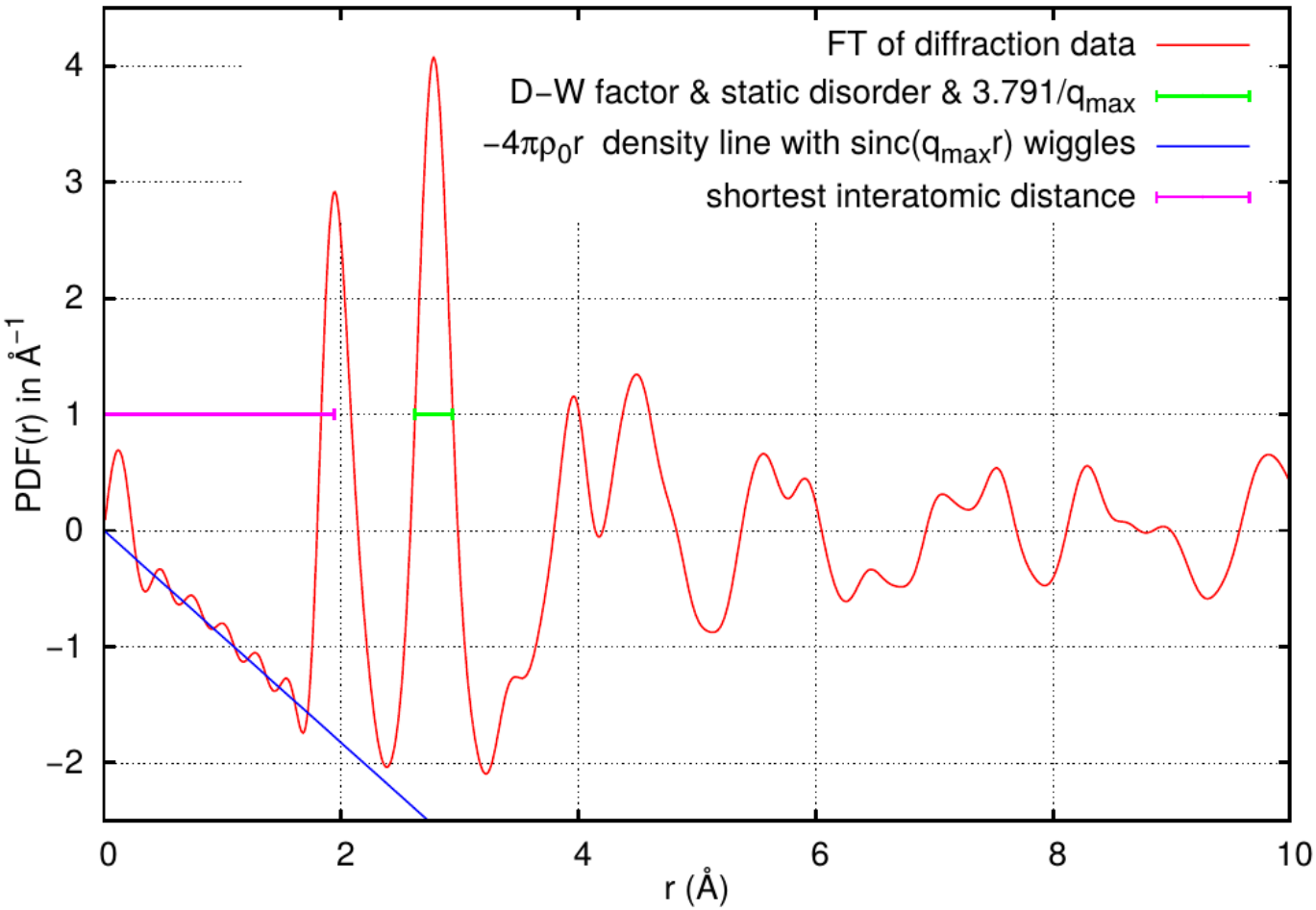
Fourier transform gives the total Pair-Distribution Function $\mathrm{PDF}(r)$ for an average atom at the origin $\Rightarrow$ peaks at all interatomic distances:



The *r*-range is limited by the crystallographic domain size (*i.e.* the range of structural correlation) and by the coherence volume of the neutron that depends on the *q*-space resolution Δq.

q-space versus *r*-space representations of data

The low-*r* slope of a properly normalized $\mathrm{PDF}(r)$ gives ρ_0, the peak areas are proportional to coordination number for atomic pairs, whose peak widths scale with their dynamic+static disorder plus the *r*-space resolution function $\Delta r(r) = \mathrm{sinc}(q_{max} r) = \sin(q_{max} r)/(q_{max} r)$ that also leads to non-physical FT ripples or "wiggles" at low-*r*:



Disorder can mean more information, not less

For an ergodic system like a monoatomic fluid at temperature T, and in the low-density limit, a *classical* mean-field theory relates $g(r)$, obtainable from diffraction, to the interatomic pair potential:

$$u(r) = -k_B T \, \ln[g(r)] \, ,$$

from which follows the interatomic force $\mathbf{F}(r) = -\vec{\rm grad}[u(r)]$, and thereby $v_{\rm sound}$, etc. For realistic densities, an iterative procedure leads to an effective pair potential $u_{\rm eff}(r)$ (*e.g.* EPSR analysis).

In effect, the $t = 0$ distribution of interatomic distances given by $g(r)$ for a liquid or glass "probes" the shape of $u(r)$, since energetically unfavorable distances will be more rare than favorable ones. By contrast, diffraction measurements on a crystalline sample cannot give such detailed information about $u(r)$ without recourse to modelling.

Note that the above expression also implies that $g(r)$, the structure measured via diffraction, is *independent of atomic mass* in a classical picture. Any observed differences in structure, *e.g.* between the $(d\sigma/d\Omega)(\mathbf{q})$ of H_2O vs D_2O as measured by x-ray diffraction, are necessarily due to QM effects.

The myth of "scattering power"

Myth of "scattering power": In all generality, diffraction measures $I = d\sigma/d\Omega = |\Sigma\, b_i \exp(i\,\mathbf{Q} \bullet \mathbf{r}_i)|^2$, a function of $\mathbf{Q}$ *only*. Changing the wavelength λ simply redistributes this intensity over Ω, so that for a *constant intrinsic* peak width of dQ, the intensity falling on a 1-D sensitive detector is integrated over $d\theta = (dQ/4\pi) \bullet \lambda/\cos(\theta)$, giving an *integrated* intensity increase ~ $\lambda/\cos(\theta)$ that *appears* as a peak-height increase for resolution-limited Bragg peaks. In fact, the (scattering_power)•(Lorentz_factor) is nothing more than this:

$$\lambda^3 / [\sin(\theta)\sin(2\theta)/2] = \lambda^3 / [\sin^2(\theta)\cos(\theta)] = (4\pi/Q)^2 \bullet \lambda/\cos(\theta)$$

leading to the same λ and θ dependence as derived above.

Is this fact well-understood in the powder diffraction community?

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