CORRELATION FUNCTIONS

We define a new function: **intermediate function**

$$I(Q,t)$$

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{k}{k_0} \frac{1}{\cdot 2\pi} \sum_{i,j} \left\langle b_i b_j \right\rangle \int_{-\infty}^{\infty} \overbrace{\frac{1}{N} \sum_i \sum_j \left\langle b_i e^{i\vec{Q}\vec{R}_i(t)} \cdot b_j e^{-i\vec{Q}\vec{R}_j(0)} \right\rangle} e^{-i\omega t} dt$$

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{k}{k_0} \frac{1}{\cdot 2\pi} \sum_{i,j} \left\langle b_i b_j \right\rangle \int_{-\infty}^{\infty} I(Q,t) e^{-i\omega t} dt$$

the scattering cross section is the fourier transform of I(Q,t) plus a prefactor $\frac{k}{k_0} \frac{1}{\cdot 2\pi}$
let's thus define the fourier transformation of I(Q,t) as S(Q,w):

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} I(\vec{Q},t) \cdot e^{-i\omega t} dt$$

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We define a new function: **scattering law**

$$S(Q, \omega)$$

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{Nk}{k_0} \sum_{i,j} \langle b_i b_j \rangle S(Q, \omega)$$

which is directly related to the scattering cross section,
and its relation with the intermediate scattering function is:

$$S(Q, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} I(Q, t) \cdot e^{-i\omega t} dt$$

And finally, we would like to have a function in real space (r and t), so that

$$I(\vec{Q},t) = \int_{-\infty}^{\infty} G(\vec{r},t) \cdot e^{i\vec{Q}\cdot\vec{r}} d\vec{Q}$$

We define a new function: **time-dependent pair correlation function**

$$G(\vec{r},t)$$

scattering law

intermediate function

$$S(\vec{Q},\omega)$$

$$S(\vec{Q},\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I(\vec{Q},t) \cdot e^{-i\omega t} dt$$

$$I(\vec{Q},t)$$

$$I(\vec{Q},t) = \int_{-\infty}^{\infty} G(\vec{R},t) \cdot e^{i\vec{Q}\vec{R}} d\vec{R}$$

 $(\vec{R},\omega)$

$$G(\vec{R},t)$$

aserejé function

time-dependent (pair) correlation function

Let's add some physics. But before:

The goal is to find an interpretation for the scattering functions
I(Q,t), S(Q,w) and G(r,t)
so that we can link those functions with the physics of the system

To do that let's first define the self part of each function!

$$I_s = \frac{1}{N} \sum_i \left\langle e^{i\vec{Q}\vec{R}_i(t)} \cdot e^{-i\vec{Q}\vec{R}_i(0)} \right\rangle$$

$$\begin{cases} S_i(Q,\omega) = \dfrac{1}{2\pi\hbar} \int_{-\infty}^{\infty} I_s(Q,t) \cdot e^{-i\omega t} dt \\[3em] G_s(\vec{r},t) = \dfrac{1}{(2\pi)^3} \int_{-\infty}^{\infty} I_s(Q,t) \cdot e^{-i\vec{Q}\vec{r}} dt \end{cases}$$

and remember the definition of I(Q,t)

$$I = \frac{1}{N} \sum_{ij} \left\langle e^{i\vec{Q}\vec{R}_i(t)} \cdot e^{-i\vec{Q}\vec{R}_j(0)} \right\rangle$$

$$\begin{cases} S(Q,\omega) = \dfrac{1}{2\pi\hbar} \int_{-\infty}^{\infty} I(Q,t) \cdot e^{-i\omega t} dt \\[3em] G(\vec{r},t) = \dfrac{1}{(2\pi)^3} \int_{-\infty}^{\infty} I(Q,t) \cdot e^{-i\vec{Q}\vec{r}} dt \end{cases}$$

COHERENT
(warning!!! it does include the self part!!!!!)

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_{coh} = \frac{k}{k_0} \frac{b_{coh}^2}{2\pi} \int_{-\infty}^{\infty} I(\vec{Q},t)e^{-i\omega t}dt = \frac{k}{k_0} \frac{\sigma_{coh}}{4\pi} NS(\vec{Q},\omega)$$

$$b_{coh}^2 = \overline{b}^2 \quad \text{and} \quad \sigma_{coh} = 4\pi\overline{b}^2$$

INCOHERENT

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right)_{inc} = \frac{k}{k_0} \frac{b_{inc}^2}{N \cdot 2\pi} \int_{-\infty}^{\infty} I_s(\vec{Q},t)e^{-i\omega t}dt = \frac{k}{k_0} \frac{\sigma_{inc}}{4\pi} NS_i(\vec{Q},\omega)$$

$$b_{inc}^2 = \overline{b^2} - \overline{b}^2 \quad \text{and} \quad \sigma_{inc} = \overline{b^2} - \overline{b}^2$$

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \left[\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right]_{coherent} + \left[\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right]_{incoherent}$$

scattering law

intermediate function

$$S(\vec{Q},\omega)$$

$$S(\vec{Q},\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I(\vec{Q},t) \cdot e^{-i\omega t} \, dt$$

$$I(\vec{Q},t)$$

$$I(\vec{Q},t) = \int_{-\infty}^{\infty} G(\vec{R},t) \cdot e^{i\vec{Q}\vec{R}} \, d\vec{R}$$

$$G(\vec{R},t)$$

**no-name function
(for the moment)**

Let's add the physics

Using $\delta(\vec{r}) = \dfrac{1}{(2\pi)^3} \displaystyle\int_{-\infty}^{\infty} e^{i\vec{Q}\vec{r}} d\vec{Q}$ *it can be proved that :*

$$G(\vec{r},t) = \frac{1}{(2\pi)^3} \frac{1}{N} \sum_{i,j} \int \left\langle \delta\left\{\vec{r}\,' - \vec{R}_i(0)\right\} \delta\left\{\vec{r}\,' + \vec{r} - \vec{R}_j(t)\right\}\right\rangle d\vec{r}\,'$$

having into account that $\displaystyle\int f(x)\delta(x-a)dx = f(a)$ *and thus* $\displaystyle\int \delta(x)\delta(x-a)dx = \delta(a)$

$$G(\vec{r},t) = \frac{1}{(2\pi)^3} \frac{1}{N} \sum_{i,j} \left\langle \delta\left\{\vec{r} - \left(\vec{R}_j(t) - \vec{R}_i(0)\right)\right\}\right\rangle$$

and assuming that all particles are identical...

$$G(\vec{r},t) = \frac{1}{(2\pi)^3} \sum_{j} \left\langle \delta\left\{\vec{r} - \left(\vec{R}_j(t) - \vec{R}_0(0)\right)\right\}\right\rangle$$

Time-dependent pair correlation function:

$$G(\vec{r},t) = \frac{1}{(2\pi)^3} \sum_j \left\langle \delta\left\{ \vec{r} - \left(\vec{R}_j(t) - \vec{R}_0(0) \right) \right\} \right\rangle$$

$\vec{R}_j(t)$

$\vec{R}_i(0)$ $\vec{R}_j(t) - \vec{R}_i(0)$ $G(\vec{R},t)$
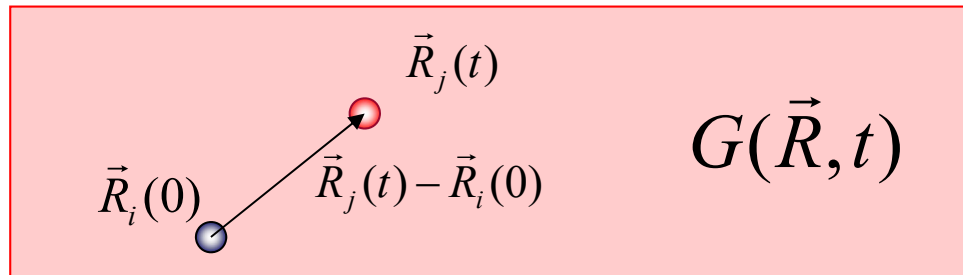
$$\left[\frac{\partial^2 \sigma}{\partial\Omega\,\partial\omega} \right]_{coherent}$$

Time-dependent pair correlation function (self):

$$G_s(\vec{r},t) = \frac{1}{(2\pi)^3} \left\langle \delta\left\{ \vec{r} - \left(\vec{R}_0(t) - \vec{R}_0(0) \right) \right\} \right\rangle$$

$\vec{R}_i(t)$

$\vec{R}_i(0)$ $\vec{R}_i(t) - \vec{R}_i(0)$ $G_s(\vec{R},t)$
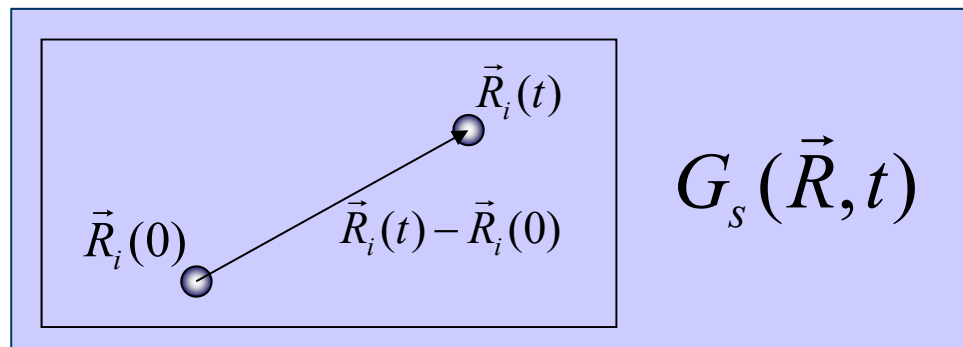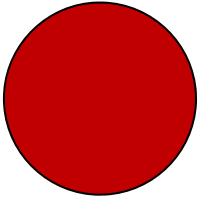
$$\left[\frac{\partial^2 \sigma}{\partial\Omega\,\partial\omega} \right]_{incoherent}$$

LIMITS OF THE CORRELATION FUNCTIONS

Limits for the scattering functions (self and coh):

	t=0	t	t=∞
$G(\vec{r},t)$			
$I(Q,t)$			
$S(Q,\omega)$			

We have:

$$G(\vec{r},t) = \sum_i \left\langle \delta\left(\vec{r} - \left(\vec{R}_i(t) - \vec{R}_0(0)\right)\right)\right\rangle$$

Let's write these contributions for t=0

That can be devided in two parts: self and distinct

$$G(\vec{r},0) = \left\langle \delta\left(\vec{r} - \left(\vec{R}_0(0) - \vec{R}_0(0)\right)\right)\right\rangle + \sum_{i\neq 0} \left\langle \delta\left(\vec{r} - \left(\vec{R}_i(t) - \vec{R}_0(0)\right)\right)\right\rangle$$

$$G_s(\vec{r},0) = \delta(\vec{r})$$

only the coherent part is interesting!!!!

$$G(\vec{r},0) = \delta(\vec{r}) + g(\vec{r})$$
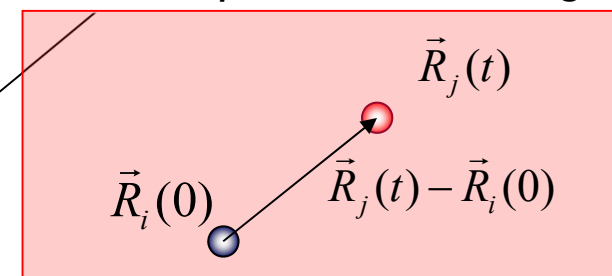
$\vec{R}_j(t)$

$\vec{R}_i(0)$ $\vec{R}_j(t) - \vec{R}_i(0)$

where g(r) is the static pair distribution function:
*average particle density **from 0** to **all i neighbours***

g(r): the static pair distribution function:
average particle density from 0 to all i neighbours
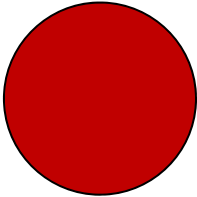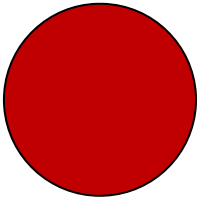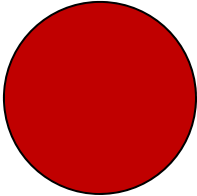
… let's assume isotropy $\quad G(\vec{R},t) \Rightarrow G(r,t)$

$$G(r,t=0) = \delta(r) + g(r)$$
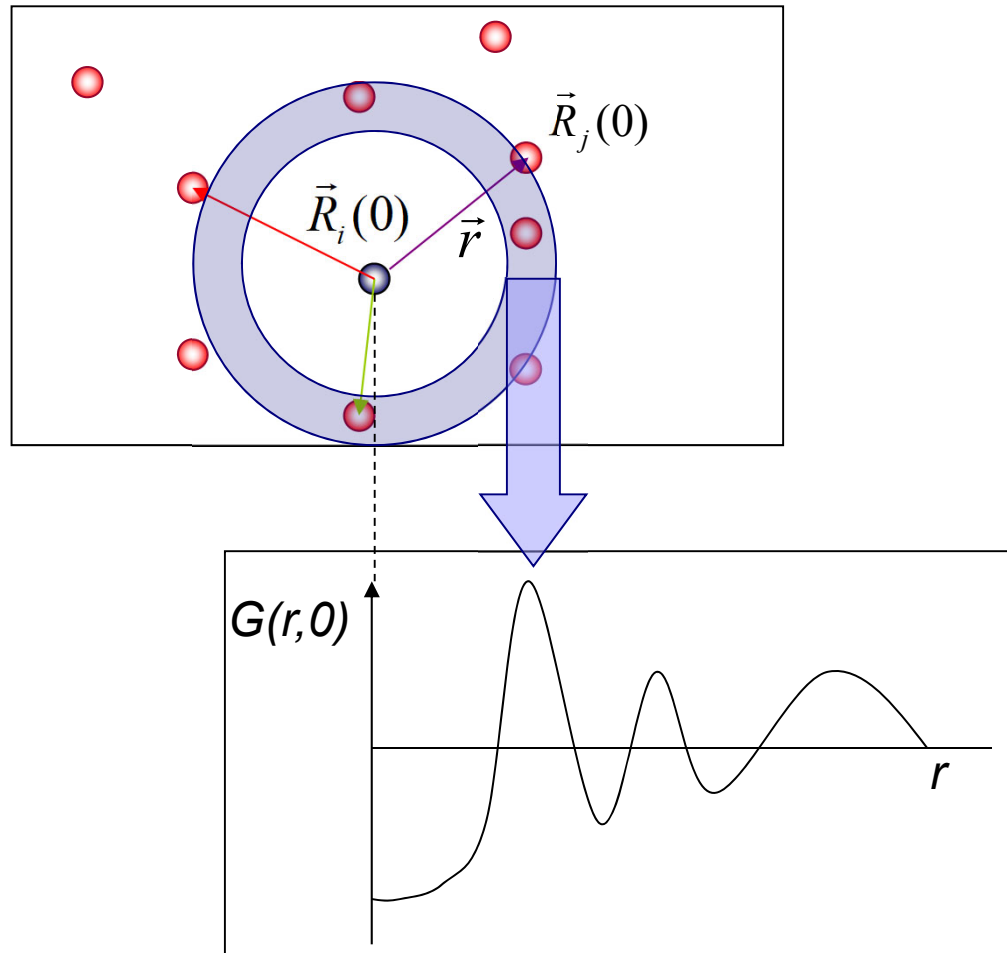
Limits for the scattering functions (self and coh):

	$t=0$	t	$t=\infty$
$G(\vec{r},t)$			
$I(Q,t)$			
$S(Q,\omega)$			

Static approximation $\quad I(\vec{Q},t) \approx I(\vec{Q},0)$ _usefull to perform diffraction_

$$I(\vec{Q},0) = \int\limits_{-\infty}^{\infty} G(\vec{R},0)\cdot e^{i\vec{Q}\vec{R}}\, d\vec{R} \;=\; \int\limits_{-\infty}^{\infty} \left(\delta(\vec{R}) + g(\vec{R})\right)\cdot e^{i\vec{Q}\vec{R}}\, d\vec{R}$$

and therefore

$$S(Q,\omega) = \frac{1}{2\pi\hbar}\int\limits_{-\infty}^{\infty} I(Q,0)\cdot e^{-i\omega t}\, dt \;=\; \frac{1}{2\pi\hbar} I(Q,0)\int\limits_{-\infty}^{\infty} e^{-i\omega t}\, dt = \frac{1}{2\pi\hbar} I(Q,0)\delta(\omega)$$

Only the elastic part participates in s(Q,w), therefore:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{coh}^{sa} = \frac{\sigma_{coh}}{4\pi} NI(\vec{Q},0)$$

This is the static approximation!
and since is elastic there i no energy change in the neutron: |k|=|k'|

Energy exchange ➔ non static ➔ k'≠k
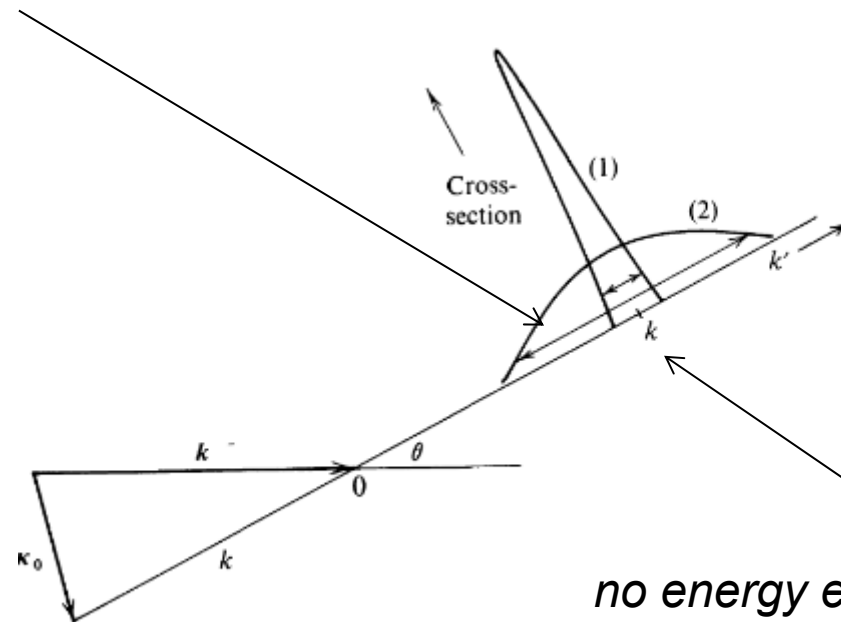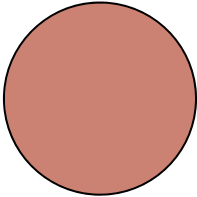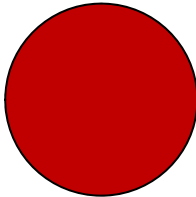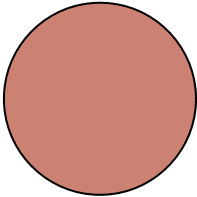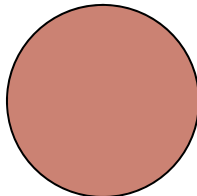
no energy exchange ➔ static ➔ k'=k

*the time the neutron takes to cross the sample must be smaller
than the vibrations characteristic time*

... this is not true for light atoms as Hydrogen... but can be corrected!

Limits for the scattering functions (inc and coh):

	$t=0$	t	$t=\infty$
$G(\vec{r},t)$			
$I(Q,t)$			
$S(Q,\omega)$			

We have:

$$G(\vec{r},t) = \sum_i \left\langle \delta\left(\vec{r} - \left(\vec{R}_i(t) - \vec{R}_0(0)\right)\right)\right\rangle$$

Let's write these contributions for t=∞

That can be devided in two (again) self and distinct:

$$G(\vec{r},\infty) = \left\langle \delta\left(\vec{r} - \left(\vec{R}_0(\infty) - \vec{R}_0(0)\right)\right)\right\rangle + \sum_{i\neq 0} \left\langle \delta\left(\vec{r} - \left(\vec{R}_i(\infty) - \vec{R}_0(0)\right)\right)\right\rangle$$
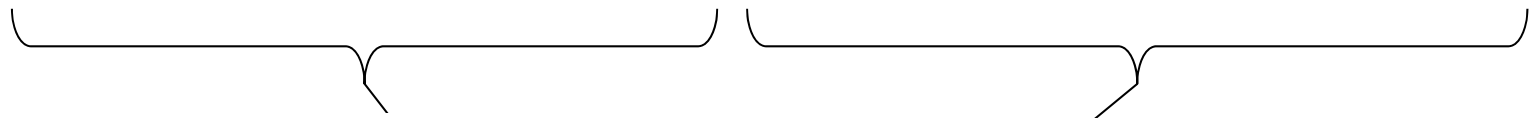
*depends on how far away
from initial position the particle goes
different from liquids and solids*

assuming ergodicity...

$$G(\vec{r},\infty) = G_s(\vec{r},\infty) + g(\vec{r})$$

where g(r) is the static pair distribution function again

Let's "attack" the self part:

$$G_s(\vec{r}, \infty) = \left\langle \delta\left(\vec{r} - \left(\vec{R}_0(\infty) - \vec{R}_0(0)\right)\right)\right\rangle$$

<u>*Solid*</u>*: particles do not go far away... and assuming isotropy*
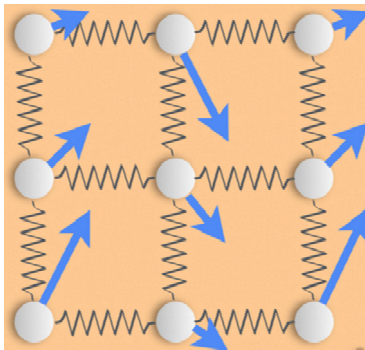
$$G_s(r, \infty) \propto \exp\left(-\frac{r^2}{2\langle u^2\rangle}\right)$$

Where <u²> is the mean square displacement

... and therefore is related to the debye waller factor (DWF)

$$\exp\left(-\frac{Q^2\langle u^2\rangle}{3}\right) = I_i(Q, \infty) = \int G_s(r, \infty)\exp\left(i\vec{Q}\vec{r}\right)d\vec{r}$$

Let's "attack" the self part:

$$G_s(\vec{r}, \infty) = \left\langle \delta\left(\vec{r} - \left(\vec{R}_0(\infty) - \vec{R}_0(0)\right)\right) \right\rangle$$

<u>*liquid*</u>*: particles are everywhere with respect to intial time*
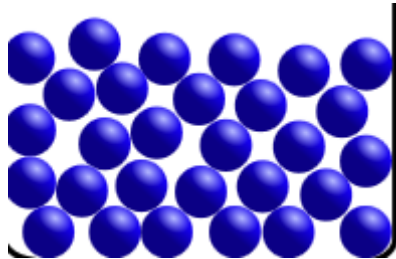
$$G_s(r, \infty) = \rho$$

... and therefore is quite boring... for t=∞!

Let's compare the cases t=0 and t=∞

$$G(\vec{r},0) = \delta(\vec{r}) + g(\vec{r})$$

$$G(\vec{r},\infty) = G_s(\vec{r},\infty) + g(\vec{r})$$

$$G_s(r,\infty) = \rho \quad G_s(r,\infty) \propto \exp\left(-\frac{r^2}{2\langle u^2 \rangle}\right)$$

$$g(\vec{r})$$
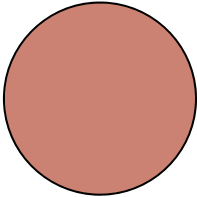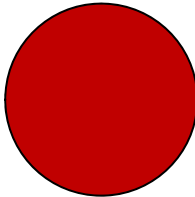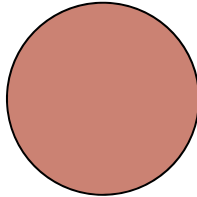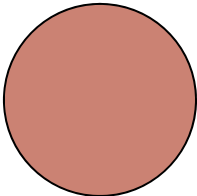
a "delta" or a smooth function   *the pair correlation function*

both are related to the distribution of distances between molecules (again)

Limits for the scattering functions (inc and coh):

	$t=0$	t	$t=\infty$
$G(\vec{r},t)$	●		●
			again, from another point of view!
$I(Q,t)$	●		
$S(Q,\omega)$	●		

Let's write (again) these contributions for t=∞

(this is much used in crystallography!!!!!)

$$G(\vec{r}, \infty) = \frac{1}{(2\pi)^3} \frac{1}{N} \sum_{i,j} \int \left\langle \delta\{\vec{r}' - \vec{R}_i(0)\} \delta\{\vec{r}' + \vec{r} - \vec{R}_j(\infty)\} \right\rangle d\vec{r}'$$

We assume particles are not correlated between t=0 and t=∞, therefore...
we can decouple de deltas at t=0 and t=∞

$$G(\vec{r}, \infty) = \frac{1}{(2\pi)^3} \frac{1}{N} \sum_{i,j} \int \left\langle \delta\{\vec{r}' - \vec{R}_i(0)\} \right\rangle \left\langle \delta\{\vec{r}' + \vec{r} - \vec{R}_j(\infty)\} \right\rangle d\vec{r}'$$

And since they are decopled we can drop "the time"

$$G(\vec{r}, \infty) = \frac{1}{(2\pi)^3} \frac{1}{N} \sum_{i,j} \int \left\langle \delta\{\vec{r}' - \vec{R}_i\} \right\rangle \left\langle \delta\{\vec{r}' + \vec{r} - \vec{R}_j\} \right\rangle d\vec{r}'$$

What is the physical meaning of each delta???

Physical meaning of the "deltas" appearing in g(r,∞):
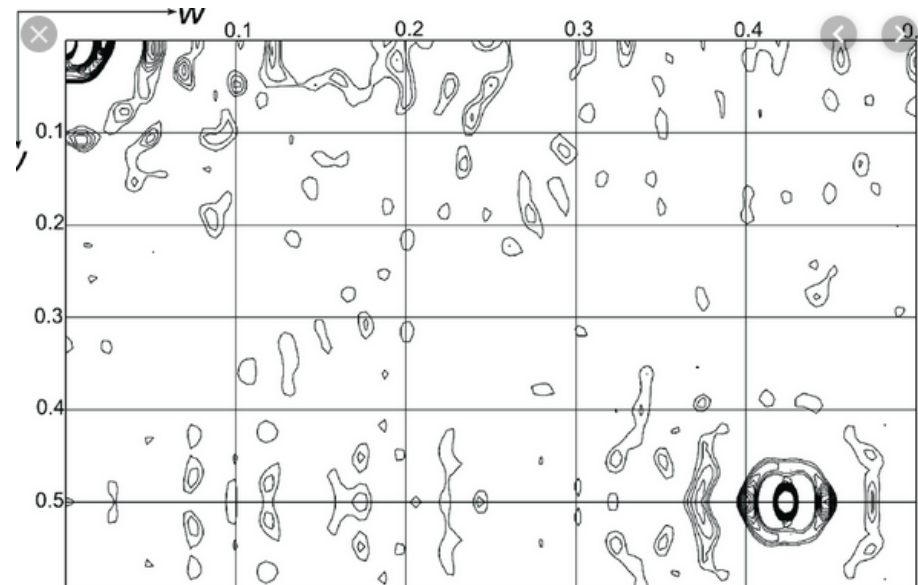
$$\rho(\vec{r}\,') = \left\langle \delta\left\{\vec{r}\,' - \vec{R}_j\right\}\right\rangle$$

it simply tells me where the molecules are
(is a 3D Probability Density Function about molecular positions

Physical meaning of the "deltas" appearing in g(r,∞):

$$\rho(\vec{r}\,') = \left\langle \delta\{\vec{r}\,' - \vec{R}_j\} \right\rangle$$

$$\rho(\vec{r} + \vec{r}\,') = \left\langle \delta\{\vec{r}\,' + \vec{r} - \vec{R}_j\} \right\rangle$$
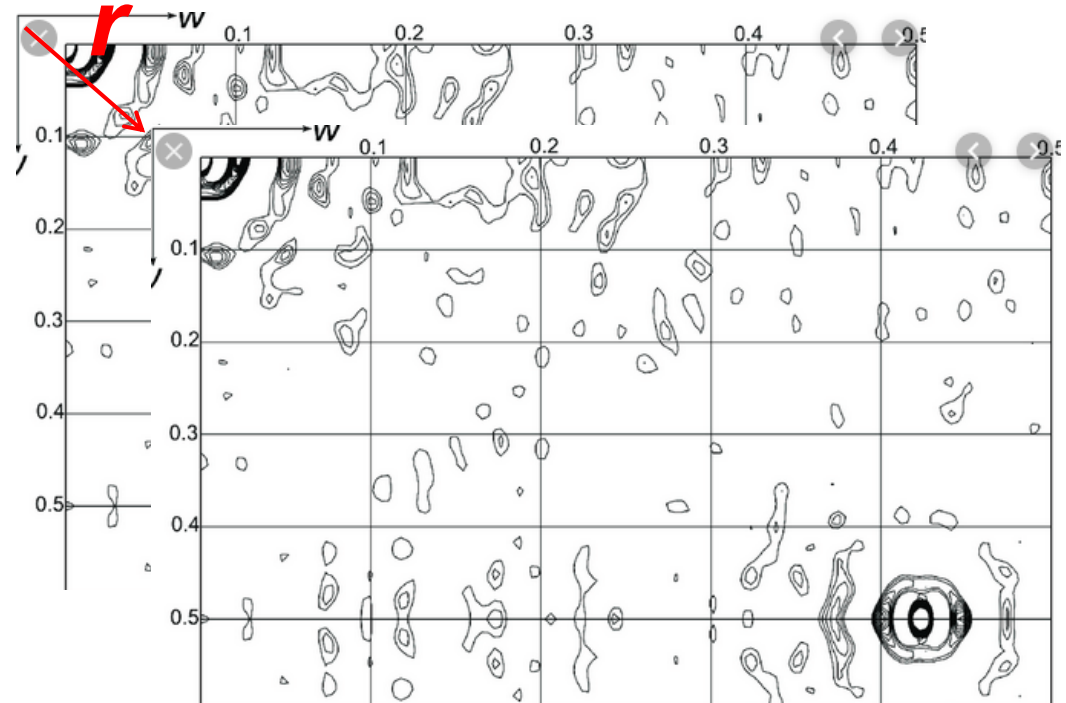
it "simply" tells me where the molecules are, when the maps is displaced

Physical meaning of the "deltas" appearing in g(r,∞):

$$\rho(\vec{r}\,')\rho(\vec{r}+\vec{r}\,') = \left\langle \delta\left\{\vec{r}\,'-\vec{R}_j\right\}\right\rangle\left\langle\delta\left\{\vec{r}\,'+\vec{r}-\vec{R}_j\right\}\right\rangle$$

is the autocorrelation function!!!!
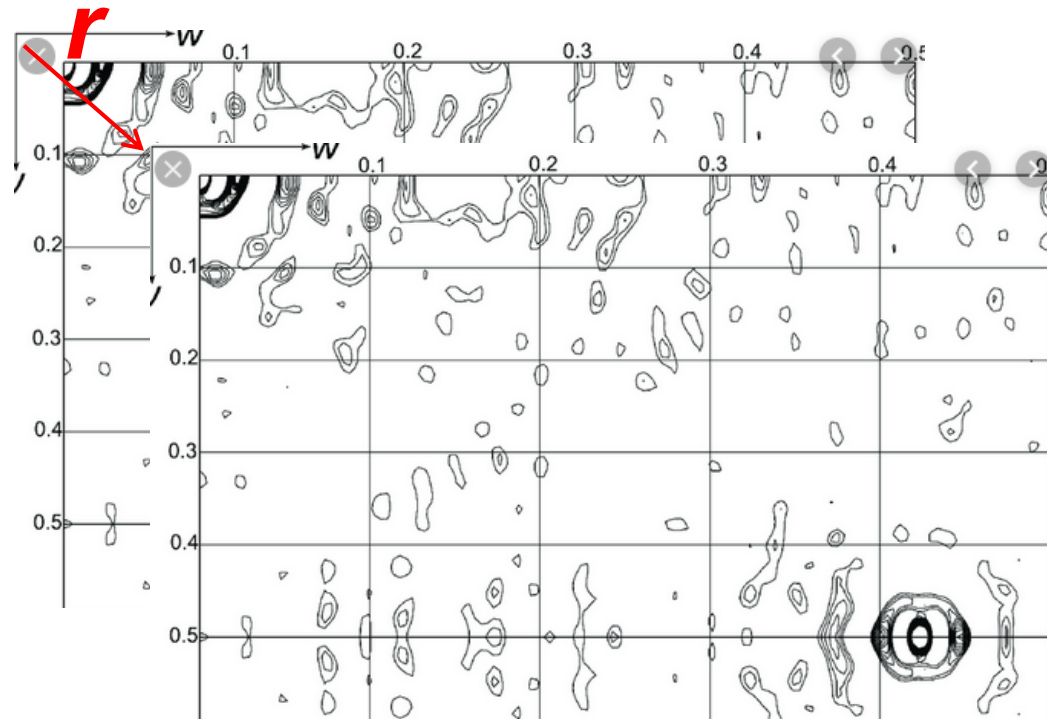
... and is maximum at the distances where there are correlations

Physical meaning of the "deltas" appearing in g(r,∞):

$$\rho(\vec{r}\,')\rho(\vec{r}+\vec{r}\,') = \left\langle \delta\left\{\vec{r}\,'-\vec{R}_j\right\}\right\rangle \left\langle \delta\left\{\vec{r}\,'+\vec{r}-\vec{R}_j\right\}\right\rangle$$

is the autocorrelation function!!!!
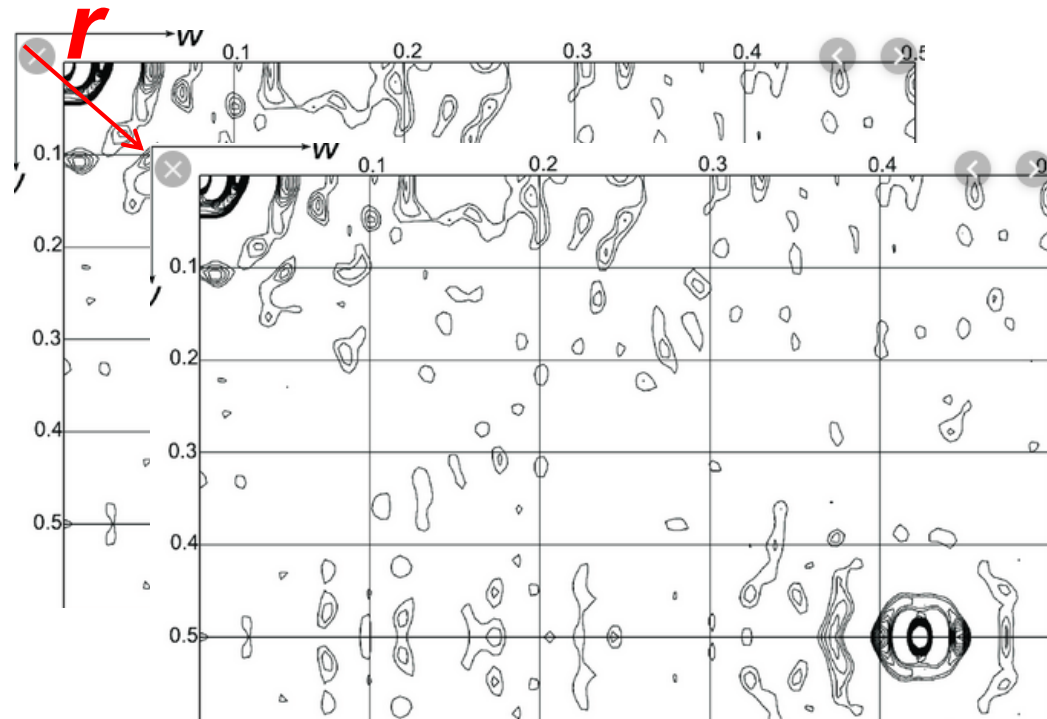
... and is maximum at the distances where there are correlations

Physical of g(r,∞) a new approach:

$$G\left(\vec{r},\infty\right) = \frac{1}{N} \int \rho(\vec{r}\,')\rho(\vec{r}+\vec{r}\,')d\vec{r}\,'$$

is the so called patterson function

a) $\rho(\vec{r}\,')$
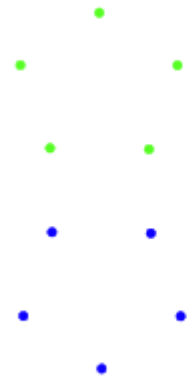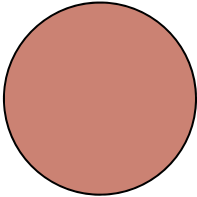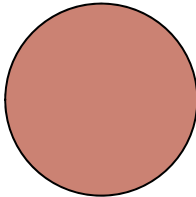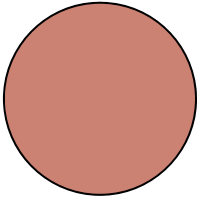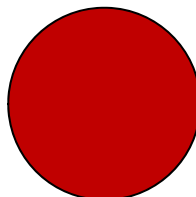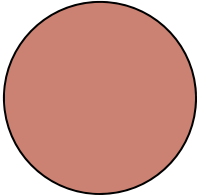
The structure

b) $G\left(\vec{r},\infty\right)$

The resulting Patterson

Its inverse
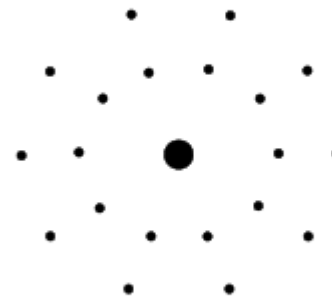
... and it is the same as the pair-distribution function... again

Limits for the scattering functions (self and coh):

	$t=0$	t	$t=\infty$
$G(\vec{r},t)$	⬤		⬤
$I(Q,t)$	⬤		⬤
$S(Q,\omega)$	⬤		

Let's have look at I(Q,t)

$$I\left(\vec{Q}=\vec{Q}_0,t\right)=I'\left(\vec{Q}=\vec{Q}_0,t\right)+I\left(\vec{Q}=\vec{Q}_0,\infty\right)$$

$I'\left(\vec{Q}=\vec{Q}_0,t\right)$

$I\left(\vec{Q}=\vec{Q}_0,\infty\right)$

t
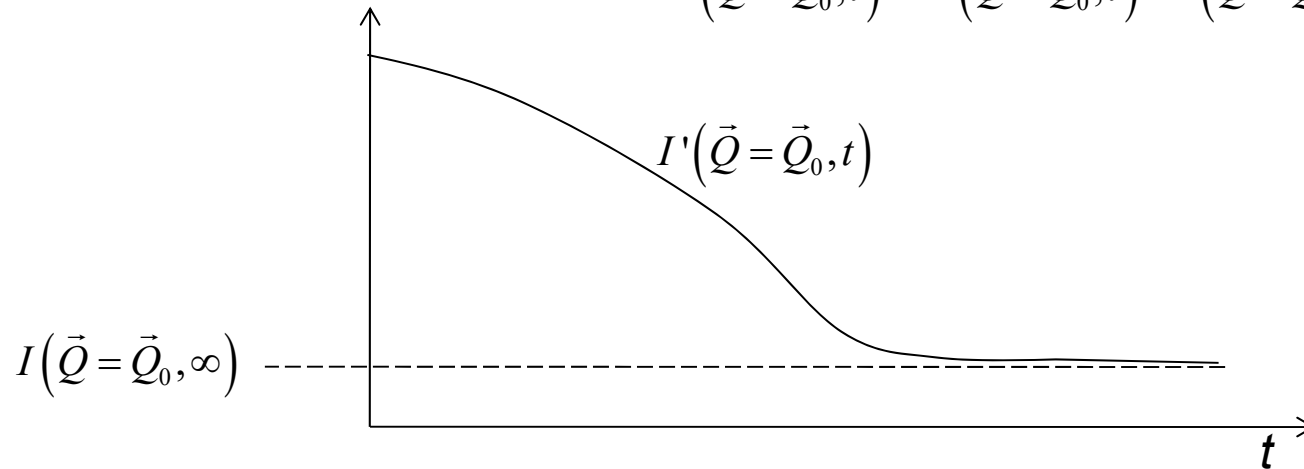
We are interested about what happens at t=∞

Two ways of interpretation

$$G(\vec{r},\infty)=G_s(\vec{r},\infty)+g(\vec{r})$$

(more used to study liquids)

$$G(\vec{r},\infty)=\frac{1}{N}\int\rho(\vec{r}\,')\rho(\vec{r}+\vec{r}\,')d\vec{r}\,'$$

(more used to study crystals)

In a liquid is better to think as:

$$G(r,\infty) = \rho + g(r)$$

Therefore:

$$I(Q,\infty) = I(Q) = \int (\rho + g(r)) \exp\left(i\vec{Q}\vec{r}\right) d\vec{r}$$

$$I(\vec{Q},\infty) = I(\vec{Q}) = \int (\rho + g(r)) \exp\left(iQr\cos\theta\right) r^2 dr\, d\cos\theta\, d\varphi$$

$$I(\vec{Q},\infty) = I(\vec{Q}) = \int (\rho + g(r)) \exp\left(iQr\cos\theta\right) r^2 dr\, d\cos\theta\, d\varphi$$

$$I(Q) = N\delta(Q) + \frac{4\pi}{Q} \int g(r)\sin(Qr) r\, dr$$

In a solid is better to think as:

$$G\left(\vec{r},\infty\right) = \frac{1}{N}\int \rho(\vec{r}\,')\rho(\vec{r}+\vec{r}\,')d\vec{r}\,'$$

Therefore:
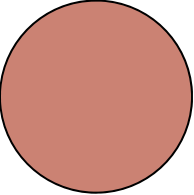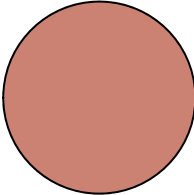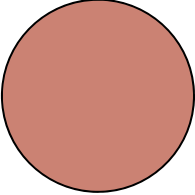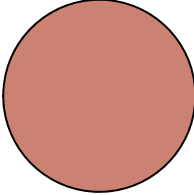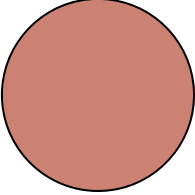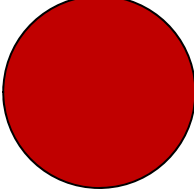
$$I\left(Q,\infty\right) = I\left(Q\right) = \int \int \rho(\vec{r}\,')\rho(\vec{r}+\vec{r}\,')d\vec{r}\,'\exp\left(i\vec{Q}\vec{r}\right)d\vec{r}d\vec{r}\,'$$

$$I\left(Q\right) = \left|\int \rho\left(\vec{r}\right)\exp\left(i\vec{Q}\vec{r}\right)d\vec{r}\right|^{2}$$

So it is the fourier transformation of the molecular position!!!
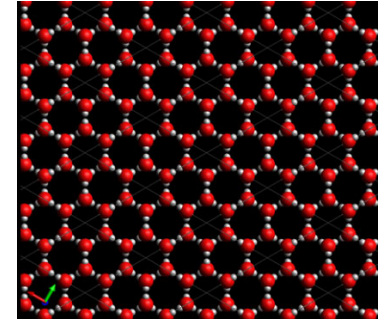
Limits for the scattering functions (self and coh):

	t=0	t	t=∞
$G(\vec{r},t)$	●		●
$I(Q,t)$	●		●
$S(Q,\omega)$	●		●

(relation with t=∞)

We finally arrive to the function we can measure!!!!

COHERENT

INCOHERENT

$$\left(\frac{\partial^2\sigma}{\partial\Omega\partial\omega}\right)_{coh} = \frac{k}{k_0}\frac{\sigma_{coh}}{4\pi}NS\left(\vec{Q},\omega\right)$$

$$\left(\frac{\partial^2\sigma}{\partial\Omega\partial\omega}\right)_{inc} = \frac{k}{k_0}\frac{\sigma_{inc}}{4\pi}NS_i\left(\vec{Q},\omega\right)$$

$$\frac{\partial^2\sigma}{\partial\Omega\partial\omega} = \left[\frac{\partial^2\sigma}{\partial\Omega\partial\omega}\right]_{coherent} + \left[\frac{\partial^2\sigma}{\partial\Omega\partial\omega}\right]_{incoherent}$$

Let's have look at I(Q,t), again

$$I\left(\vec{Q}=\vec{Q}_0,t\right)=I'\left(\vec{Q}=\vec{Q}_0,t\right)+I\left(\vec{Q}=\vec{Q}_0,\infty\right)$$

$I'\left(\vec{Q}=\vec{Q}_0,t\right)$

$I\left(\vec{Q}=\vec{Q}_0,\infty\right)$
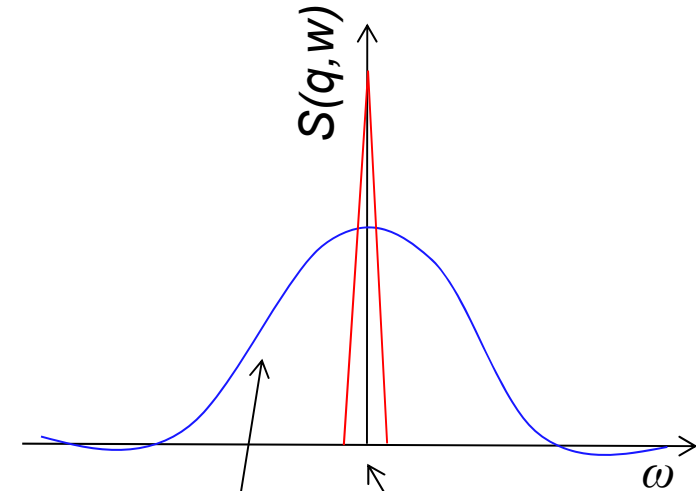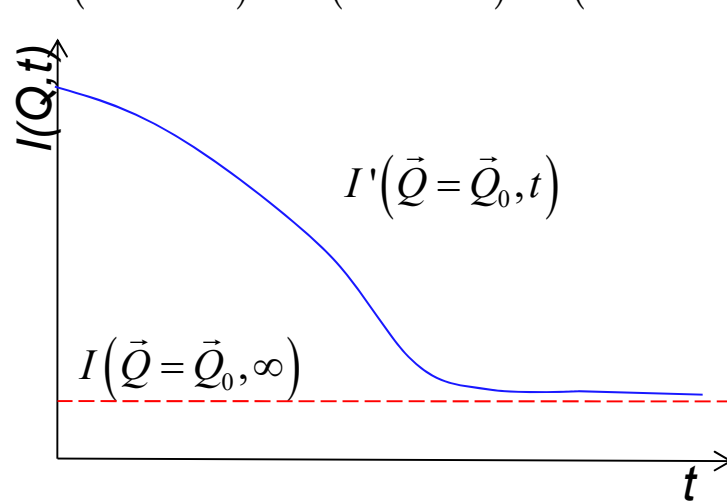
$$S(Q,\omega)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}I(Q,t)\cdot e^{-i\omega t}dt\ =\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\left[I'(Q,t)+I(Q,\infty)\right]\cdot e^{-i\omega t}dt$$

$$=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}I'(Q,t)\cdot e^{-i\omega t}dt+\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}I(\vec{Q})\cdot e^{-i\omega t}dt=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}I'(Q,t)\cdot e^{-i\omega t}dt+\frac{1}{2\pi\hbar}\delta(\omega)I(\vec{Q})$$

Inelastic scattering   *Elastic scattering*

$$I\left(\vec{Q},\infty\right)=I\left(\vec{Q}\right)\quad\text{is related to elastic scattering!!!!}$$

Therefore the relation between I(q,∞) and the cross section is:

$$\left(\frac{\partial^2 \sigma}{\partial\Omega\partial\omega}\right)_{el,coh} = \frac{k}{k_0}\frac{\sigma_{coh}}{4\pi\hbar}NS\left(\vec{Q},\omega\right) = \frac{\sigma_{coh}}{4\pi\hbar}N\delta\left(\omega\right)I\left(\vec{Q},\infty\right)$$

(since it is elastic $k_0=k$)

And integrating for all energies

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{el,coh} = \frac{\sigma_{coh}}{4\pi}NI\left(\vec{Q},\infty\right)$$

And the same holds for the incoherent part

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{el,inc} = \frac{\sigma_{inc}}{4\pi}NI_s\left(\vec{Q},\infty\right)$$

*SUMMARIZING **what we measure at** t=∞ (elastic scattering, therefore!)*

For the coherent part:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{el,coh} = \frac{\sigma_{coh}}{4\pi} NI\left(\vec{Q},\infty\right) = \frac{\sigma_{coh}}{4\pi} N\left|\int\rho(\vec{r})\exp\left(i\vec{Q}\vec{r}\right)d\vec{r}\right|^2 \qquad \text{solids}$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{el,coh} = \frac{\sigma_{coh}}{4\pi} NI\left(\vec{Q},\infty\right) = \frac{\sigma_{coh}}{4\pi} N\int\left(\rho+g(r)\right)\exp\left(i\vec{Q}\vec{r}\right)d\vec{r} \qquad \text{liquids}$$

For the incoherent part

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{el,inc} = \frac{\sigma_{inc}}{4\pi} NI_s\left(\vec{Q},\infty\right) = \frac{\sigma_{inc}}{4\pi} N\exp\left(-\frac{1}{3}Q^2\left\langle u^2\right\rangle\right) \qquad \text{solids}$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{el,inc} = \frac{\sigma_{inc}}{4\pi} NI_s\left(\vec{Q},\infty\right) = \frac{\sigma_{inc}}{4\pi} N\rho \qquad \text{liquids}$$

How does this look like for solids:

for a crystalline solid (monocrystal)   *for a crystalline solid (powder)*
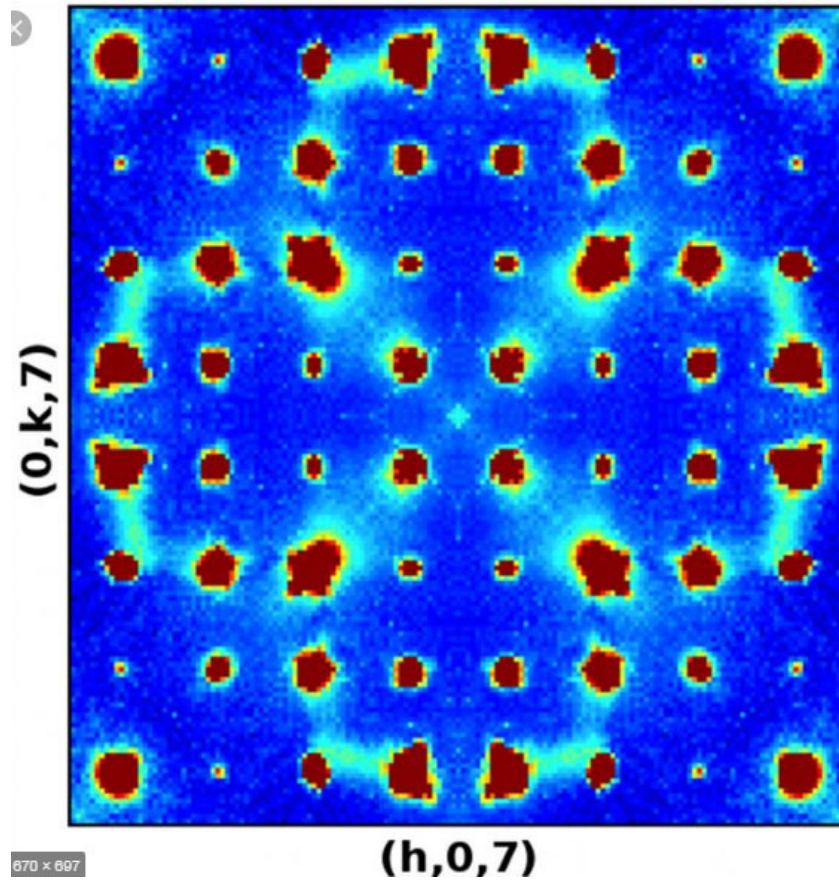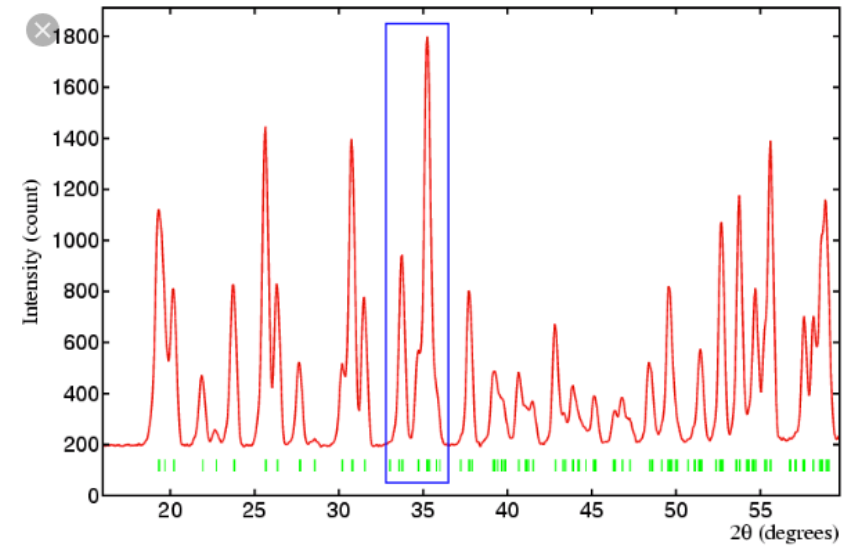
How does this look like for liquids:
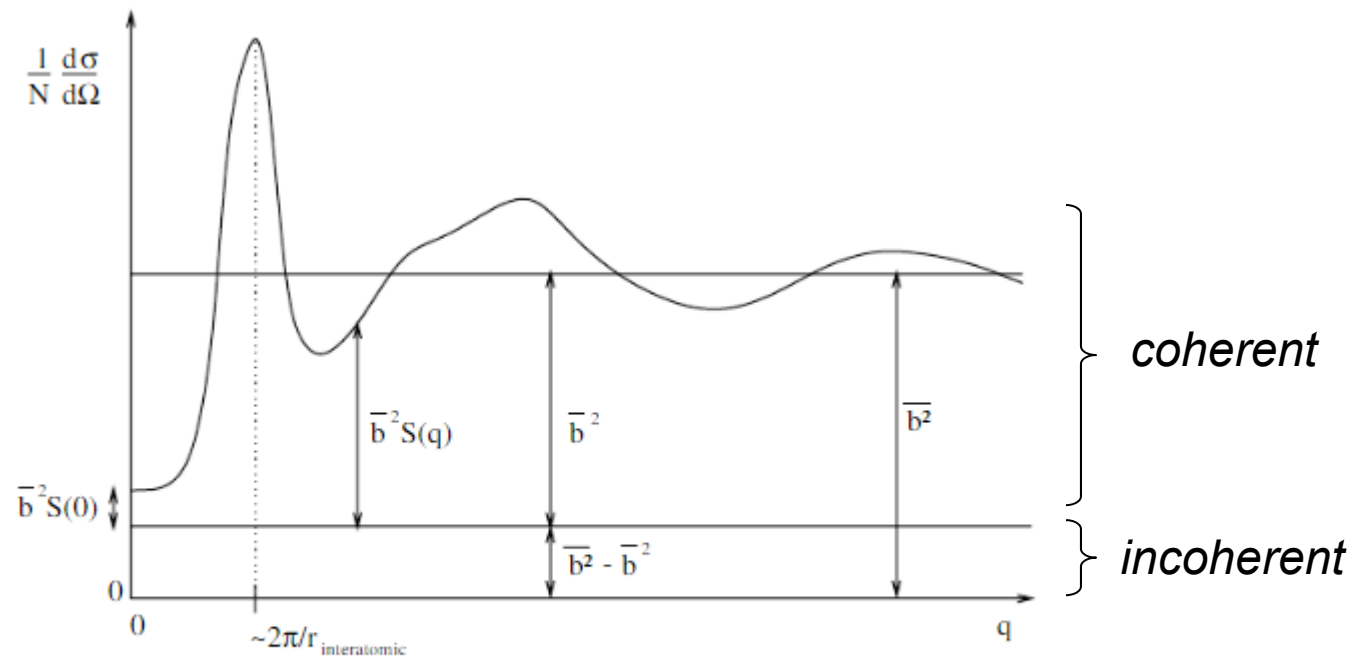
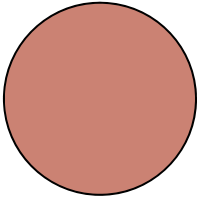**Figure 2.** Differential scattering cross-section per atom $(1/N)d\sigma/d\Omega = \bar{b}^2 S(q) + (\overline{b^2} - \bar{b}^2)$ for a monatomic liquid or glass. The position of the first peak is inversely proportional to the interatomic distance, $r_{interatomic}$.

... But, HOW DO WE EXTRACT INFORMATION FROM THIS POTATOE????
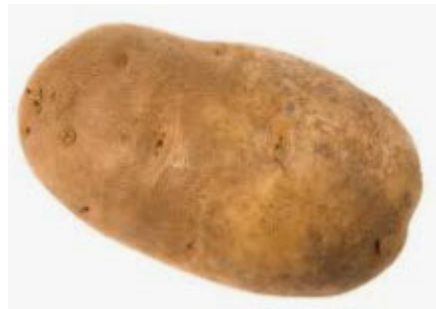
Molecular Dynamics

Force Field

Bonded   Non-bonded

$$E_{total} = \sum_{bonds} K_r(r - r_{eq})^2 + \sum_{angles} K_\theta(\theta - \theta_{eq})^2 + \sum_{dihedrals} \frac{V_n}{2}[1 + \cos(n\phi - \gamma)] + \sum_{i < j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\epsilon R_{ij}} \right]$$

Newton's laws

force   mass   acceleration

$$F = ma$$
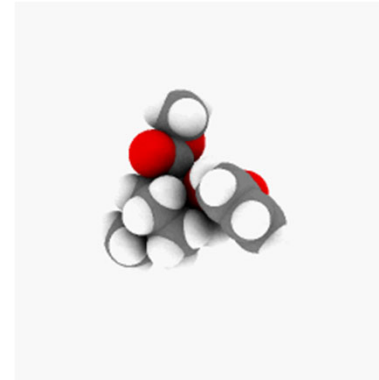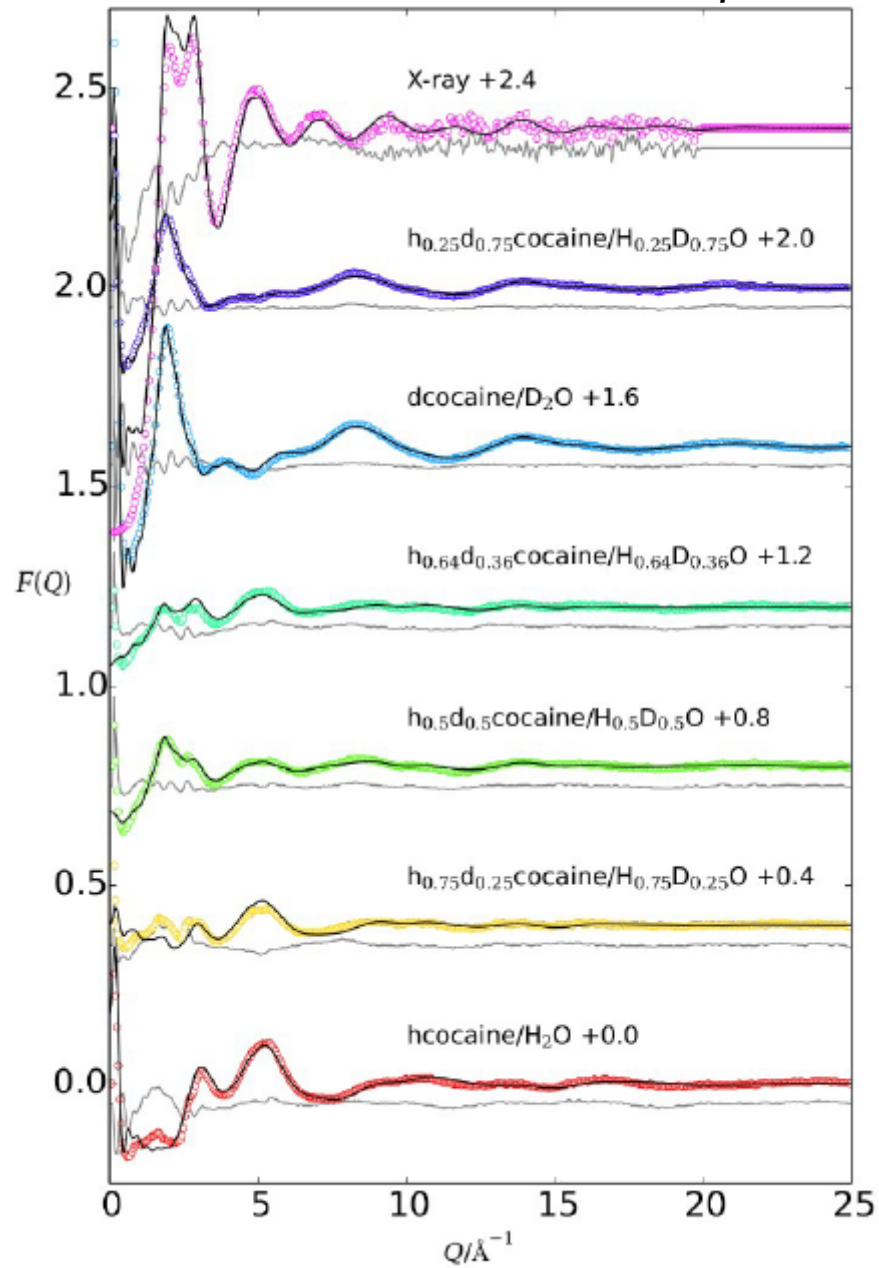
force   acceleration

How does this look like for liquids:

X-ray +2.4

$h_{0.25}d_{0.75}$cocaine/$H_{0.25}D_{0.75}O$ +2.0

dcocaine/D_2O +1.6

$h_{0.64}d_{0.36}$cocaine/$H_{0.64}D_{0.36}O$ +1.2

$h_{0.5}d_{0.5}$cocaine/$H_{0.5}D_{0.5}O$ +0.8

$h_{0.75}d_{0.25}$cocaine/$H_{0.75}D_{0.25}O$ +0.4

hcocaine/H_2O +0.0

$F(Q)$

$Q/\text{Å}^{-1}$

How does this look like for liquids:

Cocaine

X-ray +2.4

$h_{0.25}d_{0.75}$cocaine/$H_{0.25}D_{0.75}O$ +2.0

dcocaine/D_2O +1.6

$h_{0.64}d_{0.36}$cocaine/$H_{0.64}D_{0.36}O$ +1.2

$h_{0.5}d_{0.5}$cocaine/$H_{0.5}D_{0.5}O$ +0.8

$h_{0.75}d_{0.25}$cocaine/$H_{0.75}D_{0.25}O$ +0.4

hcocaine/H_2O +0.0

$F(Q)$

$Q/\text{Å}^{-1}$

How does this look like for liquids:

Cocaine

Plot of $F(Q)$ vs $Q/\text{Å}^{-1}$ with stacked curves:
- X-ray +2.4
- $h_{0.25}d_{0.75}$cocaine/$H_{0.25}D_{0.75}O$ +2.0
- dcocaine/D_2O +1.6
- $h_{0.64}d_{0.36}$cocaine/$H_{0.64}D_{0.36}O$ +1.2
- $h_{0.5}d_{0.5}$cocaine/$H_{0.5}D_{0.5}O$ +0.8
- $h_{0.75}d_{0.25}$cocaine/$H_{0.75}D_{0.25}O$ +0.4
- hcocaine/H_2O +0.0

How does this look like for liquids:

Cocaine

Limits for the scattering functions (self and coh):

	$t=0$	t	$t=\infty$
$G(\vec{r},t)$	⬤	⬤ *gas*	⬤
$I(Q,t)$	⬤		⬤
$S(Q,\omega)$	⬤		⬤

(relation with $t=\infty$)

Ideal Gas
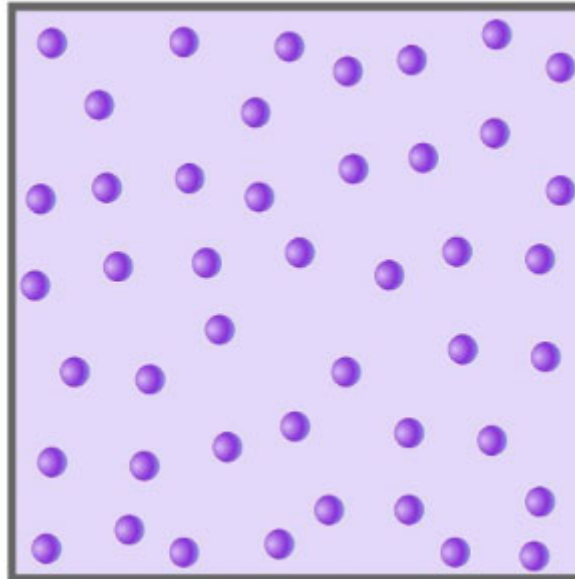
All particle are indistinguishable
The scattering of all particles is the same as that of one, but many repeated many times

That means that correlation function for one and for many is the same, and therefore:

$$G(r,t) = G_s(r,t)$$

Only simple cases can be studied

Let's study an ideal gas. There is a radial simmetry...
the probability of finding an atom between r and r+dr is:

$$P(r) = 4\pi r^2 G(r,t)$$

we can relate the r PDF to the velocity PDF of the particle:

$$P(r)dr = P(v)dv$$

and we know v from the maxwell distribution

$$P(v) = hv^2 \exp\left(-\frac{1}{2}\frac{Mv^2}{KT}\right) = hv^2 \exp\left(-\frac{1}{2}\beta Mv^2\right)$$

we apply now the change of variable

$$4\pi r^2 G(r,t)dr = hv^2 \exp\left(-\frac{1}{2}\beta Mv^2\right)dv$$

Only simple cases can be studied

Remember taht r=v·t, then for a fixed time

$$4\pi r^2 G(r,t)\,dr = h(rt)^2 \exp\left(-\frac{1}{2}\beta M (rt)^2\right) d(rt)$$

$$G(r,t) = h\exp\left(-\frac{r^2}{2\sigma^2(t)}\right)$$

being
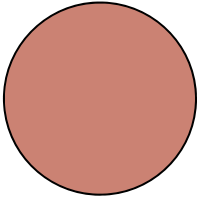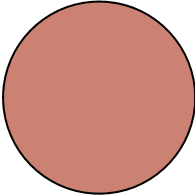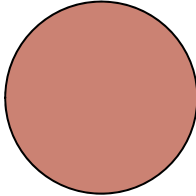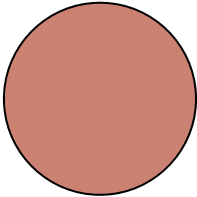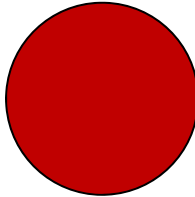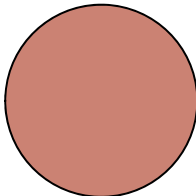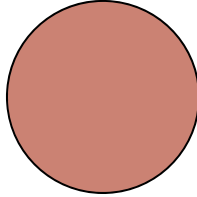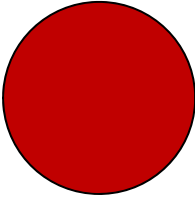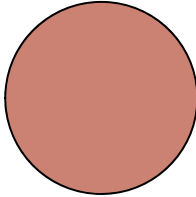
$$\sigma^2(t) = \frac{t^2}{M\beta}$$

$$h = \frac{1}{\left(2\pi\sigma^2(t)\right)^{3/2}}$$

... a gaussian that spreads with time!!!

G(r,t)   **r**

G(r,0)

G(r,t₁)

G(r,t₂)

G(r,∞)

Limits for the scattering functions (self and coh):

	$t=0$	t	$t=\infty$
$G(\vec{r},t)$		*gas*	
$I(Q,t)$		*gas*	
$S(Q,\omega)$		*gas*	

(relation with t=∞)

Only simple cases can be studied

Remember taht r=v·t, then for a fixed time

$$G(r,t) = h \exp\left(-\frac{r^2}{2\sigma^2(t)}\right)$$

$$I(Q,t) = \int_{-\infty}^{\infty} G(r,t) \cdot e^{i\vec{Q}\cdot\vec{r}} \, d\vec{Q}$$

$$I(Q,t) = \exp\left(-\frac{Q^2\sigma^2(t)}{2}\right)$$

$$S(Q,\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} I(Q,t) \cdot e^{-i\omega t} \, dt$$

$$S(Q,\omega) = \sqrt{\frac{2\beta M}{4\pi\hbar^2}} \cdot \frac{1}{Q} \exp\left(-\frac{\beta M}{2}\frac{\omega^2}{Q^2}\right)$$

Only simple cases can be studied

Remember taht r=v·t, then for a fixed time

$$G(r,t) = h \exp\left(-\frac{r^2}{2\sigma^2(t)}\right)$$

... a gaussian that spreads when increasing t

$$\sigma^2(t) = \frac{t^2}{M\beta}$$

$$I(Q,t) = \exp\left(-\frac{Q^2\sigma^2(t)}{2}\right)$$

... a gaussian that shrinks when increasing t
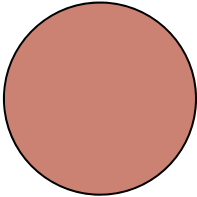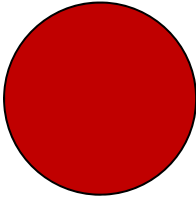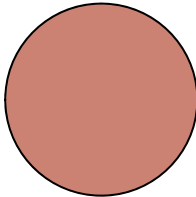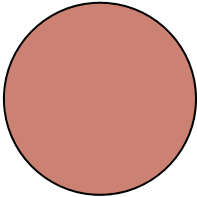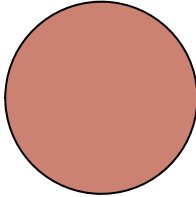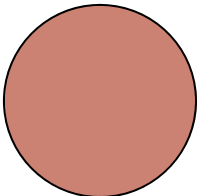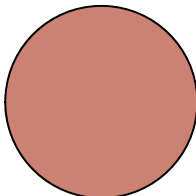
$$\sigma^2(t) = \frac{t^2}{M\beta}$$

$$S(Q,\omega) = \sqrt{\frac{2\beta M}{4\pi\hbar^2}} \cdot \frac{1}{Q} \exp\left(-\frac{Q^2\sigma^2(\omega)}{2}\right)$$

... a gaussian that shrinks when increasing energy

$$\sigma^2(\omega) = M\beta\omega^2$$

Limits for the scattering functions (self and coh):

	$t=0$	t	$t=\infty$
$G(\vec{r},t)$		*liquid inc*	
$I(Q,t)$		*liquid inc*	
$S(Q,\omega)$		*liquid inc*	

(relation with t=∞)

Diffussion: the particle tries to go to the place where the density is lower

$$D\nabla^2 G_s(r,t) = \frac{\partial G_s(r,t)}{\partial t}$$

from this equation we get again a gaussian of the particle position
from her original position

$$G_s(r,t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

Being D the "diffussion coefficient", or we could also read it as

$$G_s(r,t) = \frac{1}{(2\sigma_d^2(t))^{3/2}} \exp\left(-\frac{r^2}{2\sigma_d^2(t)}\right)$$

being $\quad \sigma_D^2(t) = 2Dt$

can be compared with ideal gas

$$\sigma_{i.g.}^2(t) = \frac{t^2}{M\beta}$$

the "spreading is faster for an ideal gas (as expected)

Diffussion: the particle tries to go to the place where teh density is lower

What is the diffussion coefficient??

$$G_s(r,t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

Mean square displacement
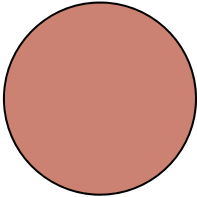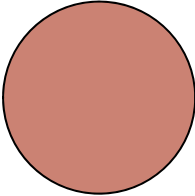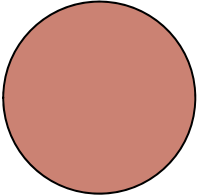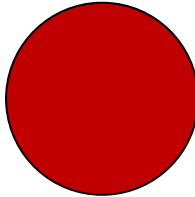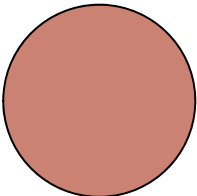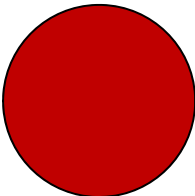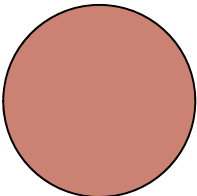
$$\langle r^2 \rangle = \langle [r(t) - r(0)]^2 \rangle$$

$$\langle r^2 \rangle = \int r^2 G_s(r,t)dr = 6Dt$$

$$D = \frac{1}{6t}\langle r^2 \rangle$$

Therefore D is related to the squared distance that a particle has advanced!!!

Limits for the scattering functions (self and coh):

	t=0	t	t=∞
$G(\vec{r},t)$		liquid	
$I(Q,t)$		liquid	
$S(Q,\omega)$		liquid	

(relation with t=∞)

We get the rest of correlation functions

$$G_s(r,t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

$$I(Q,t) = \int_{-\infty}^{\infty} G(r,t) \cdot e^{i\vec{Q}\cdot\vec{r}} \, d\vec{Q}$$
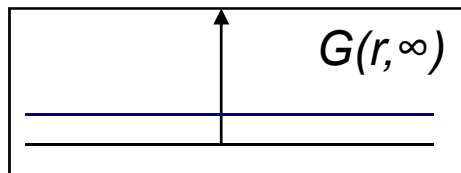
$$I_s(Q,t) = \exp\left(-Q^2 Dt\right)$$

$$S(Q,\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} I(Q,t) \cdot e^{-i\omega t} \, dt$$

Surprise surprise:
a Lorentzian!!!!

$$S_i(Q,\omega) = \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + \omega^2}$$

$$\Gamma = DQ^2$$

that spreads with energy

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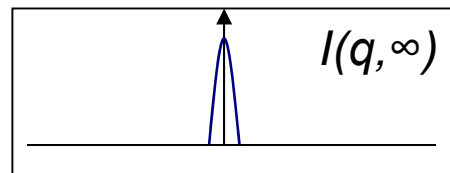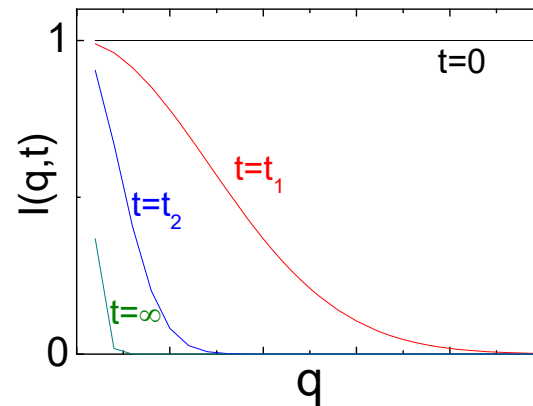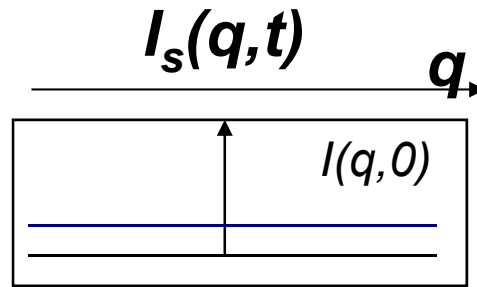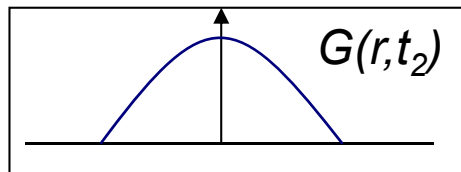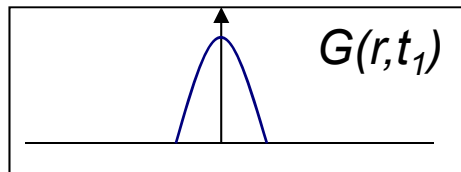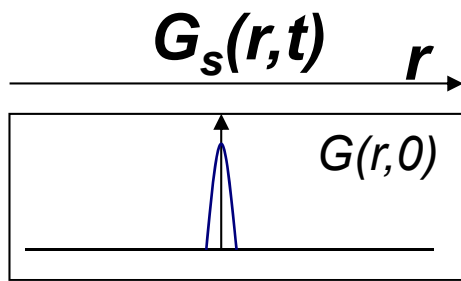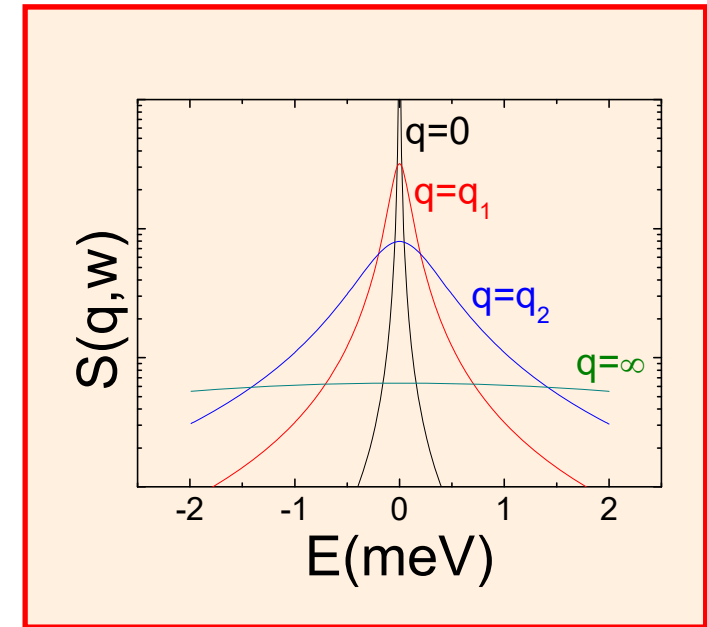
$$G_s(r,t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

D: diffusion coefficient

$$I_s(q,t) = \exp\left(-Dq^2 t\right)$$

$$S_i(q,\omega) = \frac{1}{\pi} \frac{Dq^2}{\omega^2 + (Dq^2)^2}$$
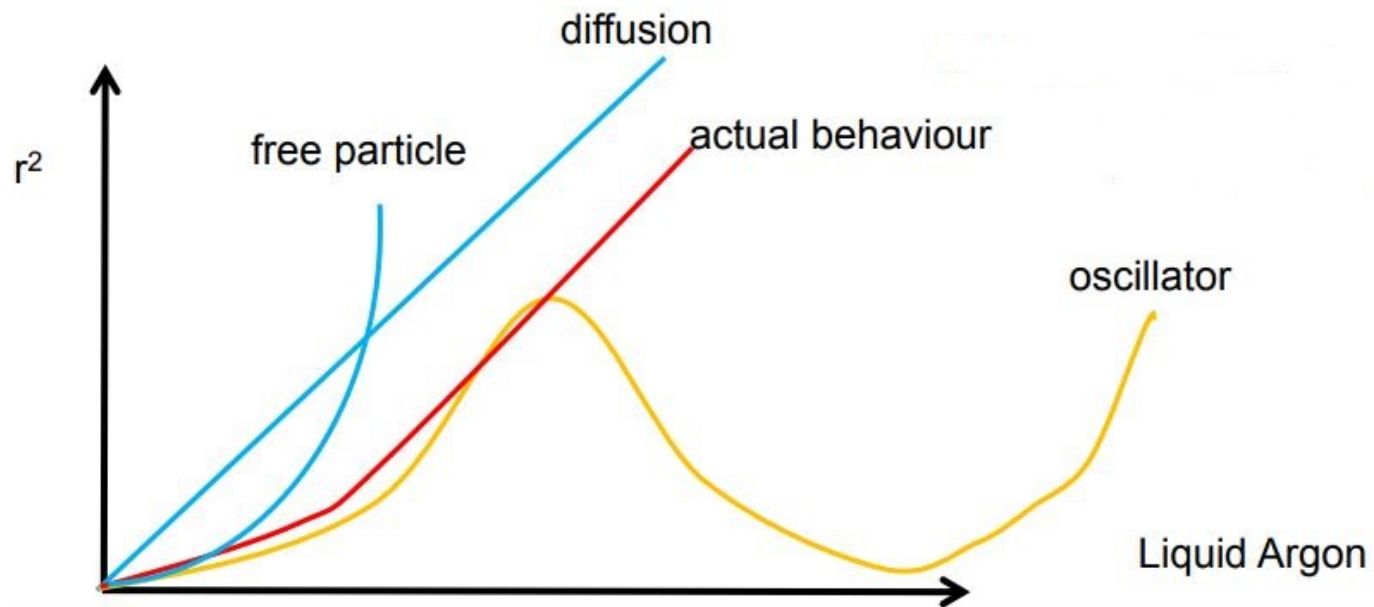
that's what we measure!!

*Gaussian **approximation**:*

Since for long and short times there is a gaussian we say that for all times:

$$G_s(r,t) = \frac{1}{\left(2\pi\sigma^2(t)\right)^{3/2}} \exp\left(-\frac{r^2}{2\sigma^2(t)}\right) \implies I(Q,t) = \exp\left(-\frac{Q^2\sigma^2(t)}{2}\right)$$
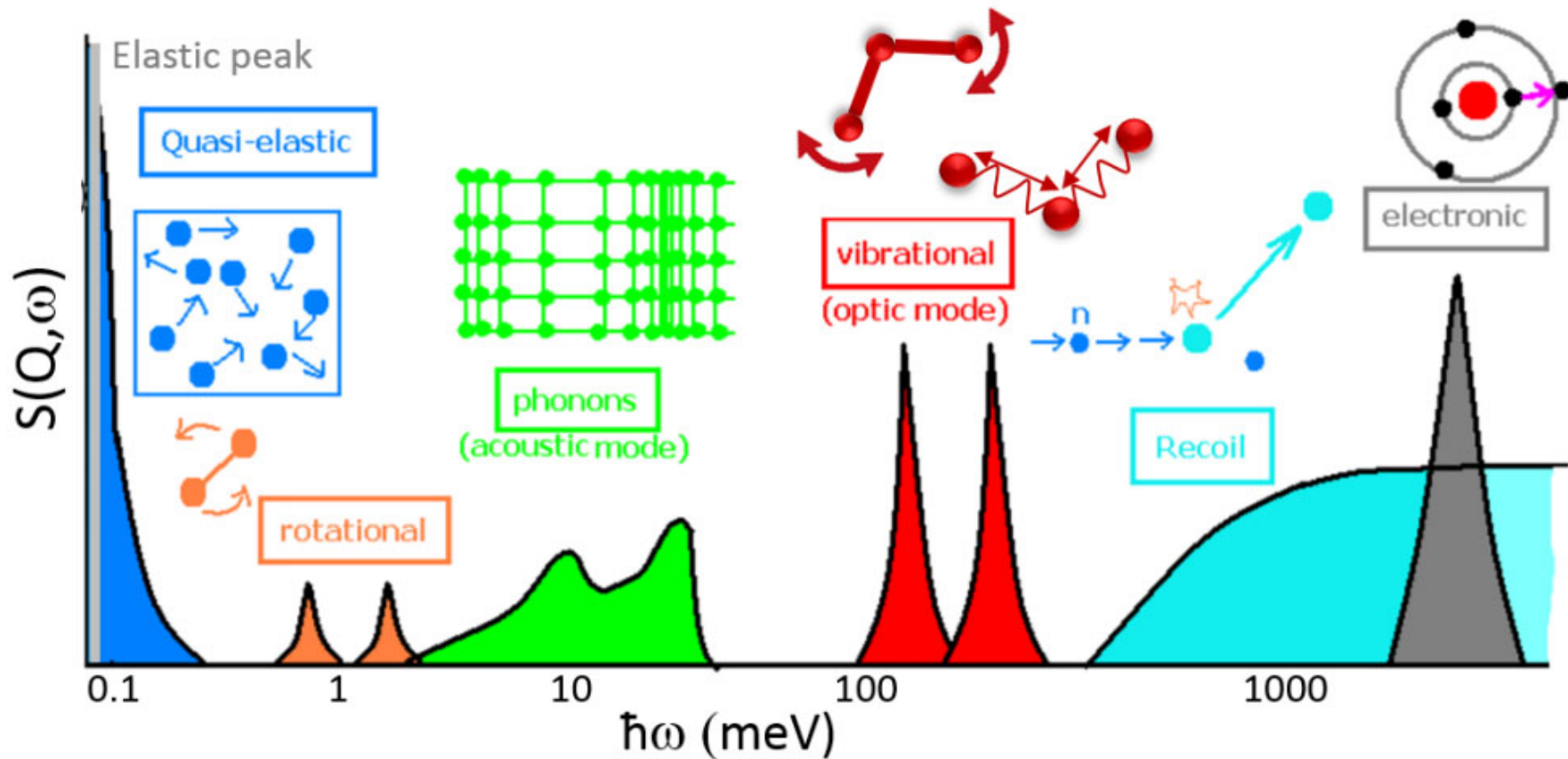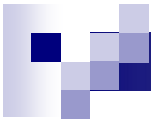
and the mean square displacement:

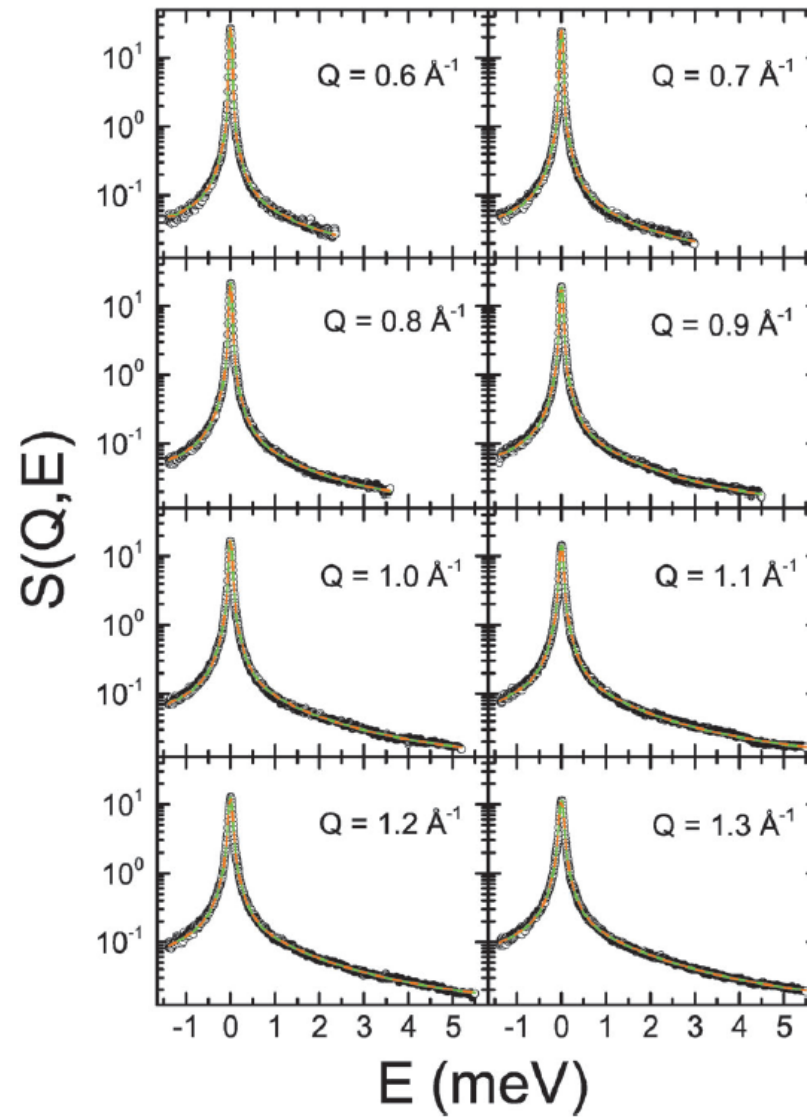$$\left\langle r^2(t) \right\rangle = 4\pi \int_0^\infty r^2 G_s(r,t)dr = 3\sigma^2(t)$$

We have a link between movement and the scattering function!!!

Incoherent scattering… beyond diffussion

A real case: glycerol

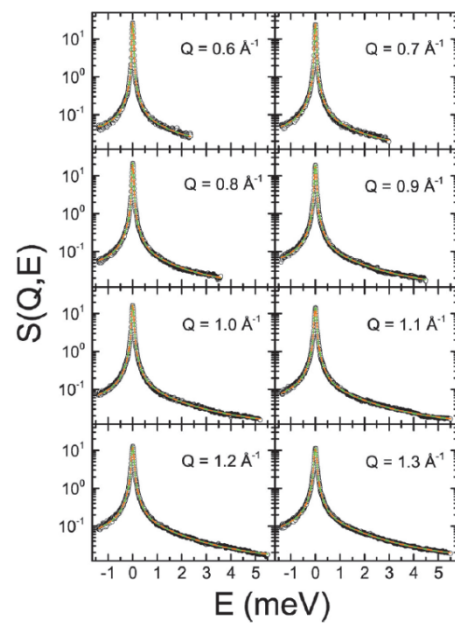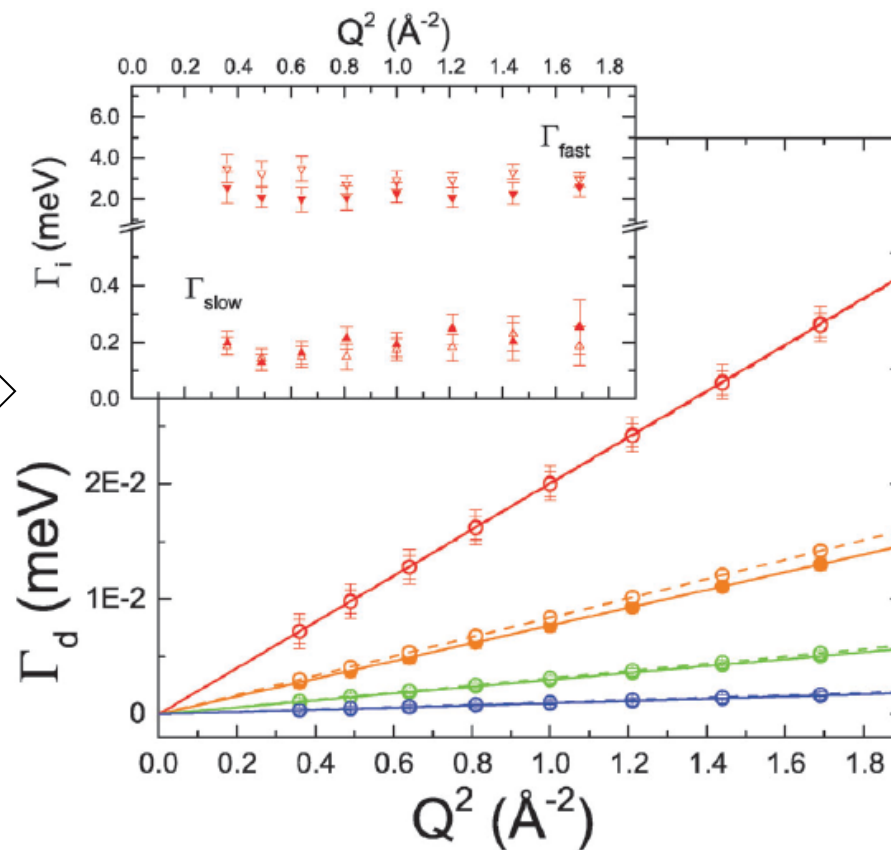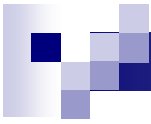*A real case: glycerol*

fitting for all Q

A real case: phospholipid membrane