

Lesson 2: From Elastic scattering to internal structure

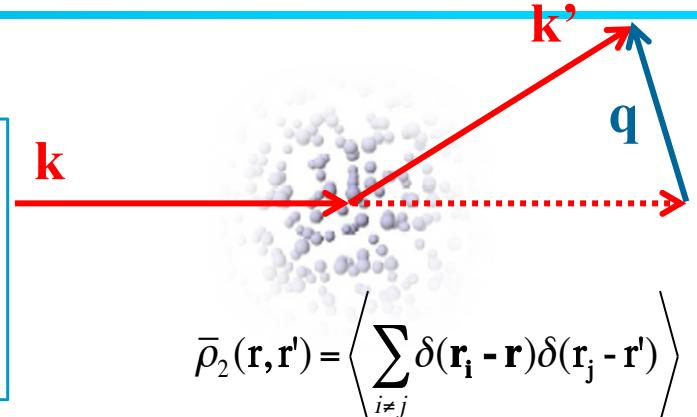
- ✓ Elastic scattering, summary
- ✓ An exemplar case: argon
 - ❖ pair correlation function of argon (gas, liquid and solid)
 - ❖ Static structure factor across state transitions
- ✓ A complex polyatomic case: water
- ✓ Compressibility and Ornstein Zernike relation
- ✓ Global properties of $S(k)$ across different states

Structure of liquids - module of the course "structure of matter"

In the previous lesson...

$$I(\mathbf{q}) - N\delta_{\mathbf{q},0} = S(\mathbf{q}) = \frac{1}{N} \iint d\mathbf{r}_1 d\mathbf{r}_2 \exp(-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)) \rho_2(\mathbf{r}_1, \mathbf{r}_2) - N\delta_{\mathbf{q},0}$$

$$S(\mathbf{q}) = 1 + \frac{\rho^2}{N} \int [g(\mathbf{r}_1, \mathbf{r}_2) - 1] e^{i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} d\mathbf{r} d\mathbf{r}' \quad g(\mathbf{r}_1, \mathbf{r}_2) = \frac{\bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2}$$



Fluids, glasses

$$\bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(r) \quad S(\mathbf{q}) = 1 + \rho \int [g(r) - 1] e^{-i\mathbf{q}\mathbf{r}} dr$$

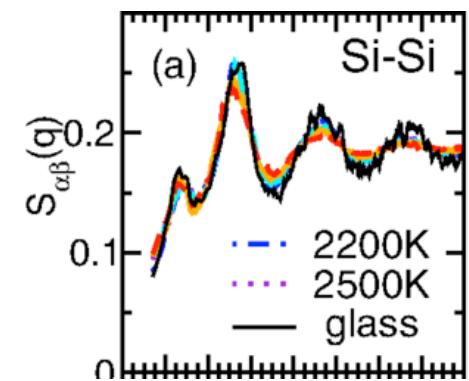
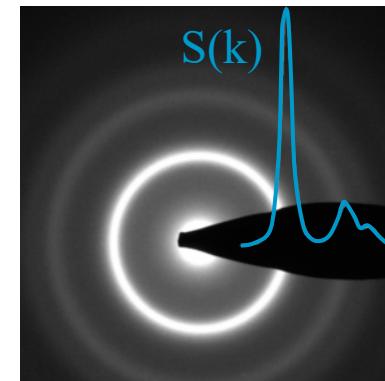
Perfect gases (non interacting classical particles)

$$\rho(\mathbf{r}) = \rho \quad g(\mathbf{r}, \mathbf{r}') = 1 \quad \bar{\rho}_2(\mathbf{r}, \mathbf{r}') = \rho^2 \quad dN = 4\pi\rho r^2 dr$$

$$\Rightarrow S(\mathbf{q}) = 1$$

$$\Rightarrow g(r) = 1$$

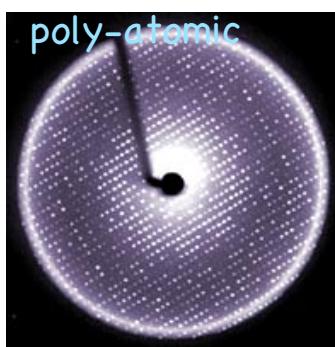
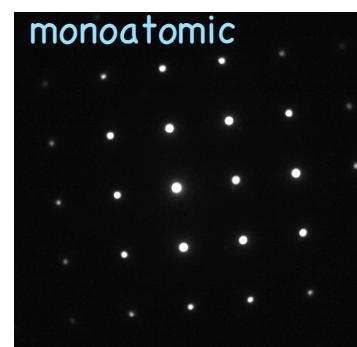
i.e. uniform scattering, no constructive interference, only forward scattering



Crystals

$$\bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2) \approx \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) - \delta(\mathbf{r}_1 - \mathbf{r}_2)\rho(\mathbf{r}_1)$$

$$S(\mathbf{q}) + N\delta_{0,\mathbf{q}} = \frac{1}{N} \left| \int \rho(\mathbf{r}) e^{i\mathbf{q}(\mathbf{r})} d\mathbf{r} \right|^2$$



$$\rho(\mathbf{r}) = \sum_I \sum_i f_i (\mathbf{r} - \mathbf{r}_i - \mathbf{R}_I) \xrightarrow{FT} \frac{N}{V} \sum_J \sum_i \bar{f}_i(k) e^{i\mathbf{k}\mathbf{r}_i} \delta_{\mathbf{k}, \mathbf{K}_J}$$

poly-atomic

Structure of liquids - module of the course "structure of matter"

What's next... Connecting structure to other properties

$$S(k) - 1 = \rho \int [g(r) - 1] e^{ikr} d\mathbf{r} = \rho \int_0^\infty 4\pi r^2 [g(r) - 1] \frac{\sin(kr)}{kr} dr$$

Operatively, scattering is a way to measure the internal structure of a fluid:

The (measured) structure factor $S(k)$ is related to the (radial) pair distribution function $g(r)$ by a FT

$g(r)$ describes the probability of finding a particle at a distance r from another

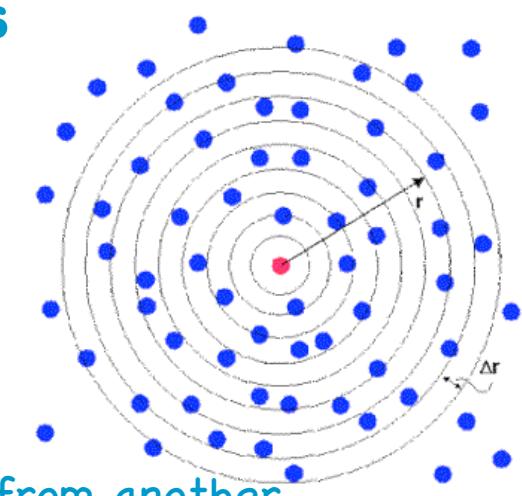
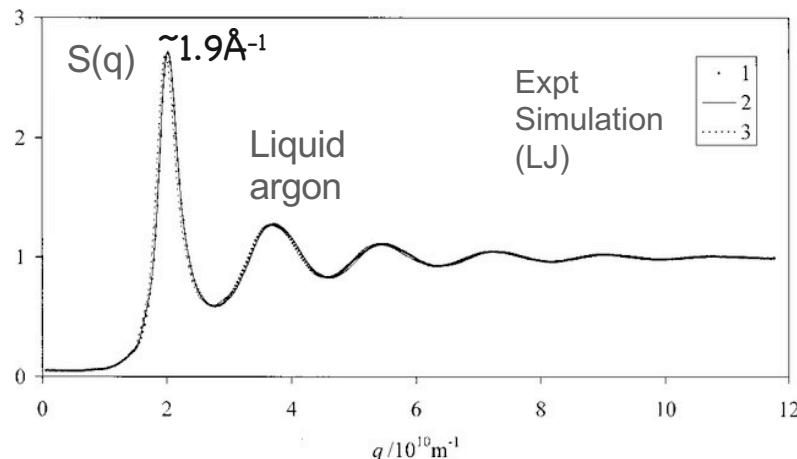
The number of particles at distance between r and $r+dr$ from a given one is

$$dN = \rho 4\pi r^2 g(r) dr \text{ note the } r^2 \text{ behavior!!}$$

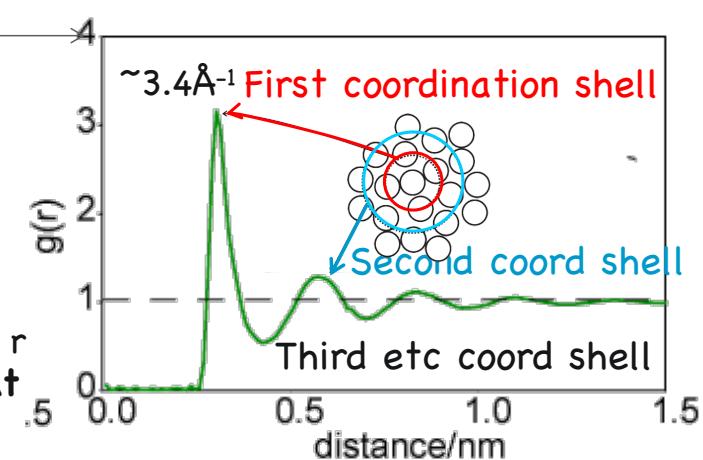
It is also useful to define the total correlation function (or hole function)

$$h(r) = g(r) - 1 = \frac{1}{8\pi^3 \rho} \int [S(k) - 1] e^{-ikr} dk = \frac{1}{2\pi^2 \rho r} \int_0^\infty [S(k) - 1] k \sin(kr) dk$$

An example: Argon, a "Lennard Jones" fluid



- ✓ As an effect of FT, the location of first peaks of $S(k)$ and $g(r)$ are $k_1 \times r_1 \sim 2\pi$
- ✓ The location of $g(r)$ peaks corresponds to coordination shells
- ✓ $g(r)$ is exactly null at small r
- ✓ $S(k)$ is small but not null at small k



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In the polyatomic case

One must generally define particle-type separate structure and pair correlation functions:

$$S_{\alpha\beta}(k) - 1 = \rho \int [g_{\alpha\beta}(r) - 1] e^{ikr} dr$$

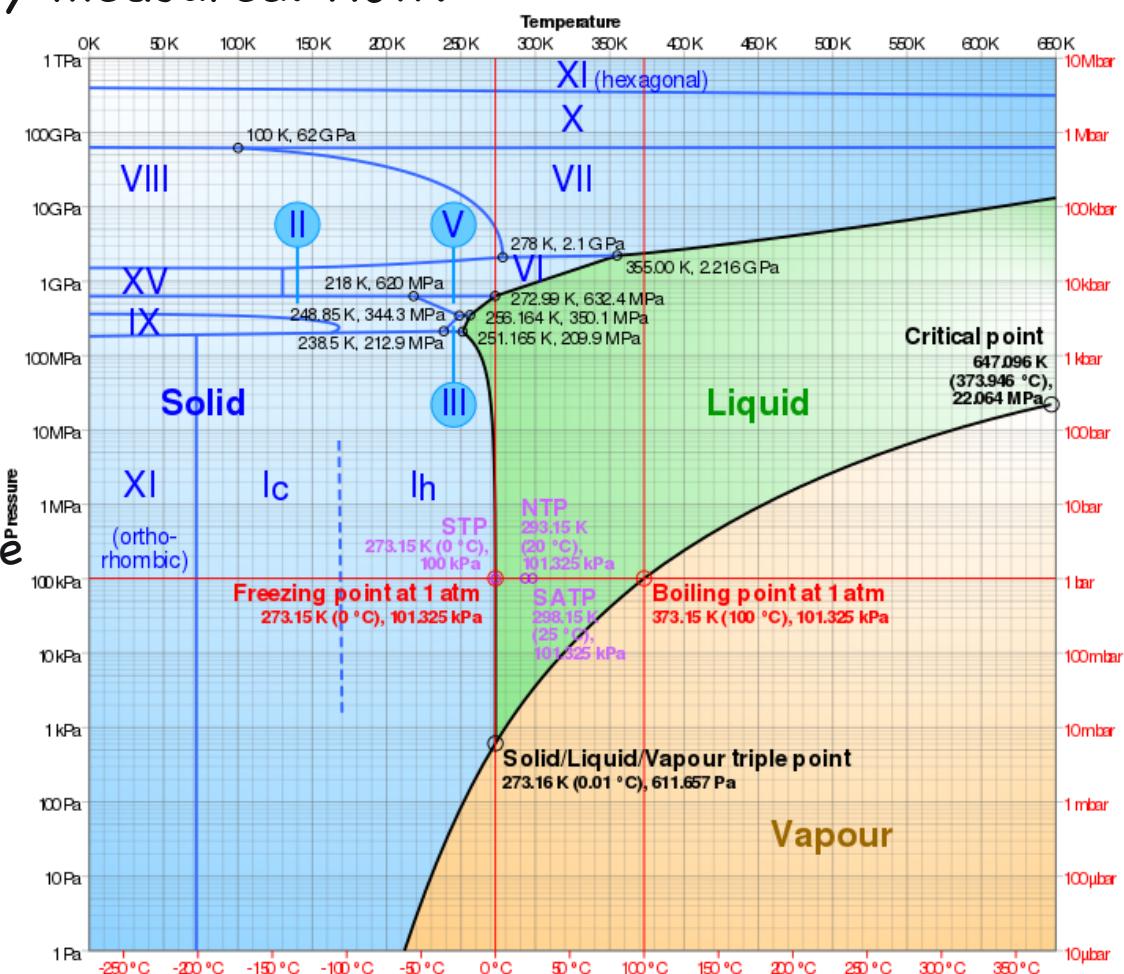
Which can generally be separately measured. How?

Exploiting the different atomic scattering form factor of the different atoms

- ✓ X-ray-scattering is blind to hydrogen atoms
- ✓ Neutron scattering is sensitive to different atoms and different isotopes, therefore the relative weight of different component can be changed by isotopic substitutions

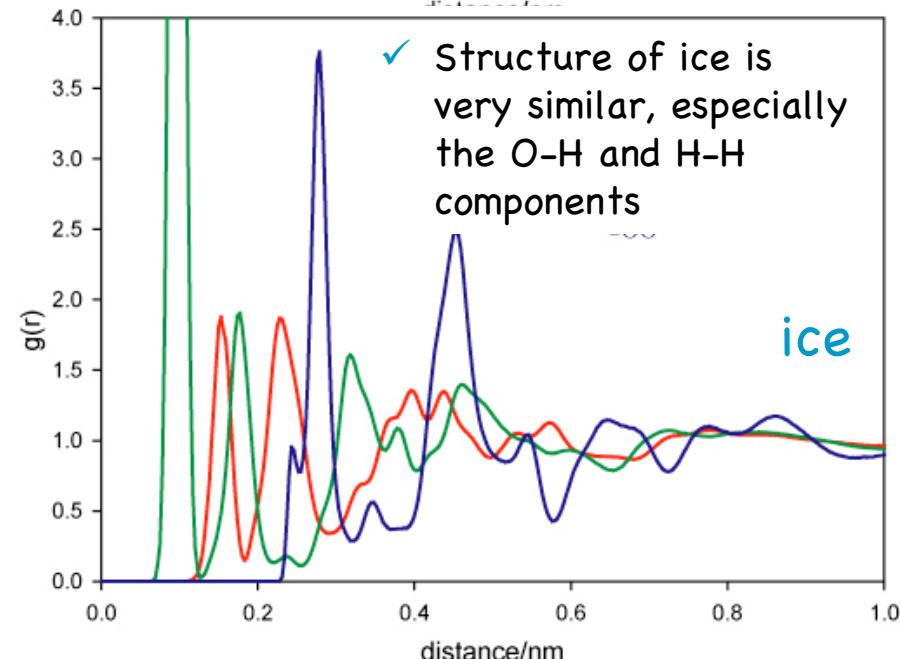
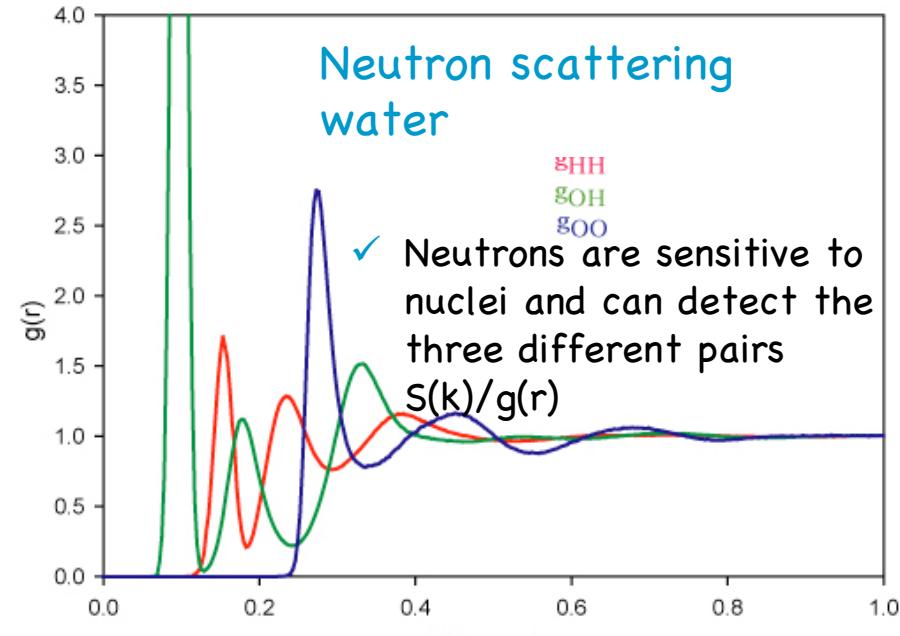
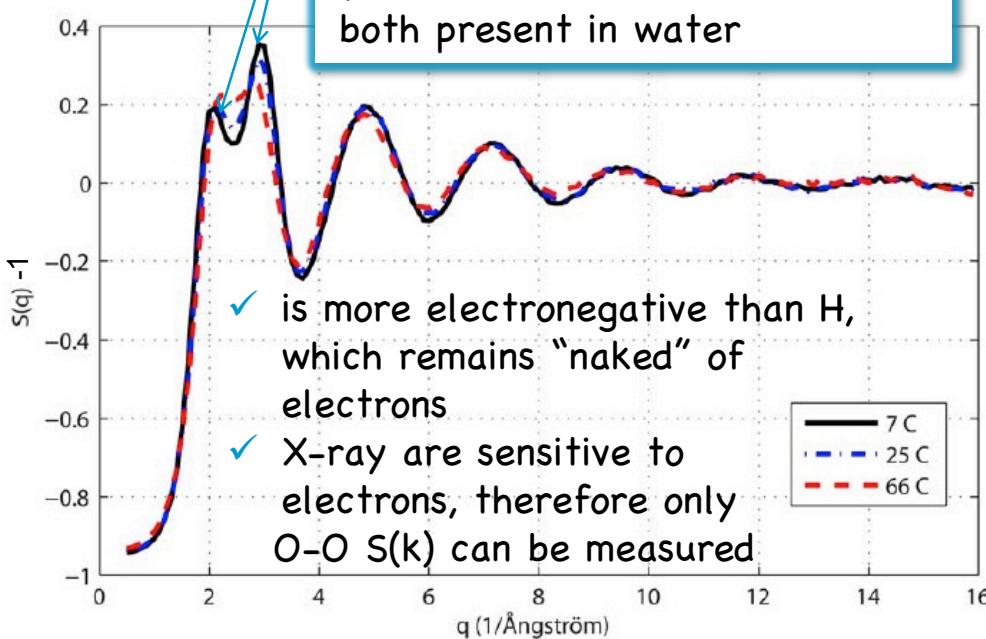
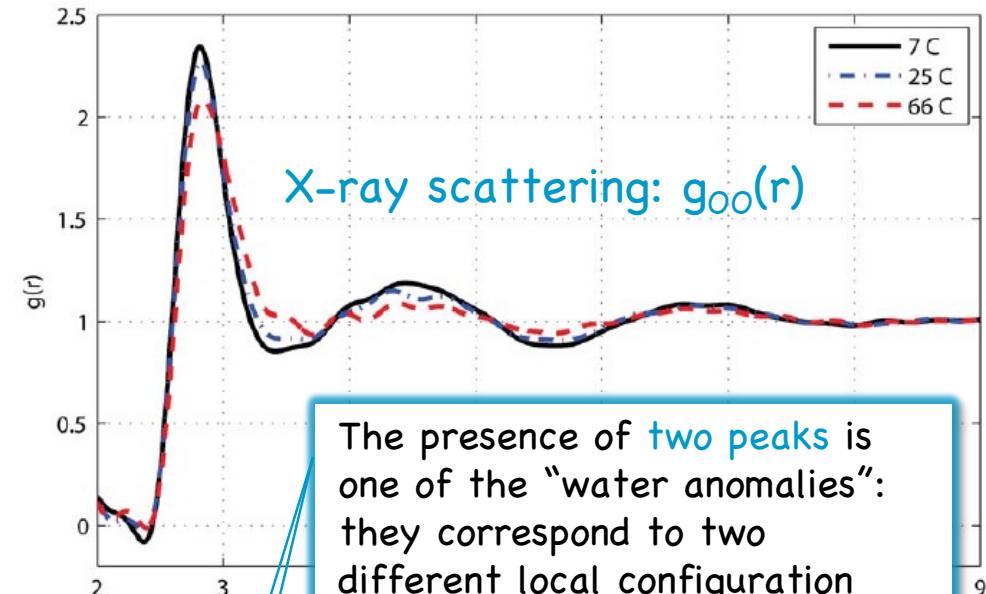
Examples

A complex polyatomic case: Water



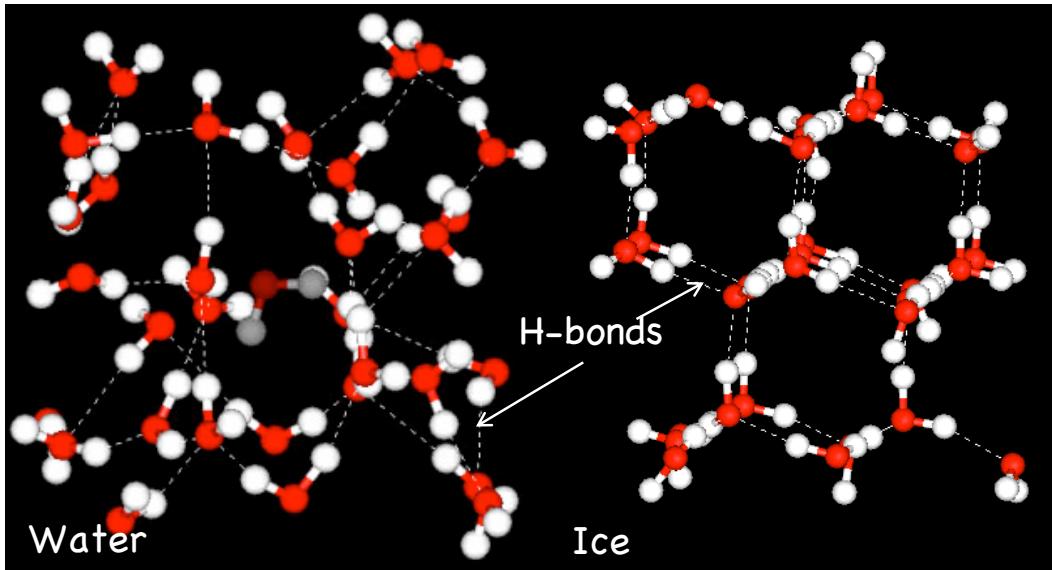
Structure of liquids – module of the course “structure of matter”

Examples A complex polyatomic case: Water

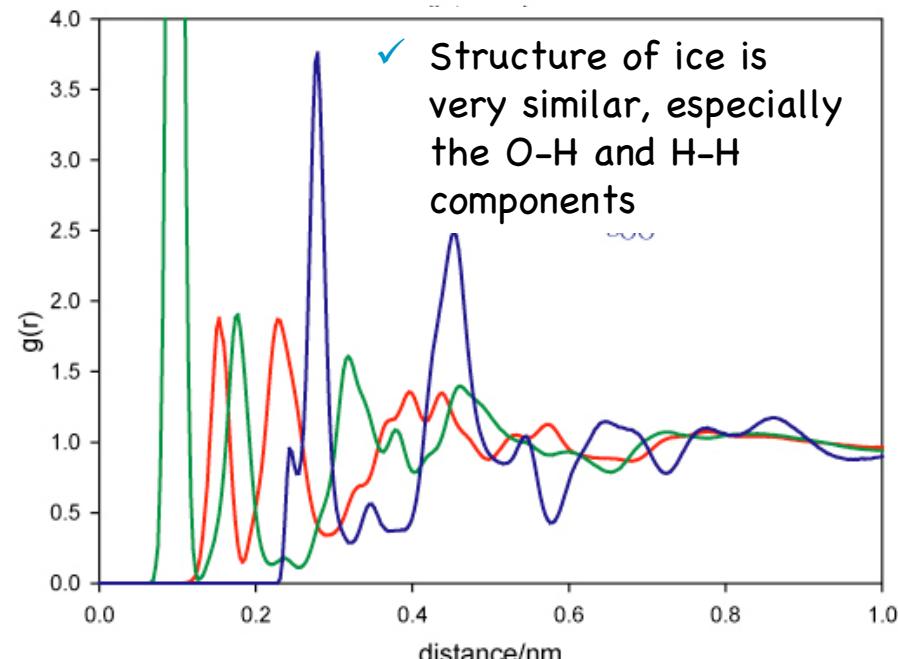
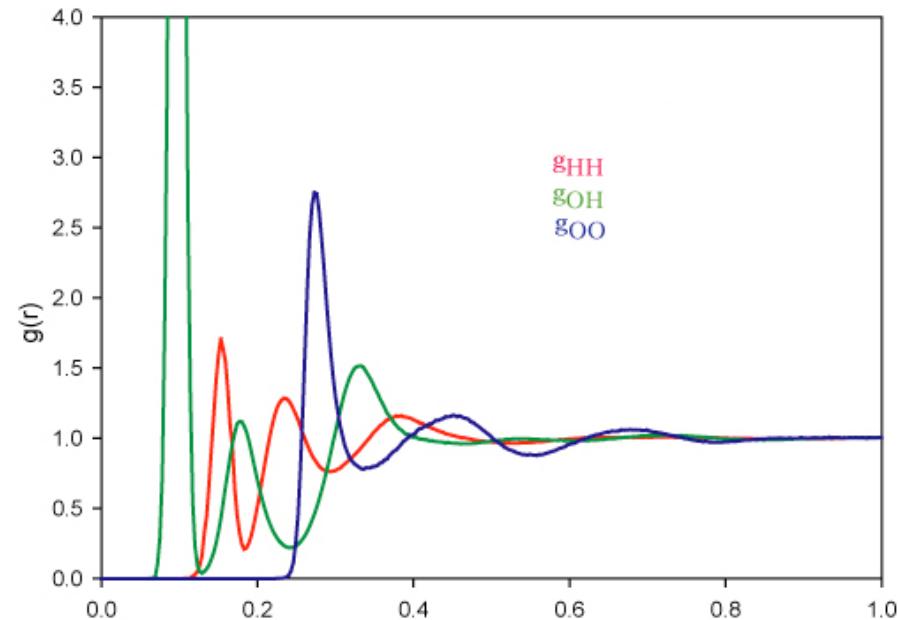


Structure of liquids – module of the course “structure of matter”

Examples A complex polyatomic case: Water



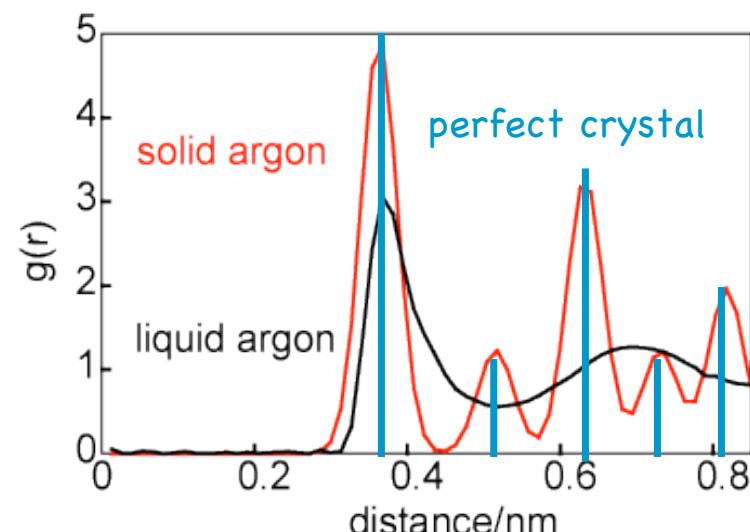
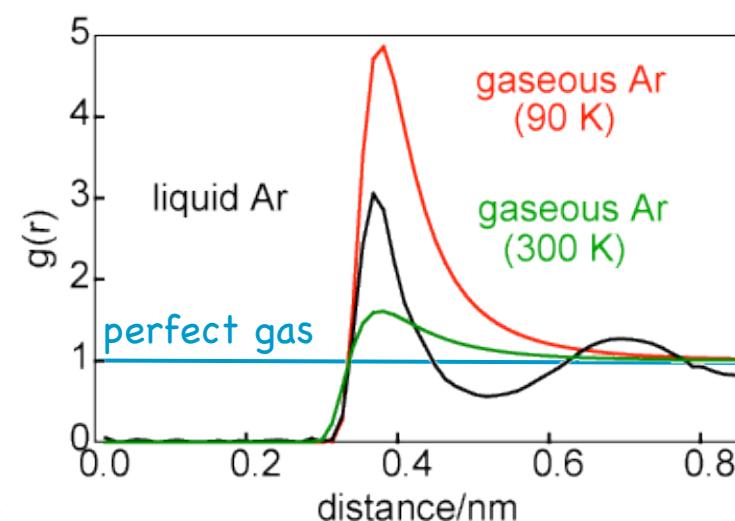
- ✓ Ice is crystalline, while water is disordered
- ✓ However both are stabilized by a network of H-bonds using H as bridges between Os and involving also lone pairs of O
- ✓ In ice these bonds are stable and regular, in water they are mobile
- ✓ However, even in water the local order is very strong, as shown by the very high peaks in $g(r)$, especially those involving H
- ✓ This locally ordered structure, even in liquid water, is responsible for the unusual properties of water, and of its very complex phase diagram



Structure of liquids – module of the course “structure of matter”

An example: Argon, a “Lennard Jones” fluid

- ✓ Liquid argon
- ✓ The $g(r)$ of liquid is modulated and oscillates
- ✓ As the temperature increases and the transition to gas occurs, the structure is lost. Secondary peaks disappear and the first one decreases
- ✓ The $g(r)$ of a perfect gas is constant and equal to 1: the particles do not see each other, are interpenetrating and therefore $g(r)$ does not vanish at $r=0$ as in real systems, and the probability of finding a particle at distance r in any direction is barely $\propto 4\pi r^2$
- ✓ Noble gases at high temperature are good approximation of perfect gases, except for the short range part where the repulsive excluded volume interaction is non negligible
- ✓ In solid argon, there are sharp peaks, gaussian-like. In fact in this case one has $g(\mathbf{r}_1, \mathbf{r}_2) \propto \rho(\mathbf{r}_1) \rho(\mathbf{r}_2)$
- ✓ The first peak is located approximately in the same location as in the liquid (first neighbors)
- ✓ Peaks in the liquid $g(r)$ are “reminiscent” of those in solid
- ✓ As the temperature decreases, the peaks become sharper

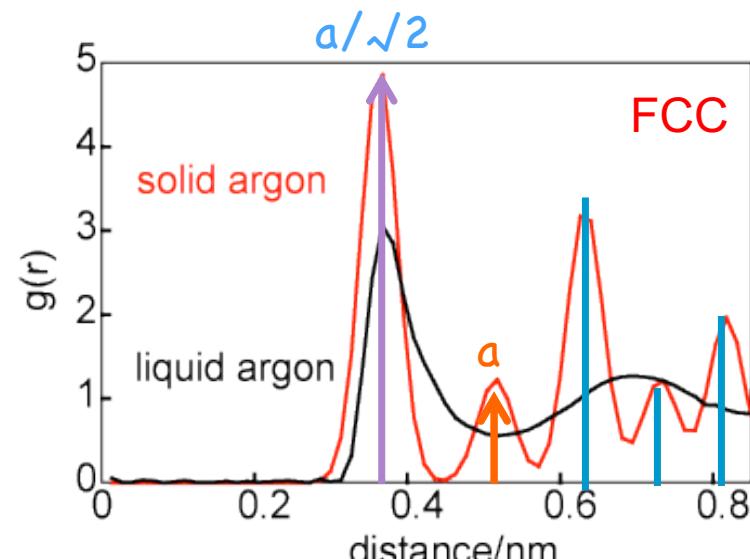
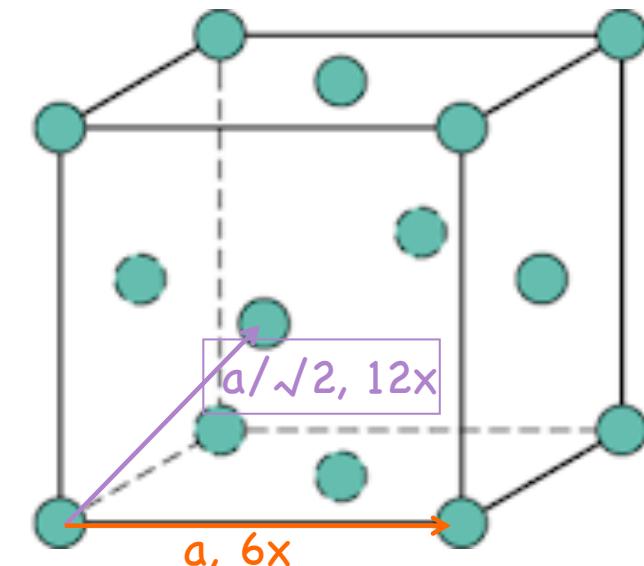


Structure of liquids - module of the course "structure of matter"

An example: Argon, a "Lennard Jones" fluid

Direct evaluation of $g(r)$ in solid argon

- ✓ Solid argon = FCC crystal
- ✓ In the perfect crystal (exactly localized atoms) the $g(r)$ is non null only when $r=R$ lattice vectors
- ✓ The location of the first two "stars" of lattice vectors stemming from a given atom is at $a/\sqrt{2}$ and a , respectively, being a the lattice parameter (the third is at $a/\sqrt{2}$ etc.)
- ✓ Therefore, the first two peaks of $g(r)$ in the solid are located at those values
- ✓ The height of the peaks is proportional to m/r^2 , m being the multiplicity of the star (i.e. 12 for the first, 6 for the second) and r the distance. Therefore the ratio between second and first peak is $(6/a^2)/(12/(a^2/2))=1/4$
- ✓ Because at room temperature the atoms are not frozen on the lattice sites, there is a smearing of the $g(r)$ due to thermal fluctuations (red line)

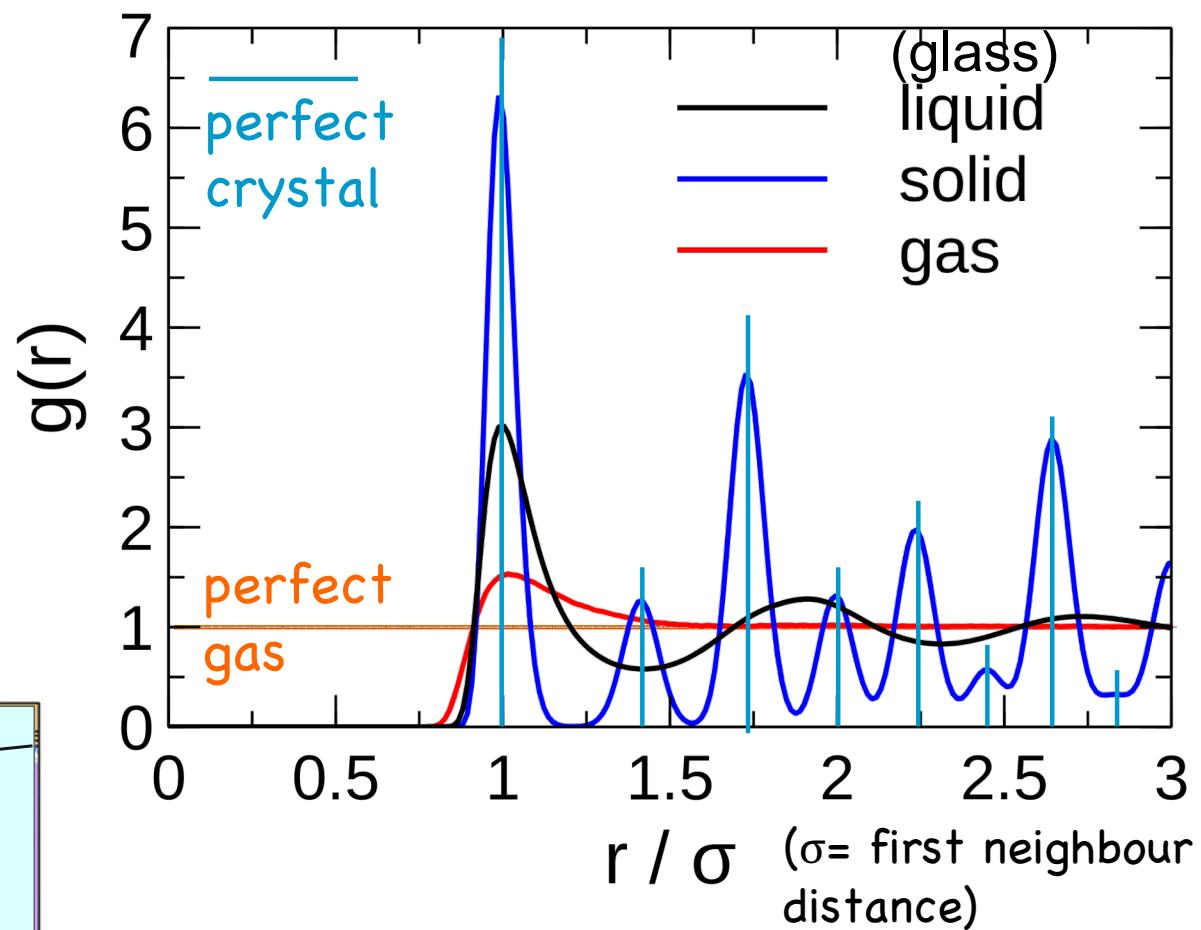
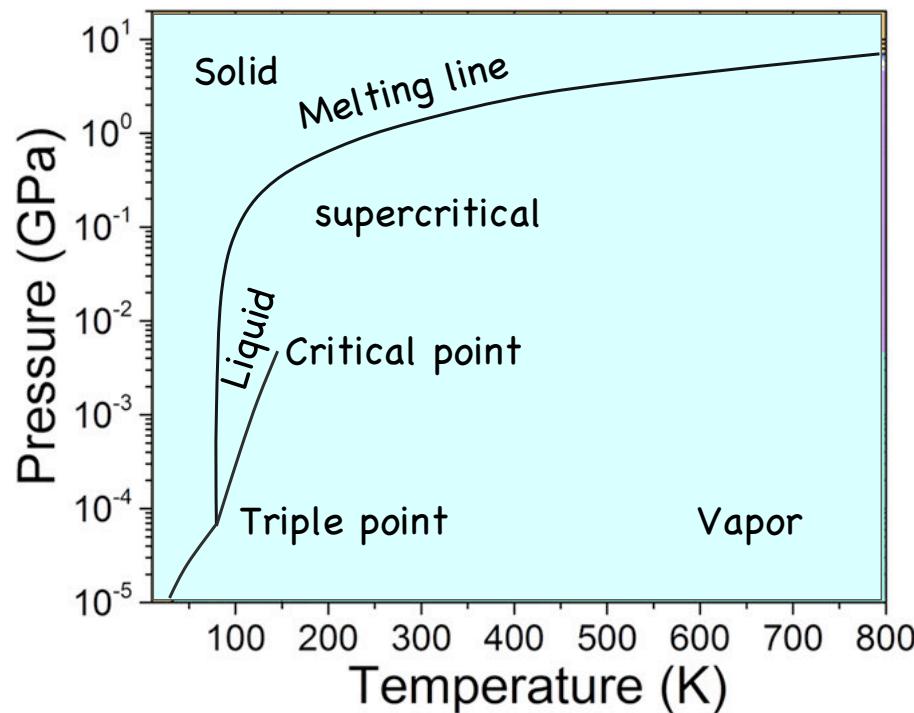


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In summary

In the classical regime (btw, what about very low temperatures? Can it exist the “ideal crystal”) the form of $g(r)$ can be related to the phase of the material (except for specific cases, e.g comparison between liquid and glasses)

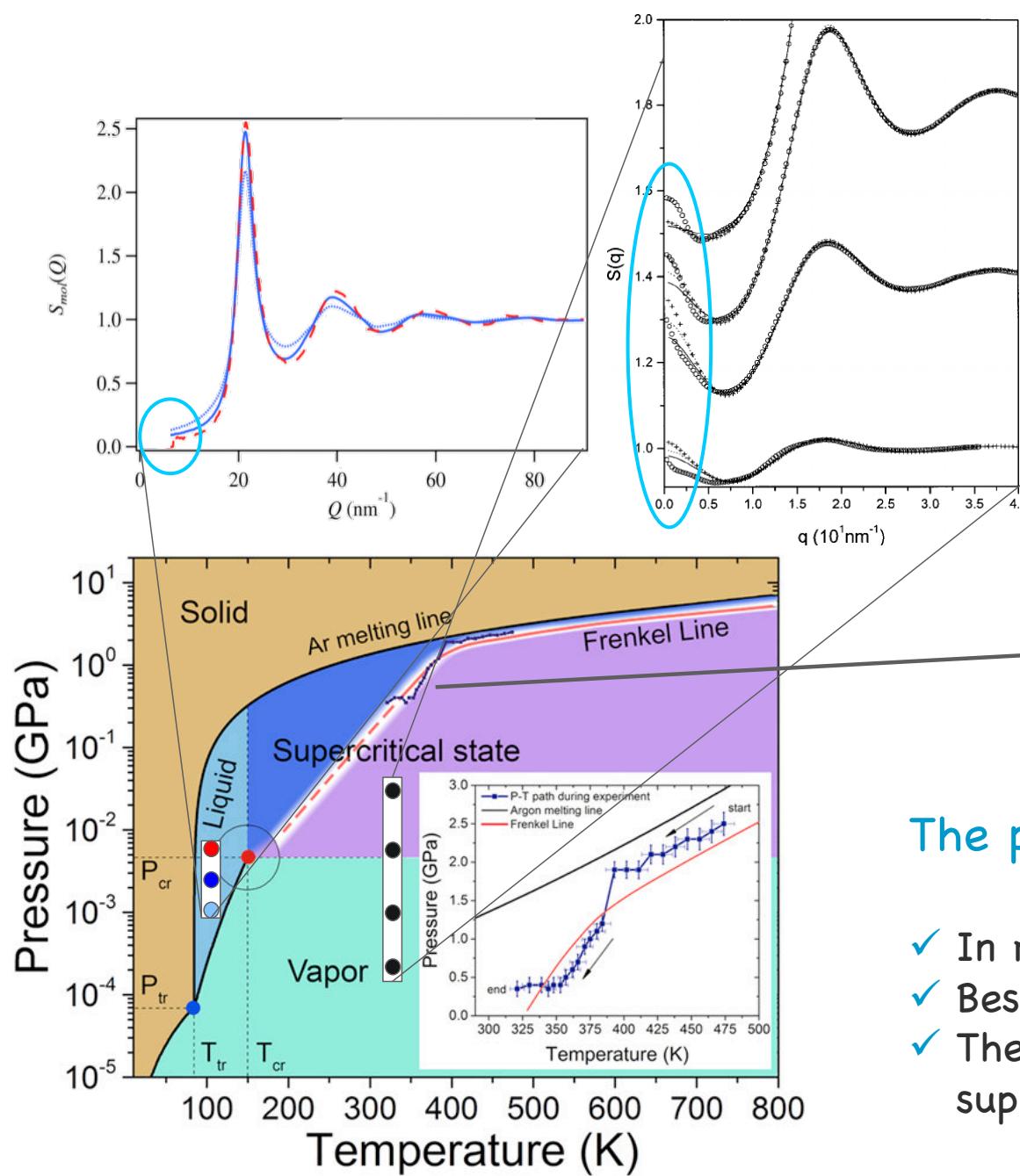
But what about the $S(k)$?



The phase diagram of Argon

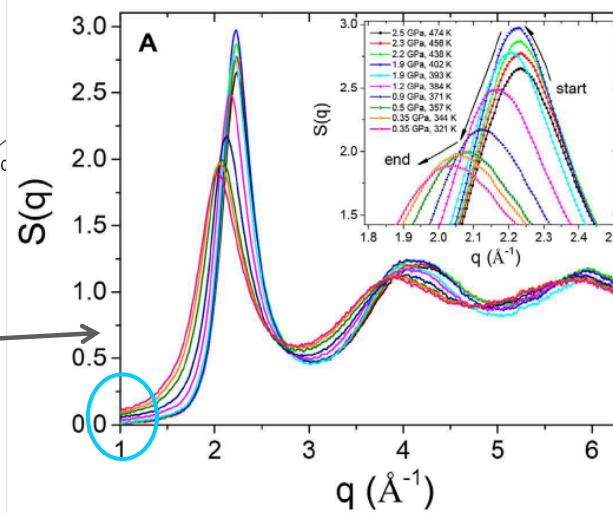
- ✓ Three normal phases
- ✓ A critical point and supercritical region in which there's “no distinction” between liquid and gas

Structure of liquids – module of the course “structure of matter”



- ✓ While $g(r)$ is always null at $r=0...$
- ✓ $S(k=0)$ is very different in the different phases!

Why?



The phase diagram of Argon

- ✓ In reality, more complicate
- ✓ Besides the normal phases
- ✓ There seems to exist transition in the supercritical state (Frenkel line)

Structure of liquids - module of the course "structure of matter"

The large wavelength (small k) limit of S(k)

$$S(k=0) = 1 + \rho \int [g(r) - 1] d\mathbf{r} = 1 + \frac{1}{N} \iint \rho^2 g(r) d\mathbf{r} d\mathbf{r}' - \rho \int d\mathbf{r}$$

$$\bar{\rho}_2(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \right\rangle$$

$$\iint \bar{\rho}_2(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' = \langle N^2 \rangle - \langle N \rangle$$

$$S(k=0) = 1 + \frac{\langle N^2 \rangle - \langle N \rangle}{\langle N \rangle} - \langle N \rangle = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{\langle \Delta N^2 \rangle}{\langle N \rangle}$$

Gibbs-Duhem relation

$$Nd\mu + SdT - Vdp = 0$$

$$\left. \frac{\partial \mu}{\partial p} \right|_{T,V} = \frac{V}{N} = \frac{1}{\rho}$$

Therefore: in a system with constant number of particles S(k) vanishes at k=0 (perfect crystals)
Otherwise S(0) is proportional to the relative fluctuation of number of particles of the system.
To evaluate these, one must consider the general thermodynamic relationship, e.g. in the grand canonical formalism

$$N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V} \quad \langle \Delta N^2 \rangle = kT \left(\frac{\partial N}{\partial \mu} \right)_{T,V} = kT \frac{\left(\frac{\partial N}{\partial p} \right)_{T,V}}{\left(\frac{\partial \mu}{\partial p} \right)_{T,V}} = kT \frac{\left(\frac{\partial N}{\partial p} \right)_{T,V}}{1/\rho} = V \rho kT \left(\frac{\partial \rho}{\partial p} \right)_{T,V} = V \rho^2 kT \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_{T,V} \quad \kappa_T$$

$$\langle \Delta N^2 \rangle = N k T \rho \kappa_T$$

$$\lim_{k \rightarrow 0} S(k) = \rho k T \kappa_T \quad \text{Ornstein - Zernike relation}$$

isothermal compressibility

$$\langle \Delta M^2 \rangle = kT \left. \frac{\partial M}{\partial H} \right|_{T,V,\dots}$$

This is the "static part" of the fluctuation dissipation theorem, linking fluctuations of any quantity (e.g. M) to the linear response function to external "field" (H)

Structure of liquids - module of the course "structure of matter"

The large wavelength (small k) limit of S(k)

In a perfect gas

$$\kappa_T = \frac{1}{\rho} \frac{\partial \rho}{\partial p} = \frac{1}{\rho} \frac{\partial N/V}{\partial p} \xrightarrow{pV = NkT} = \frac{1}{\rho} \frac{\partial(p/kT)}{\partial p}$$

$$\kappa_T = \frac{1}{\rho kT} \Rightarrow S(q=0)=1$$

But, as we already know, in this case $S(k)=1$ for every k

In a crystal $S(k=0) \sim 0$ (ideally incompressible)

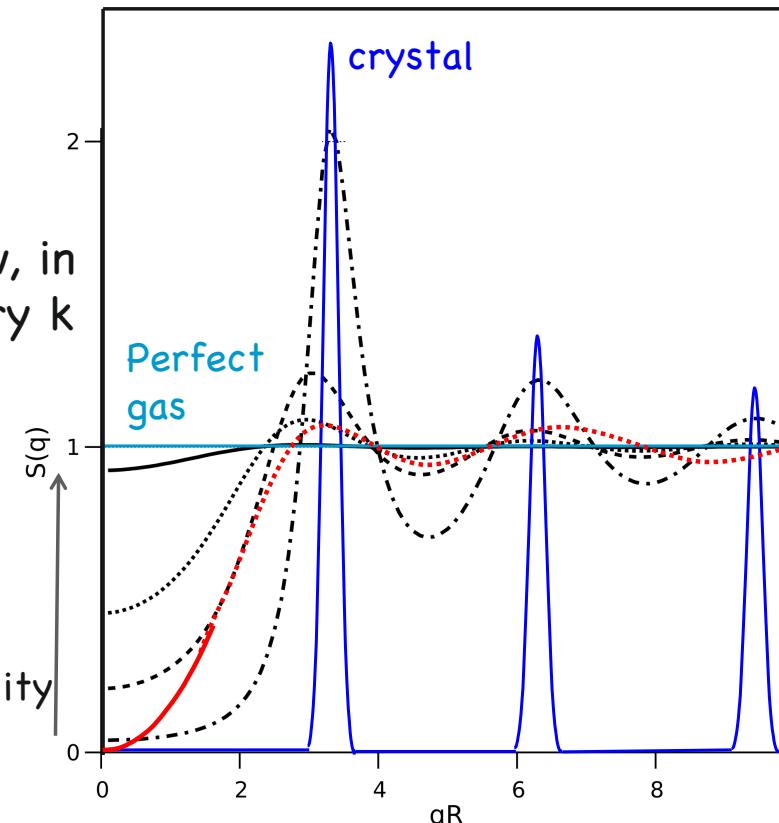
In a plasma (e.g. electrons on uniform background) the compressibility of the system is determined by the fact that compression creates a charge separation and therefore a macroscopic electrostatic field



$$\lim_{k \rightarrow 0} S(k) = -\frac{kT}{\rho} \chi(k, \omega=0)$$

Solving the Poisson equation one gets $\lim_{k \rightarrow 0} S(k) = \frac{kT}{4\pi\rho e^2} k^2$

k^2 coming from ∇^2 in Poisson equation, or equivalently, from $1/r^2$ long range potential i.e.: at variance with normal cases, in which the $S(k=0)$ behavior is determined by the repulsive core (local compressibility), in the plasma case it is determined by the long range behavior



Static linear response function, related to dielectric function

$$\lim_{k \rightarrow 0} S(k) = \rho k T \kappa_T \quad \text{Ornstein - Zernike relation}$$

Structure of liquids – module of the course “structure of matter”

The large wavelength (small k) limit of S(k)

In a perfect gas

$$\kappa_T = \frac{1}{\rho kT} \Rightarrow S(0) = 1$$

In a plasma

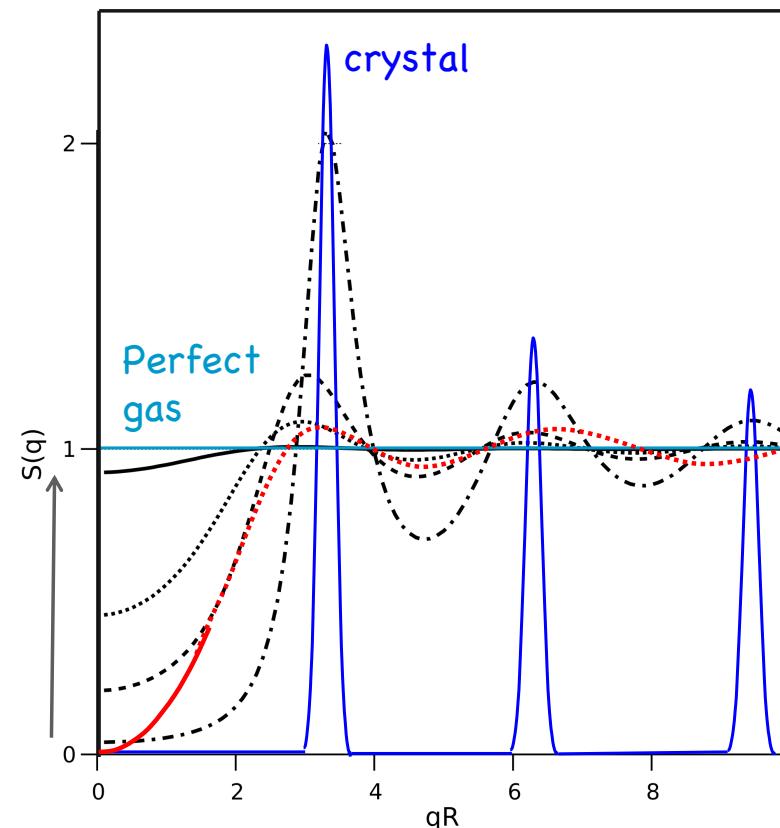
$$\lim_{k \rightarrow 0} S(k) = \frac{kT}{4\pi\rho e^2} k^2$$

$$S(k=0) = 1 + \rho \int [g(r) - 1] dr$$

$$\left. \frac{\partial}{\partial k} S(k) \right|_0 \propto \rho \int r [g(r) - 1] dr$$

$$\left. \frac{\partial^2}{\partial k^2} S(k) \right|_0 \propto \rho \int r^2 [g(r) - 1] dr$$

Fluids with increasing compressibility



In general, the features of S(k) depend “non locally” on g(r) (global properties, e.g. compressibility and other momenta of the g(r)).

In turn, g(r) depends on the features of the interparticle potential

What is the general relationship between S(k) (g(r)) and the interparticle potential? → Theories of structure!

$$\lim_{k \rightarrow 0} S(k) = \rho k T \kappa_T \quad \text{Ornstein - Zernike relation}$$