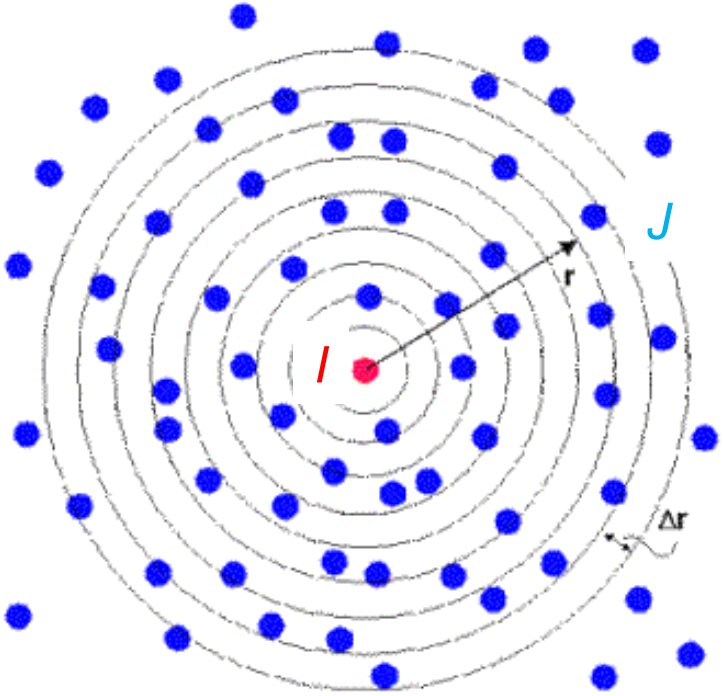
Course 04/2

Static property: pair correlation function

- Definition and properties
- Method of calculation
- Relation with structure factor
- Examples

Density as a function of distance from a given atom



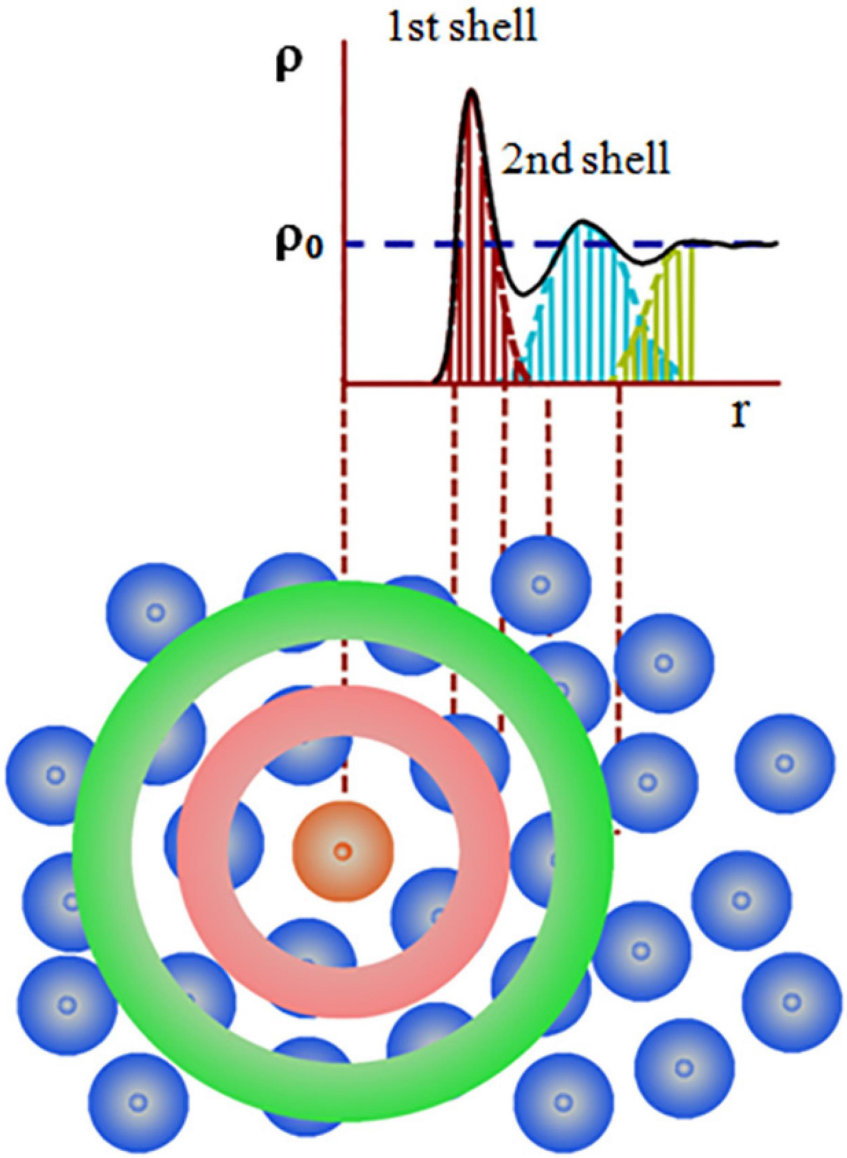
We define a density as a function of distance from a given atom *I*

$$\rho(\vec{r}) = \sum_{J=1}^{N} \delta(\vec{r} - \vec{r}_{IJ})$$

For an isotropic material, this definition is self-averaging:

$$\rho(\vec{r}) = \rho(r)$$

Density as a function of distance from a given atom

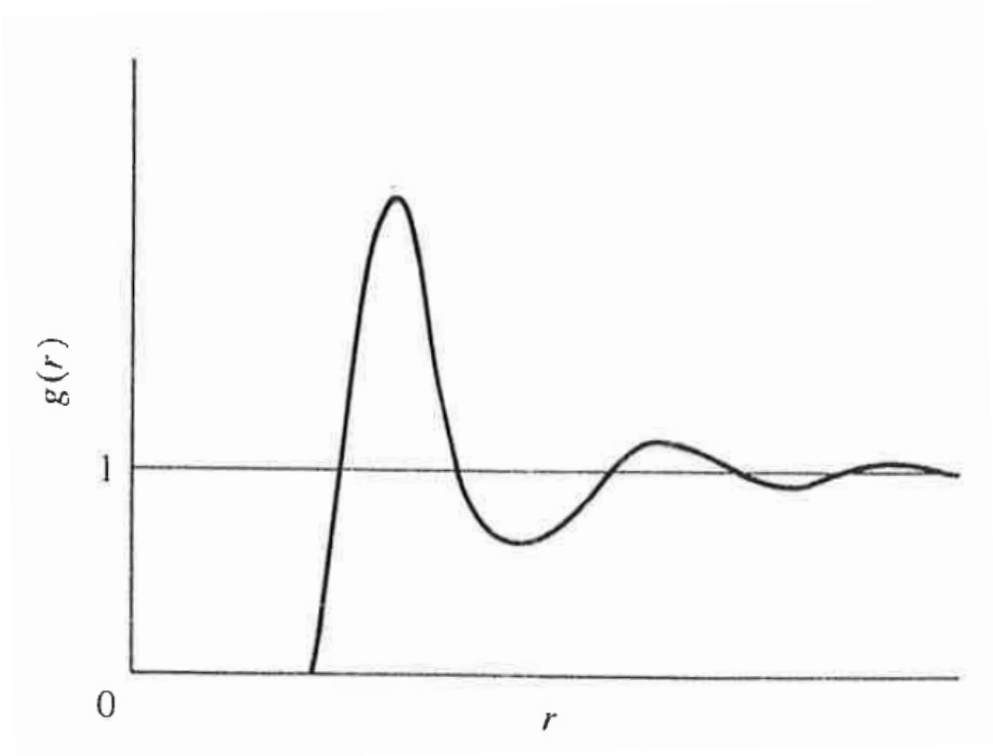


Pair correlation function

Definition of pair correlation function $g(r)$

$$g(r) = \frac{\rho(r)}{\rho_0}$$

where ρ_0 is the average density.



General properties of $g(r)$

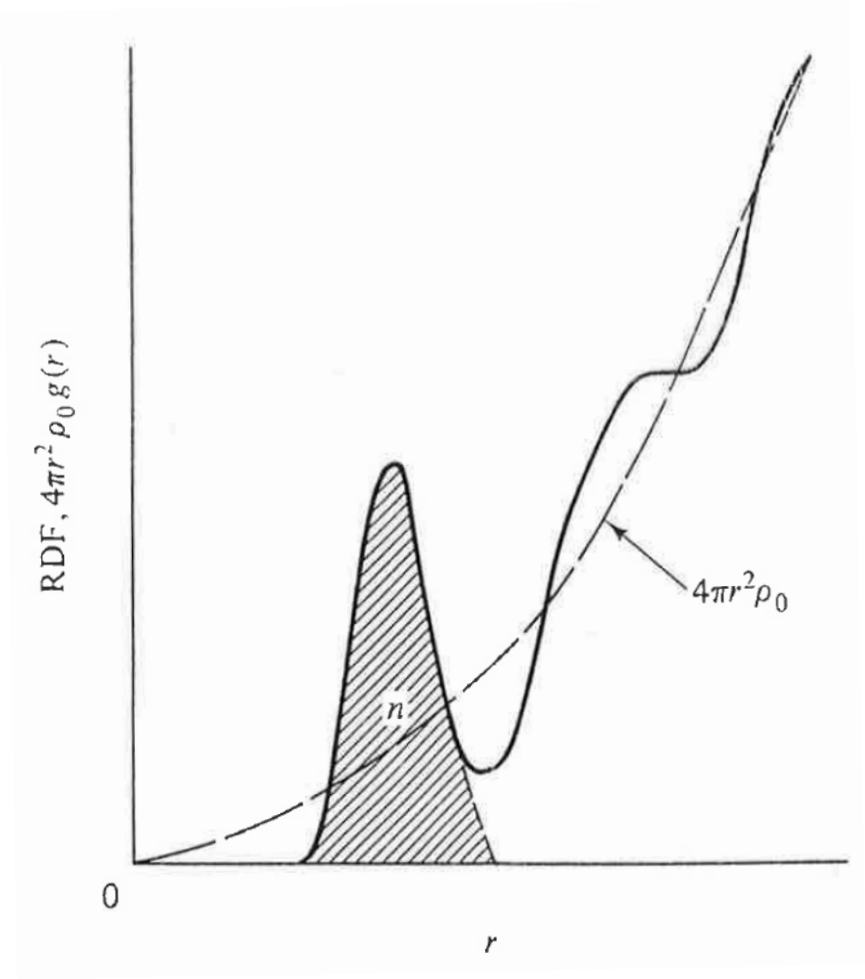
1. $\lim_{r \to 0} g(r) = 0$

2. $\lim_{r \to \infty} g(r) = 1$

Pair correlation function

General properties of $g(r)$

3. Coordination



$$\rho(r) = \rho_0 \, g(r)$$

Radial distribution function (RDF)

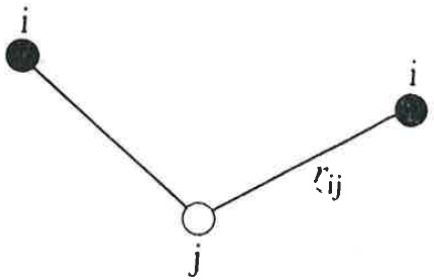
$$\text{RDF} = 4\pi r^2 \rho_0 \, g(r)$$

Coordination number n

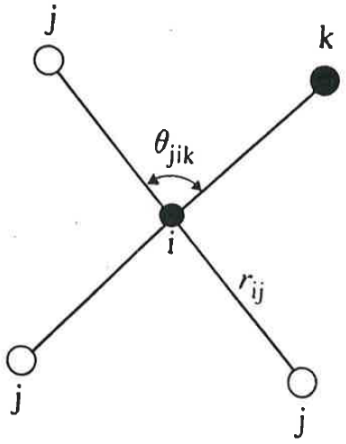
$$n = \int_{r_1}^{r_2} 4\pi r^2 \rho_0 \, g(r) \, dr$$

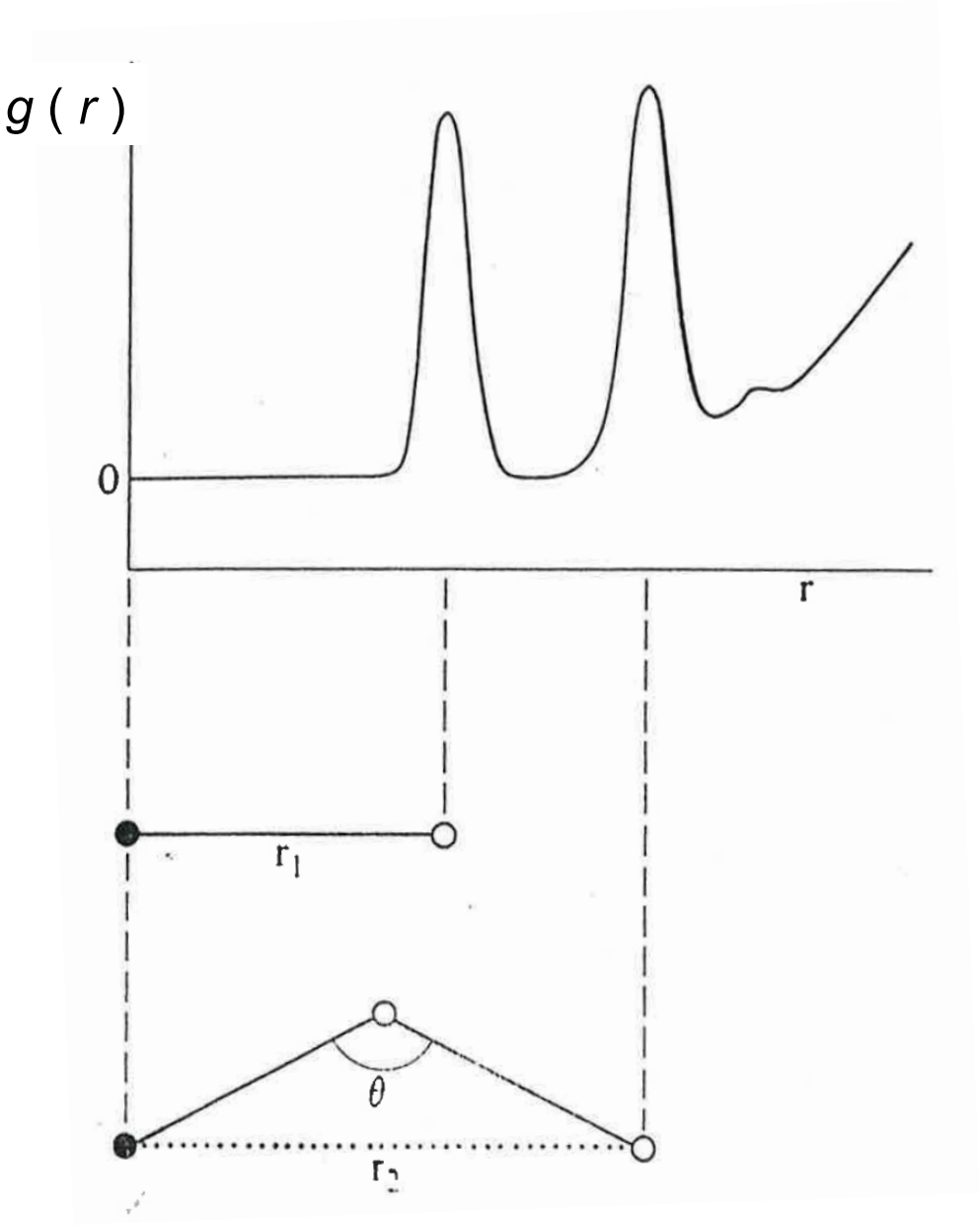
Information on short range order

Bond distances



Bond angles



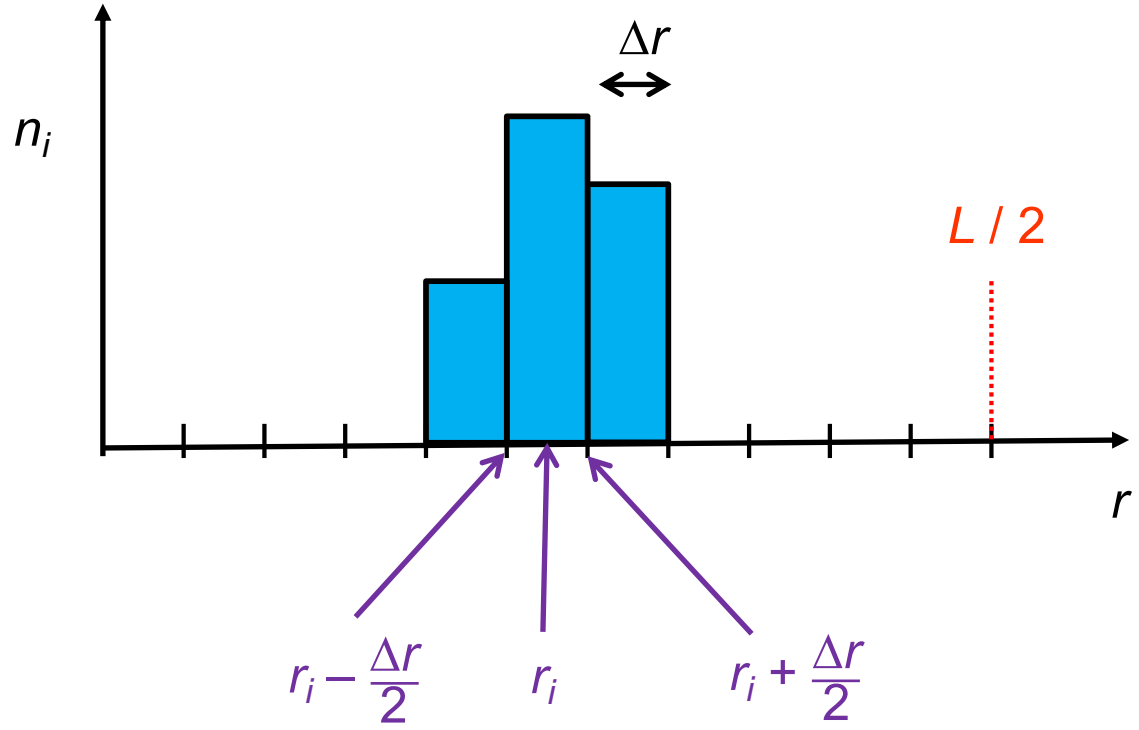


Method of calculation

Histogram: collect statistics for an " atom *I* " going through all other " atoms *J* ".

$$\begin{cases} n_i(I, J) = 1 & \text{if } r_i - \frac{\Delta r}{2} < r_{IJ} < r_i + \frac{\Delta r}{2} \\ n_i(I, J) = 0 & \text{otherwise} \end{cases}$$

$$n_i(I) = \sum_{\substack{J=1 \\ J \neq I}}^{N} n_i(I, J)$$



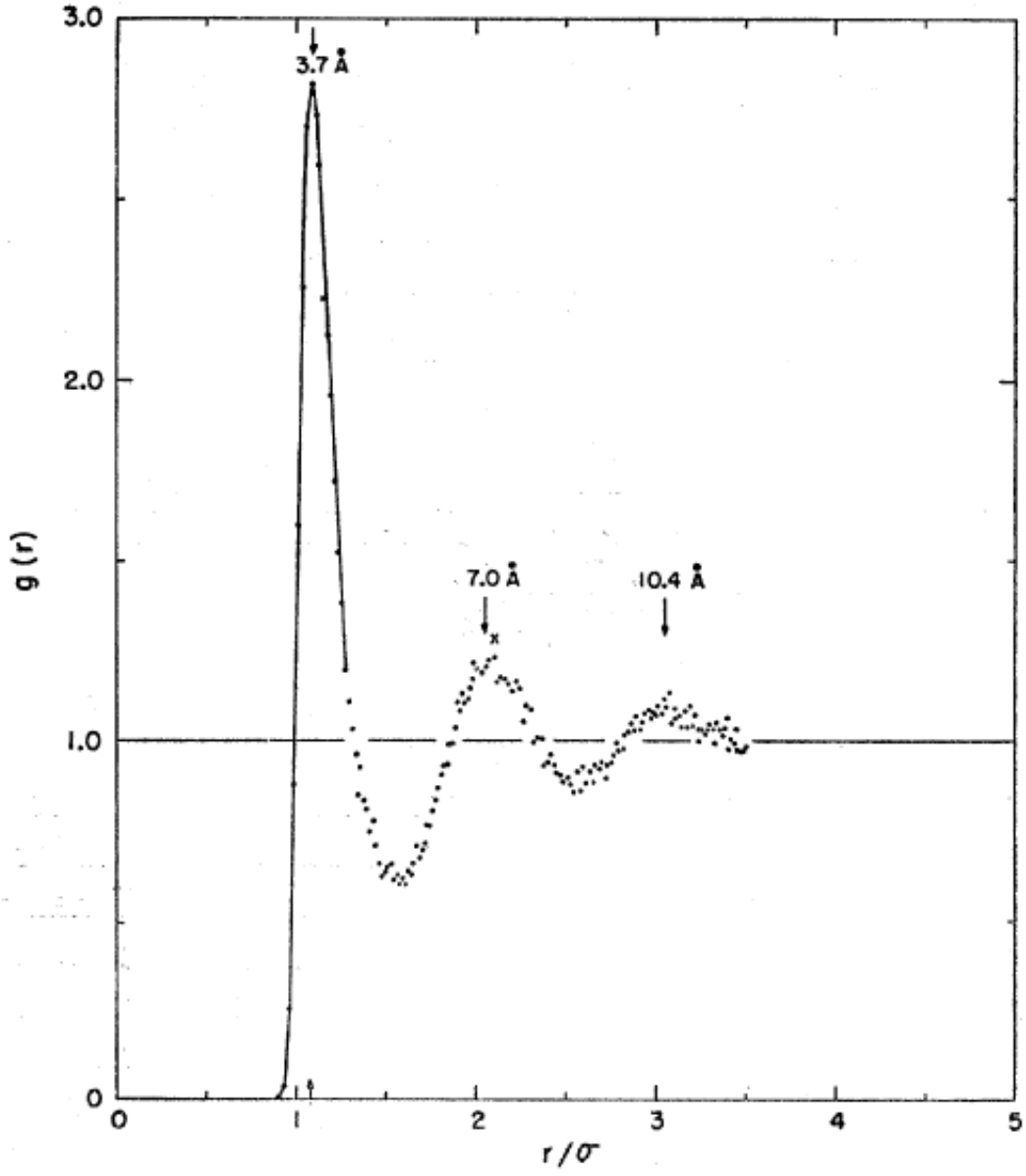
Method of calculation

$$g(r_i) = \frac{1}{\rho_0} \underbrace{\frac{1}{N} \sum_{I=1}^{N}} \left[\frac{\langle n_i(I) \rangle}{4\pi r_i^2 \Delta r} \right]$$

average over
all atoms I

- Average over all atoms I as possible origin
- Use $\rho_0 = \frac{N-1}{V}$ so that $\lim_{r \to \infty} g(r) = 1$
- Average over all configurations $\langle \ldots \rangle$

Pair correlation function of Lennard-Jones liquid

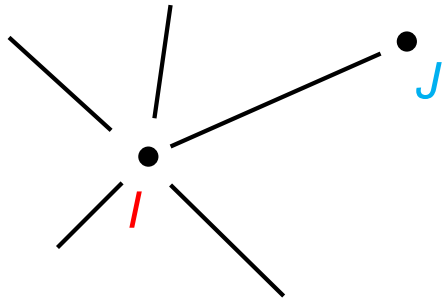


Relation with structure factor

Density with respect to atom I

$$\rho_I(r) = \left\langle \sum_{J \neq I} \delta(\vec{r} - (\vec{r}_J - \vec{r}_I)) \right\rangle$$

$$= \left\langle \sum_{J} \delta(\vec{r} - (\vec{r}_J - \vec{r}_I)) \right\rangle - \delta(r)$$



Density averaged over all atoms I

$$\rho(r) = \frac{1}{N} \sum_{I} \rho_I(r)$$

$$= \frac{1}{N} \left\langle \sum_{IJ} \delta(\vec{r} - (\vec{r}_J - \vec{r}_I)) \right\rangle - \delta(r)$$

Pair correlation function

$$g(r) = \frac{\rho(r)}{\rho_0}$$

Relation with structure factor

We have obtained:

$$\rho_0\, g(r) = \frac{1}{N} \left\langle \sum_{IJ} \delta(\vec{r} - (\vec{r}_J - \vec{r}_I)) \right\rangle - \delta(r)$$

$$\rho_0\, (g(r) - 1) = \frac{1}{N} \left\langle \sum_{IJ} \delta(\vec{r} - (\vec{r}_J - \vec{r}_I)) \right\rangle - \rho_0 - \delta(r)$$

We now apply a Fourier transform:

$$\rho_0 \int [g(r) - 1]\, e^{-i\vec{Q}\cdot\vec{r}}\, d\vec{r} = \underbrace{\frac{1}{N} \sum_{IJ} \left\langle e^{-i\vec{Q}\cdot(\vec{r}_J - \vec{r}_I)} \right\rangle - N\, \delta_{\vec{Q}0}}_{\text{structure factor } S(\vec{Q})} - 1$$

Relation with structure factor

$$S(Q) = 1 + \rho_0 \int [g(r) - 1]\, e^{-i\vec{Q}\cdot\vec{r}}\, d\vec{r}$$

$$\rho_0 [g(r) - 1] = \frac{1}{(2\pi)^3} \int [S(Q) - 1]\, e^{i\vec{Q}\cdot\vec{r}}\, d\vec{Q} \qquad \text{(inverse Fourier)}$$

Corresponding expressions with radial integrations

$$\int e^{i\vec{Q}\cdot\vec{r}}\, d\Omega = 2\pi \int_{-1}^{1} e^{iQr\cos\theta}\, d\cos\theta = 4\pi \frac{\sin Qr}{Qr}$$

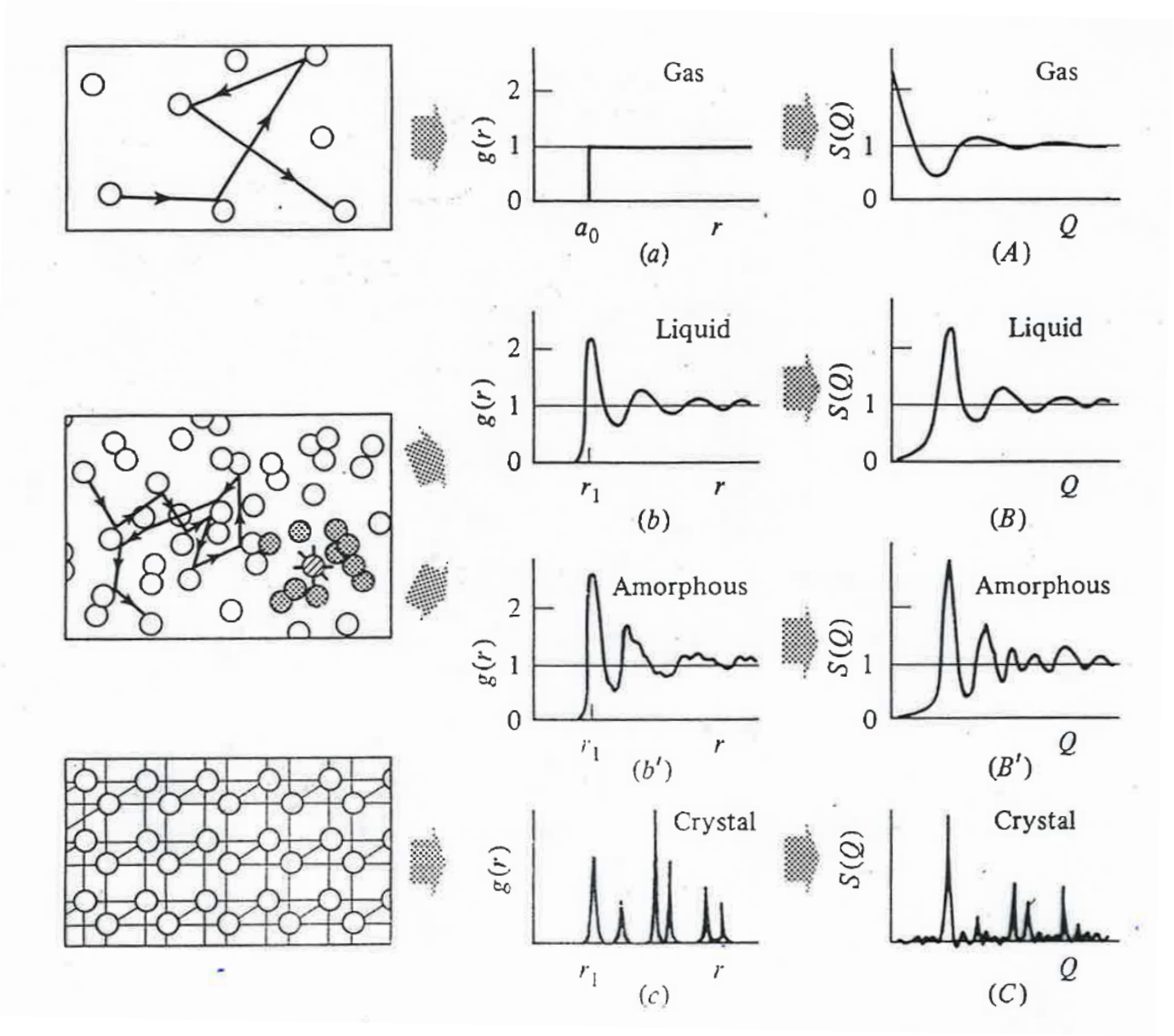
$$S(Q) = 1 + 4\pi\rho_0 \int_0^{\infty} [g(r) - 1] \frac{\sin Qr}{Qr} r^2\, dr$$

$$r\rho_0 [g(r) - 1] = \frac{1}{2\pi^2} \int_0^{\infty} [S(Q) - 1]\, Q \sin Qr\, dQ$$

Structure factor of Lennard-Jones liquid

Peaks in $S(\kappa)$	Rahman	Expt. X-rays
$\kappa_1\ \sigma$	6.8	6.8
$\kappa_2\ \sigma$	12.5	12.3
$\kappa_3\ \sigma$	18.5	18.4
$\kappa_4\ \sigma$	24.8	24.4

$g(r)$ and $S(Q)$ of various phases



Ar

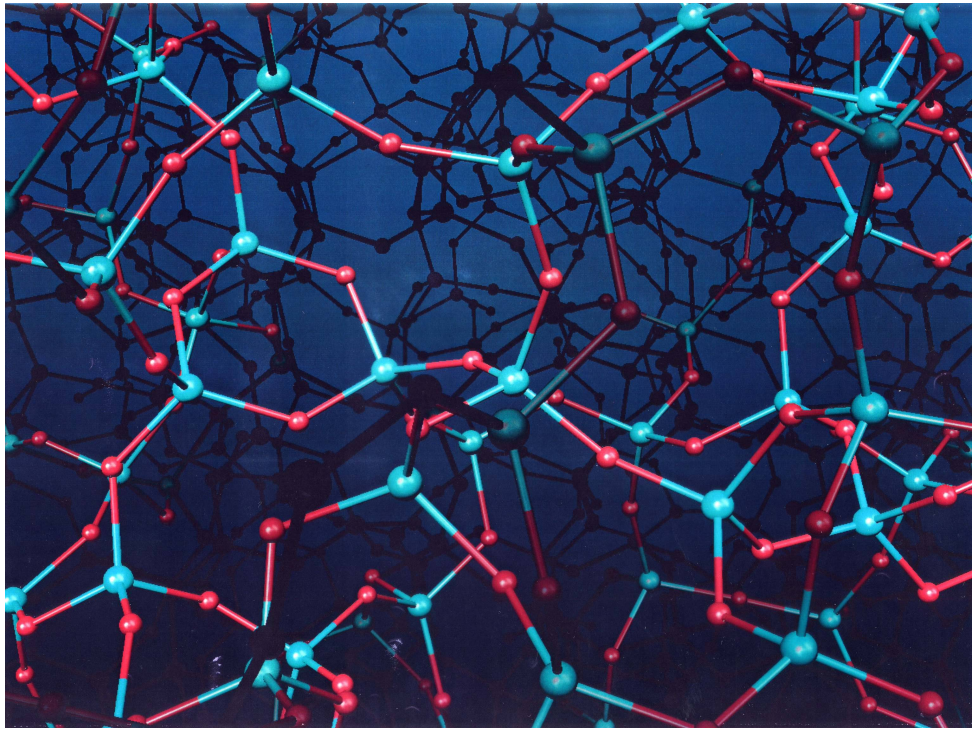
Ni

Ni

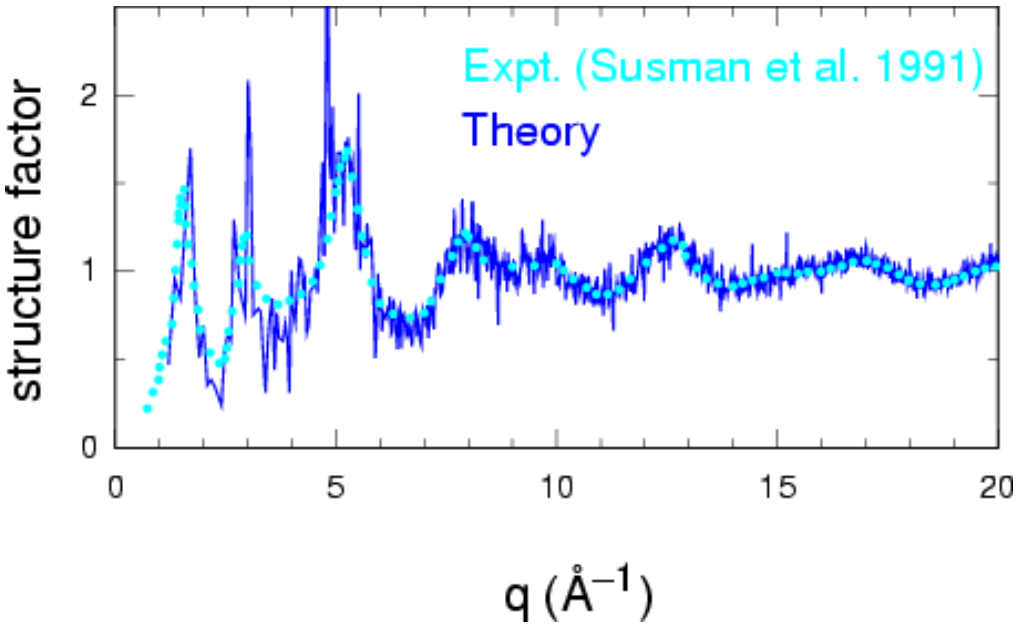
Al

The atomic structure of vitreous silica

Structural model
generated by *ab initio* MD

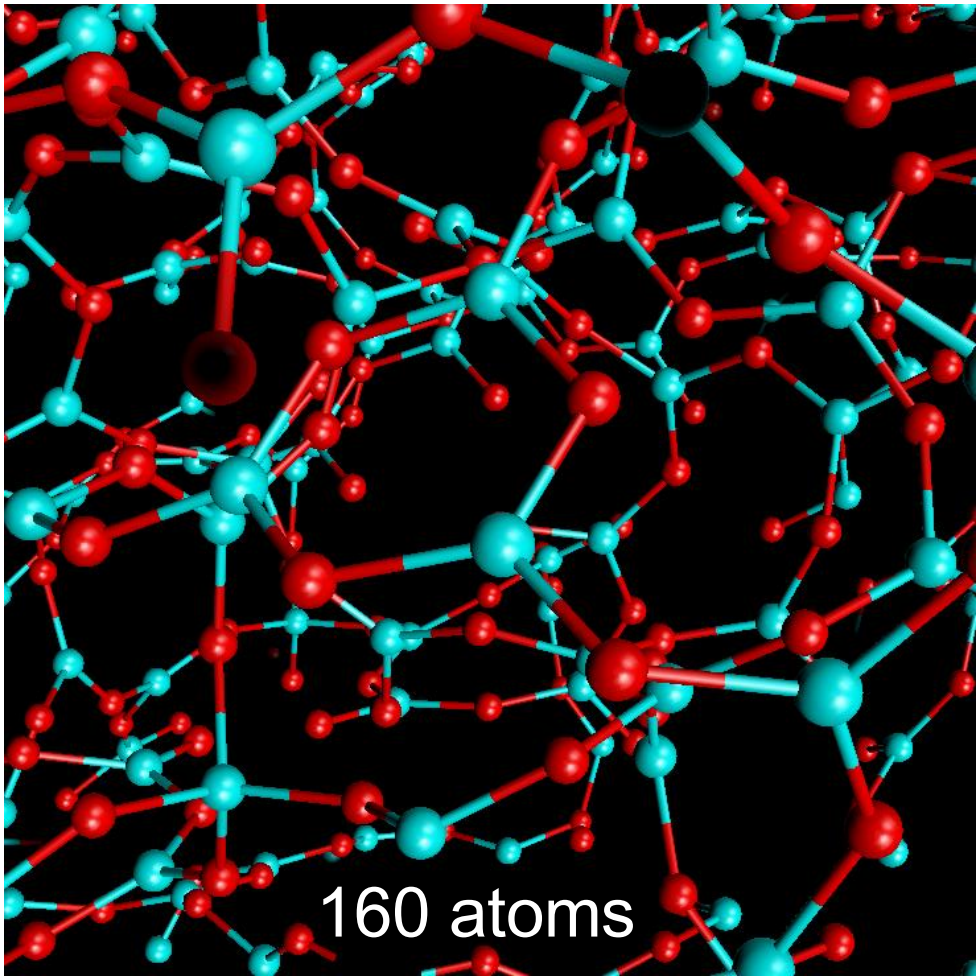


Neutron diffraction

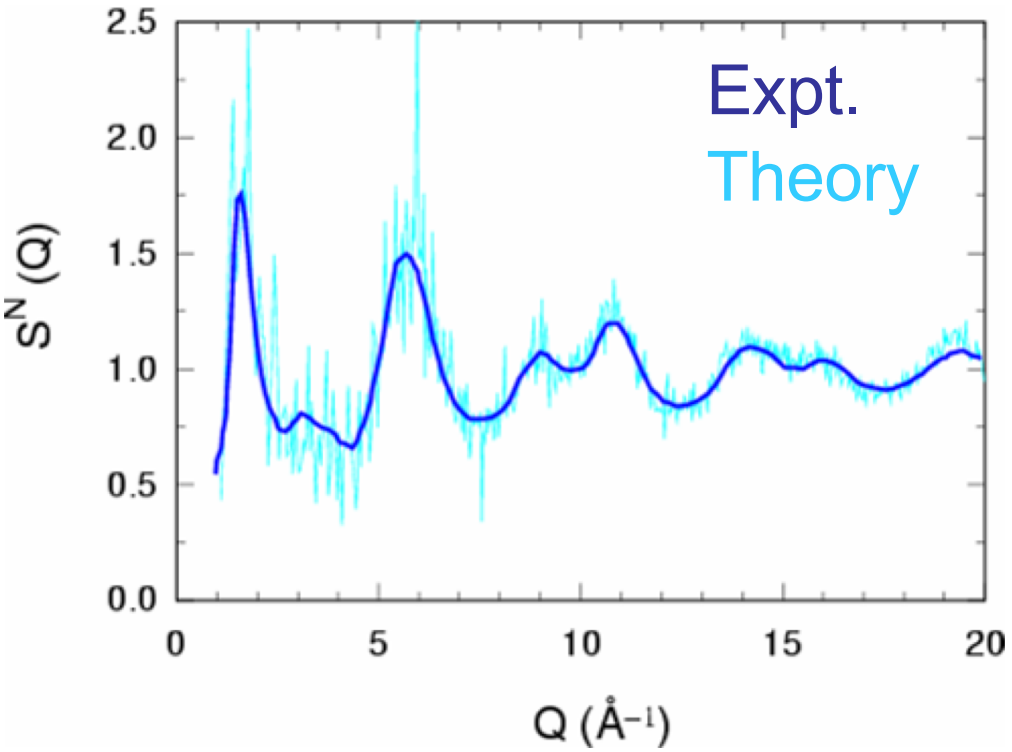


The atomic structure of vitreous B_2O_3

Model generated by *ab initio* MD



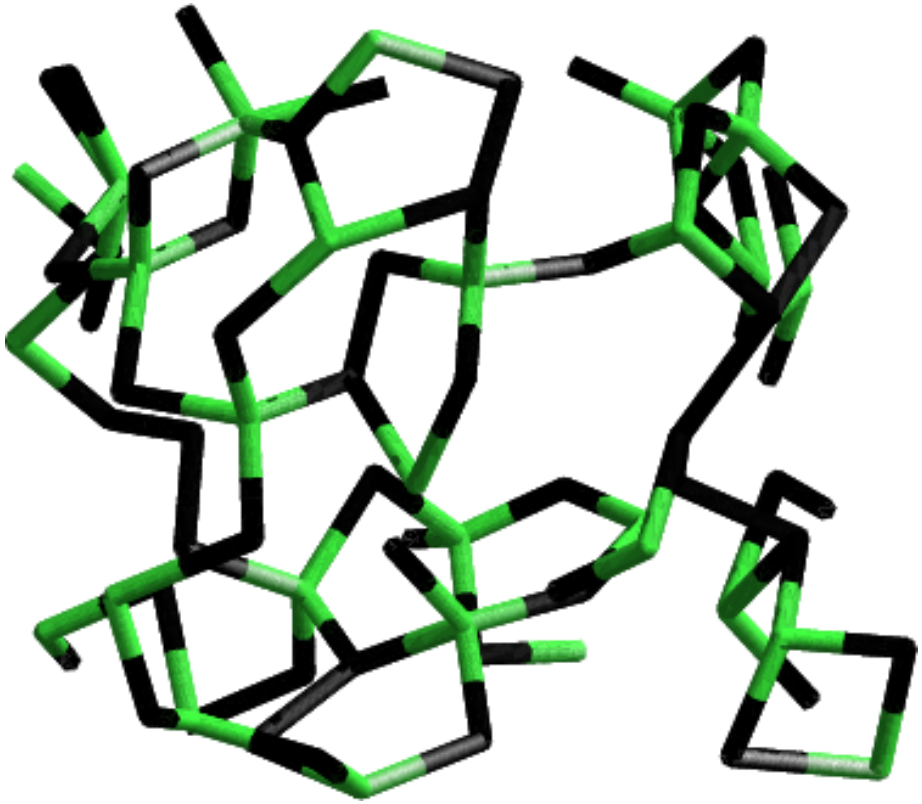
Neutron structure factor



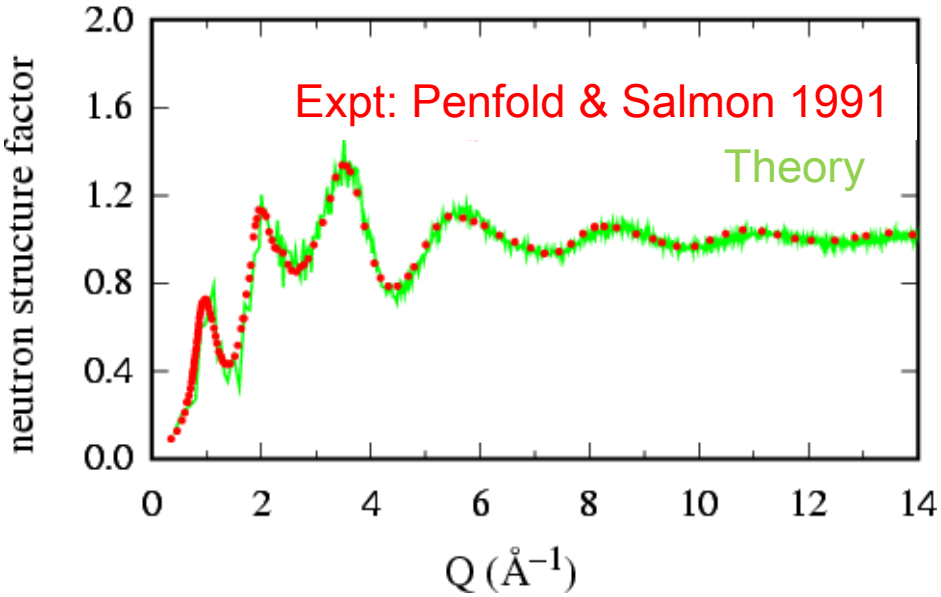
Expt: Hannon et al. 1994

The atomic structure of liquid $GeSe_2$

Snapshot of the liquid
generated by *ab initio* MD



Neutron structure factor



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