The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

1866-16

School on Pulsed Neutrons: Characterization of Materials

15 - 26 October 2007

Glasses & Amorphous Materials

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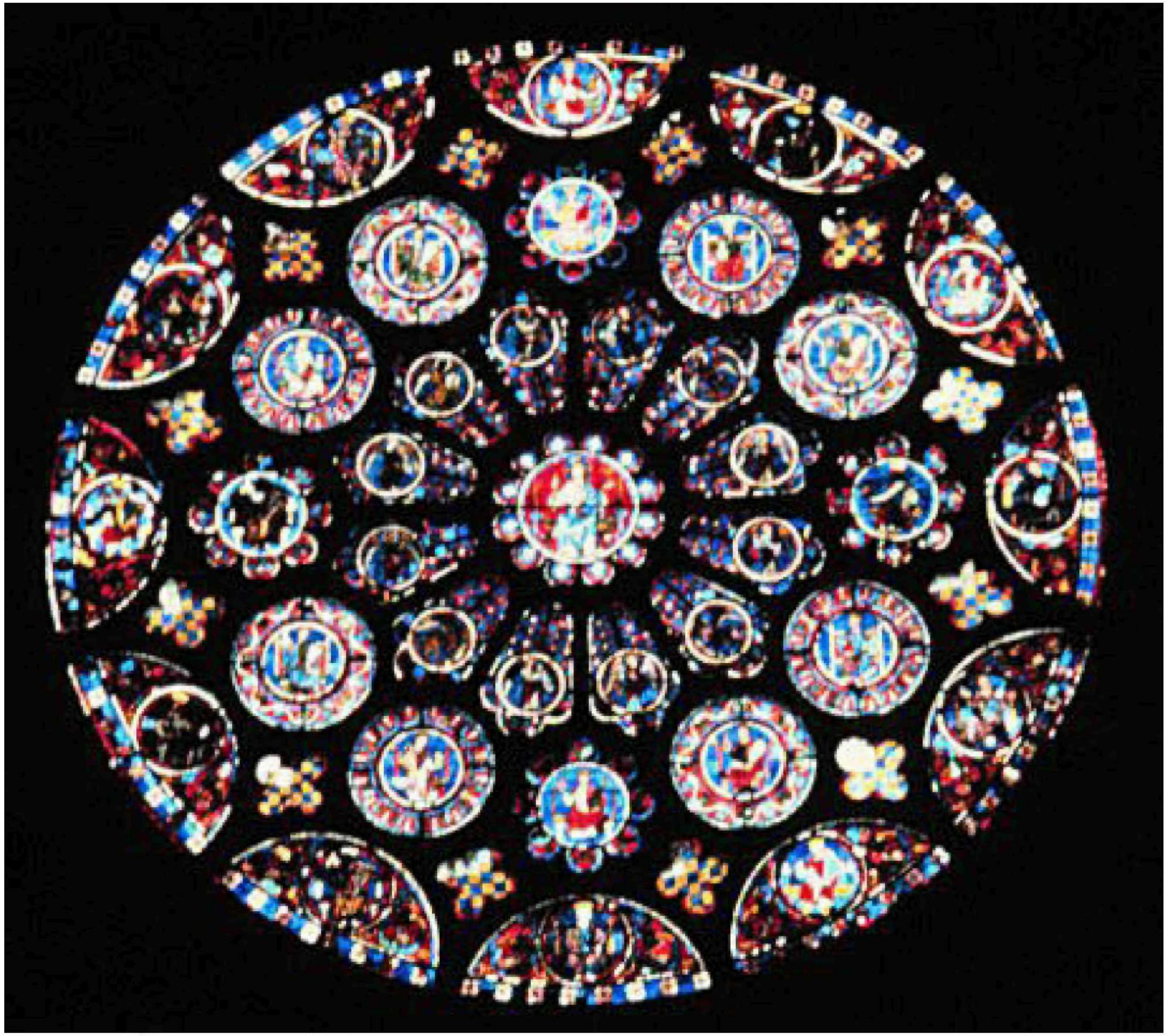
The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. This could be the next breakthrough in the coming decade. The solution of the problem of spin glass in the late 1970s had broad implications in unexpected fields like neural networks, computer algorithms, evolution, and computational complexity. The solution of the more important and puzzling glass problem may also have a substantial intellectual spin-off. Whether it will help make better glass is questionable."

P. W. Anderson [*Science* **1995**, *267*, 1615]

ISIS

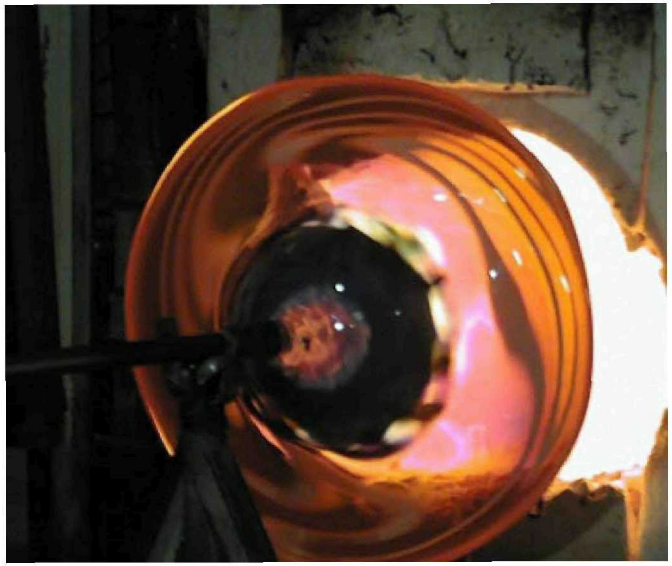
What is a Glass?



ISIS

What is Glass?

A supercooled liquid?



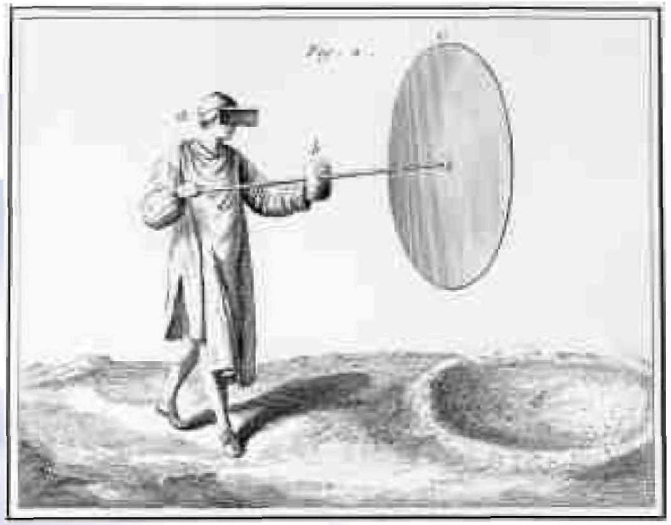
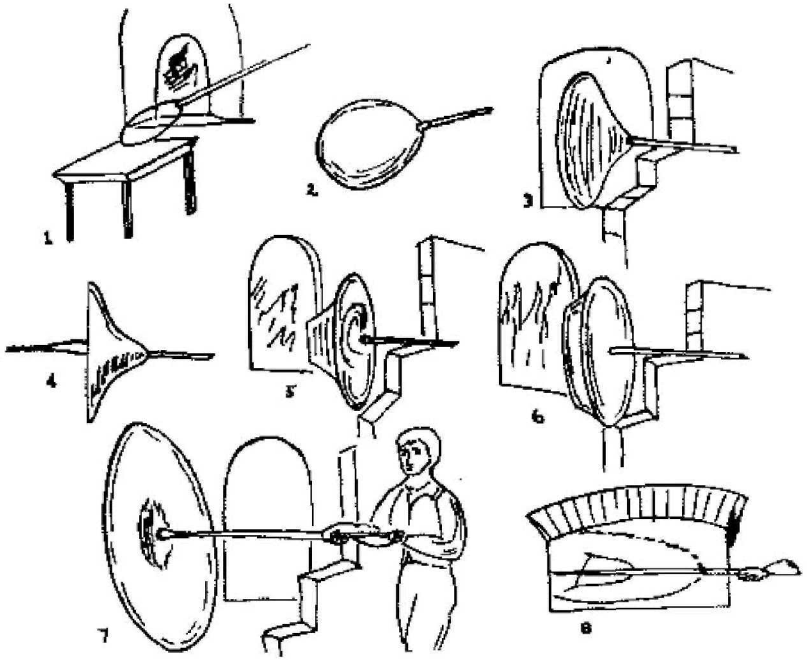
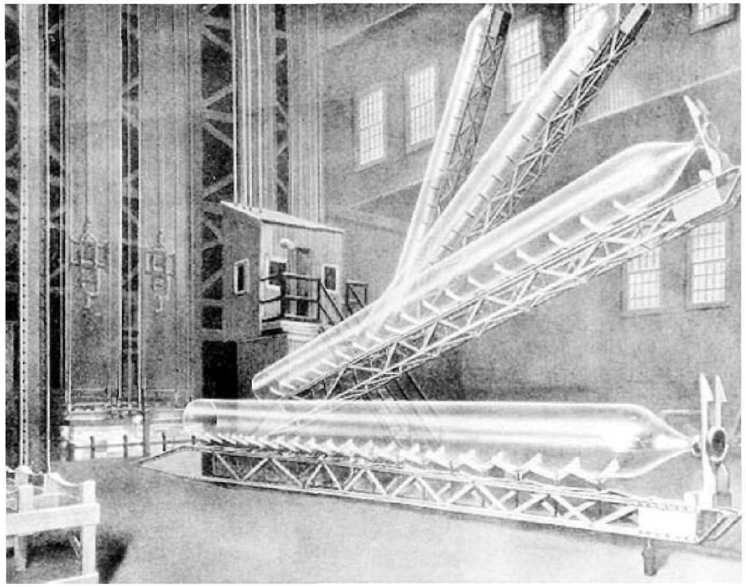


FIG. 48 Method of making crown glass. A large bubble was blown, a pontil rod was attached opposite the blowpipe, and the blowpipe was cracked off, leaving a hole in the bubble. The bubble was then reheated and twirled several times so that it became flat and disk-shaped. The disk was cooled and cut into panes of glass. (*Photo by The Corning Museum of Glass; illustration copied from K. M. Wilson's drawing in* Glass in New England, *an Old Sturbridge Village booklet*)





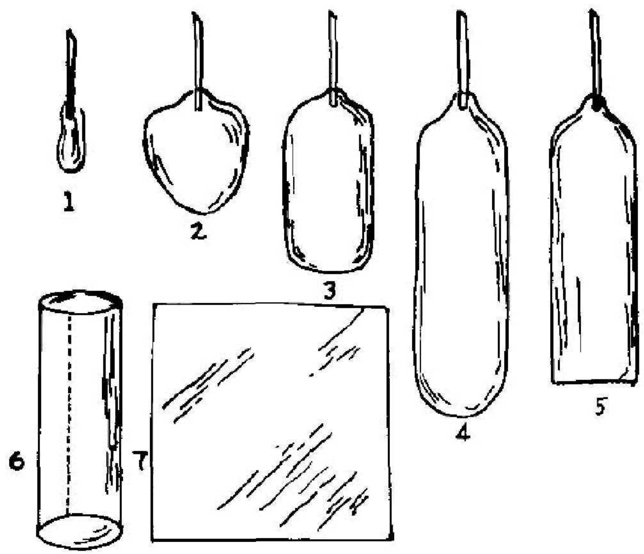
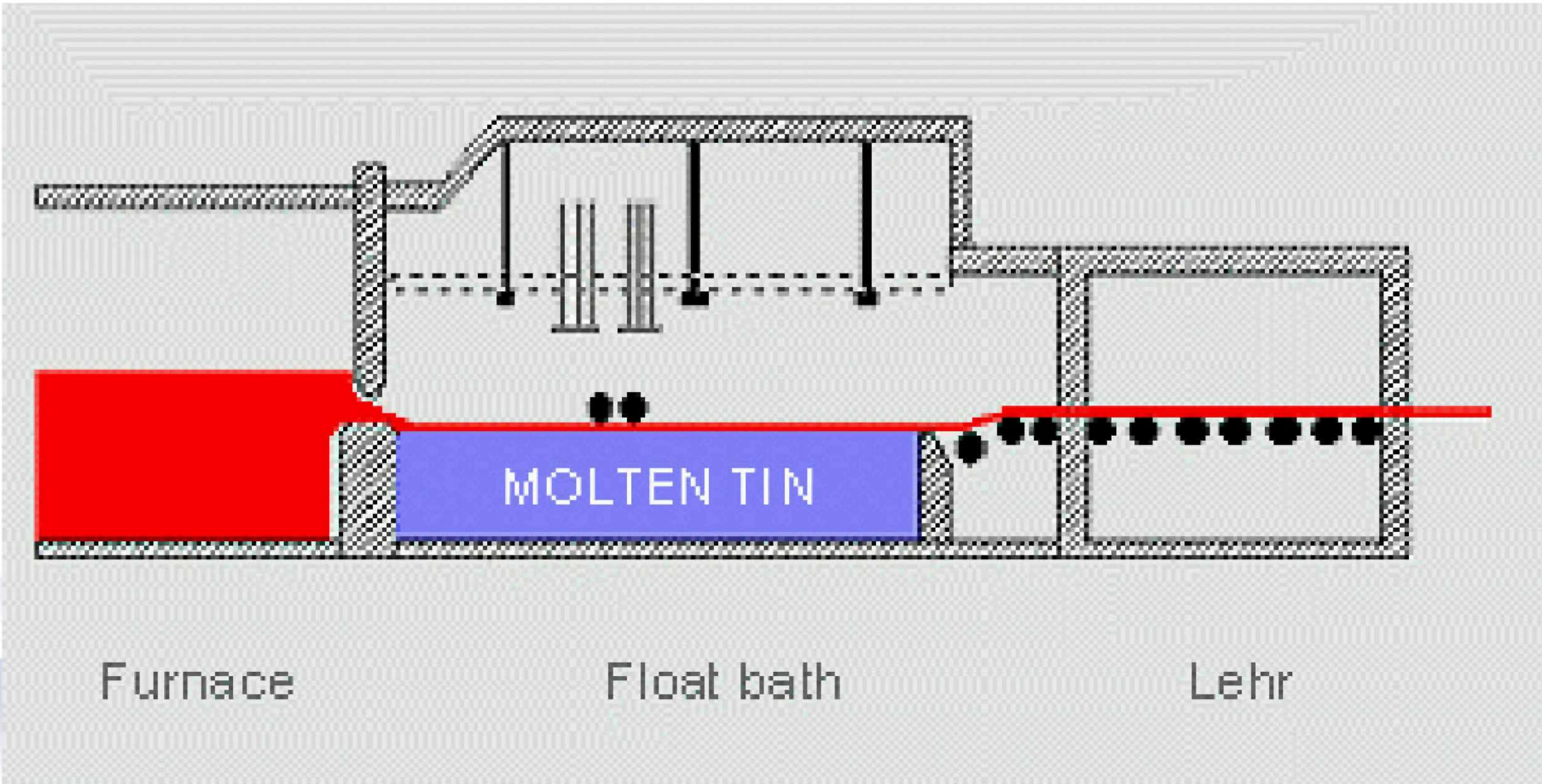


FIG. 41 Steps in the process of making window glass by the cylinder-glass method. A cylinder about five feet long and one foot in diameter was blown; then the end was cut off, the blowpipe was cracked off, and the cylinder was slit and opened out into a flat sheet. (*Photo by The Corning Museum of Glass, illustration copied from K. M. Wilson's drawing in* Glass in New England, *an Old Sturbridge Village booklet*)


MOLTEN TIN
Furnace
Float bath
Lehr

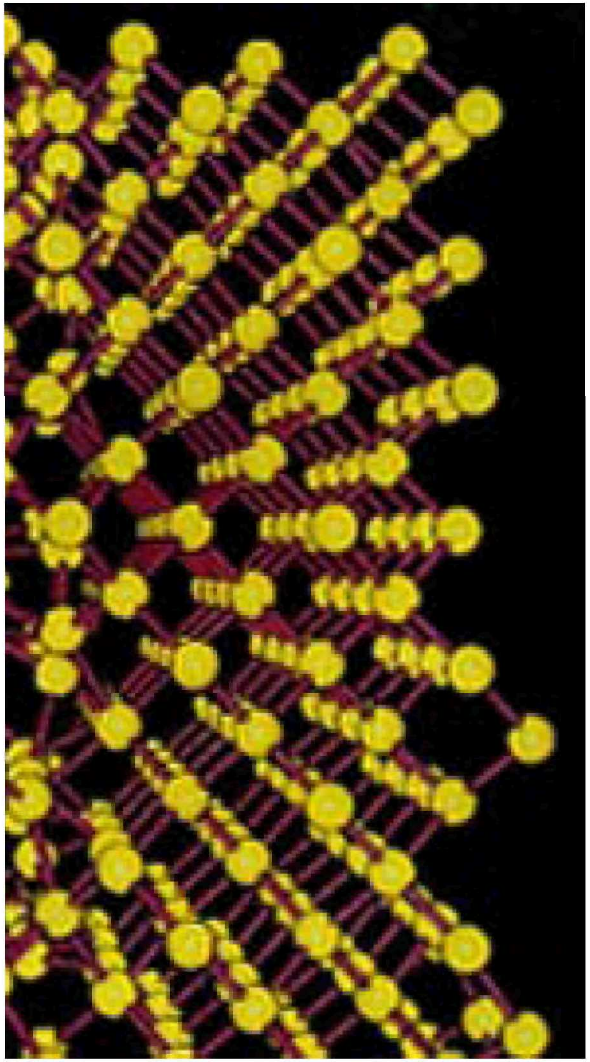
What is a Glass?

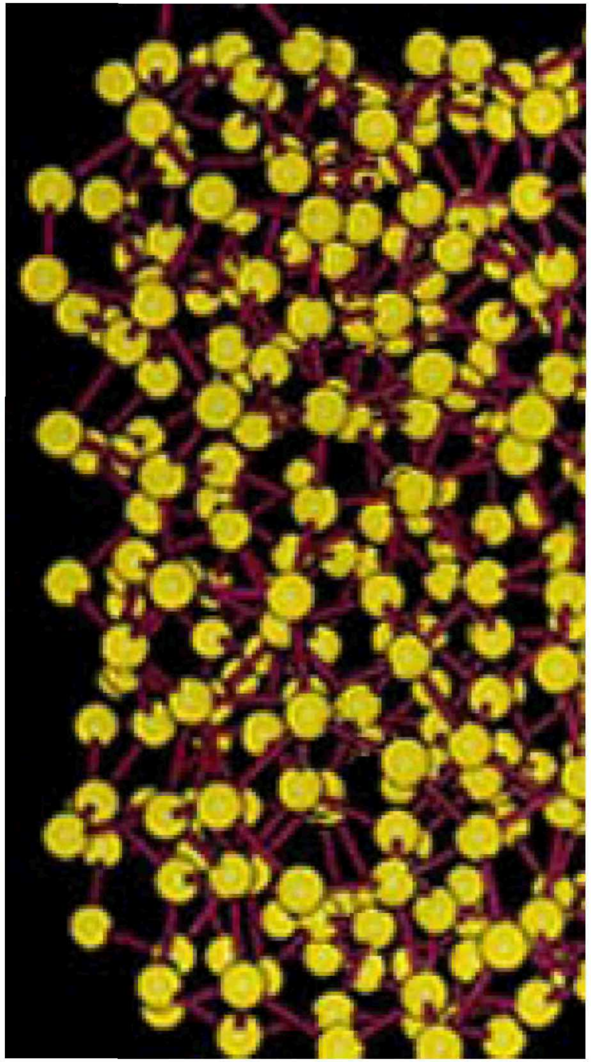
A glass is a non-ergodic state of matter which has become non-ergodic by virtue of the continuous slow-down of one or more of its degrees of freedom

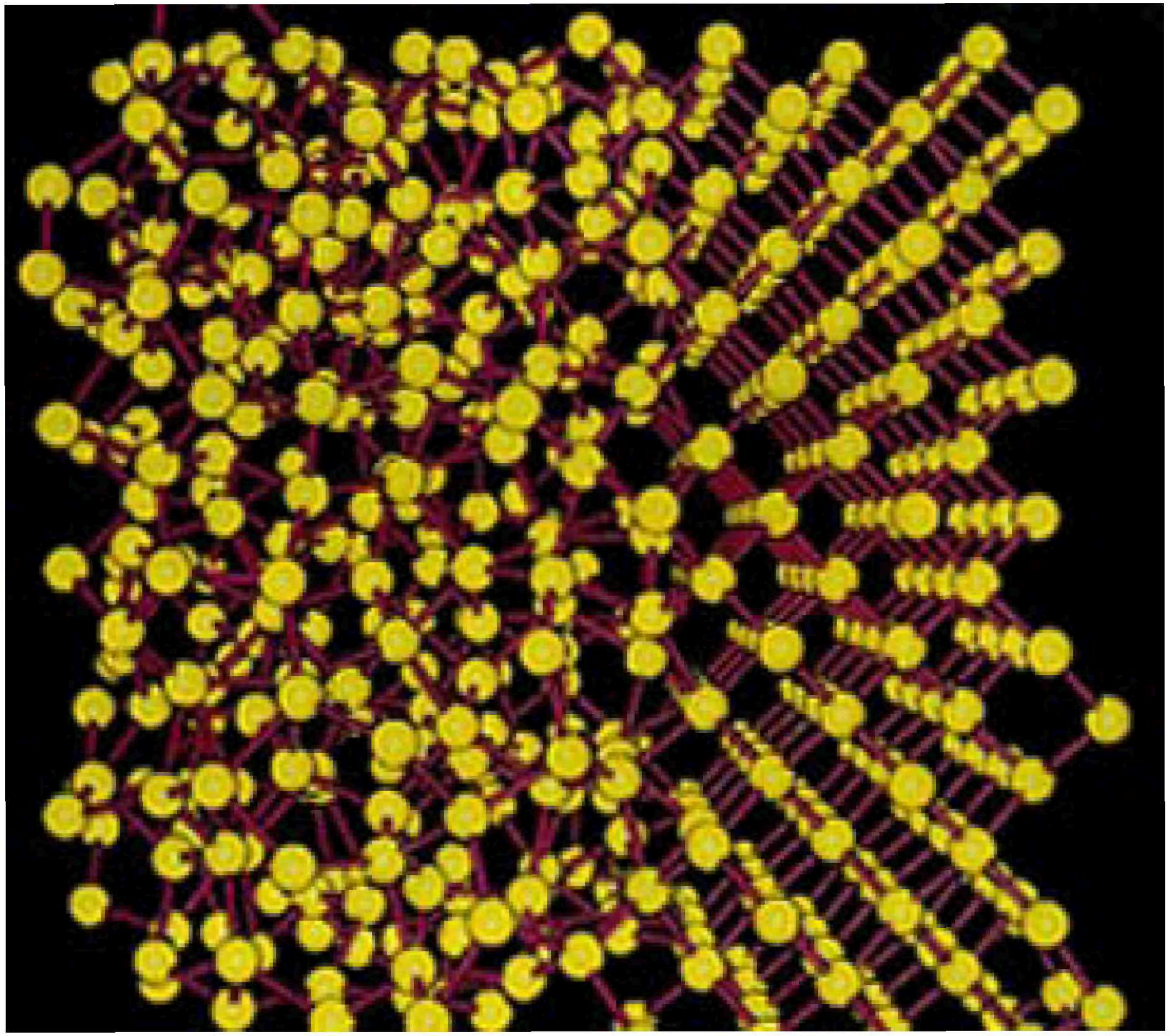
A structural glass is an amorphous solid which is capable of passing into the viscous liquid state, usually, but not necessarily, accompanied by an abrupt increase in heat capacity (the glass transition)

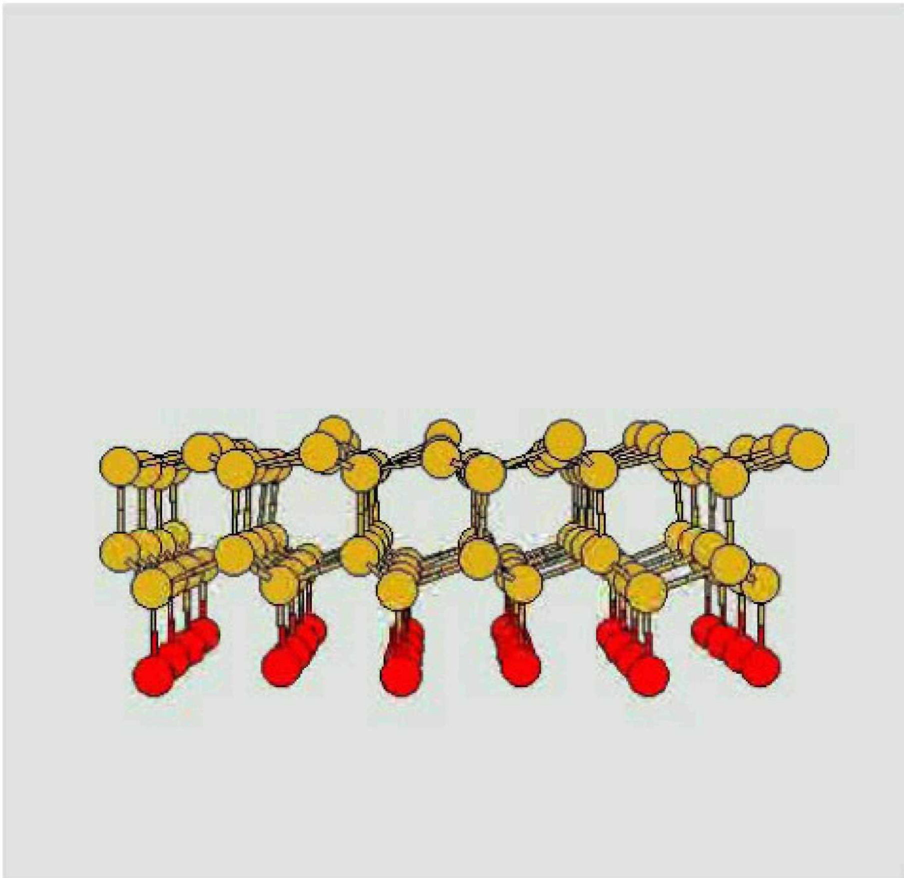
An amorphous solid is a solid which lacks long range (crystalline) order

ISIS



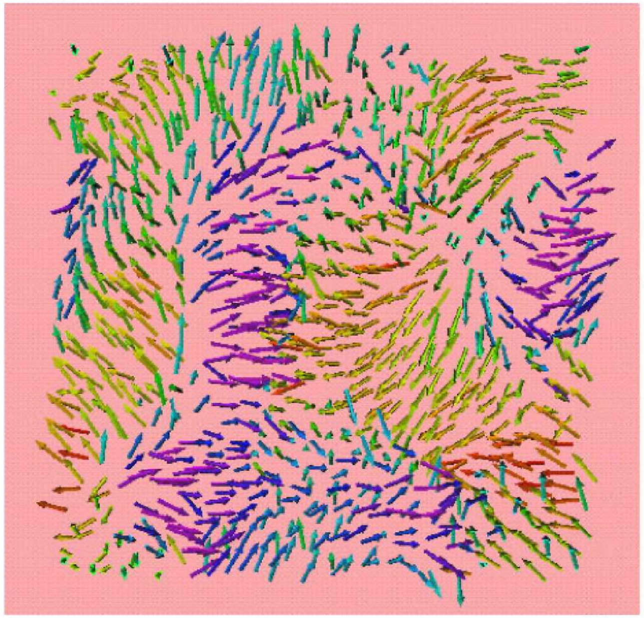






What is a Glass?

Structural glasses
Spin glasses
Orientational glasses
Vortex glasses

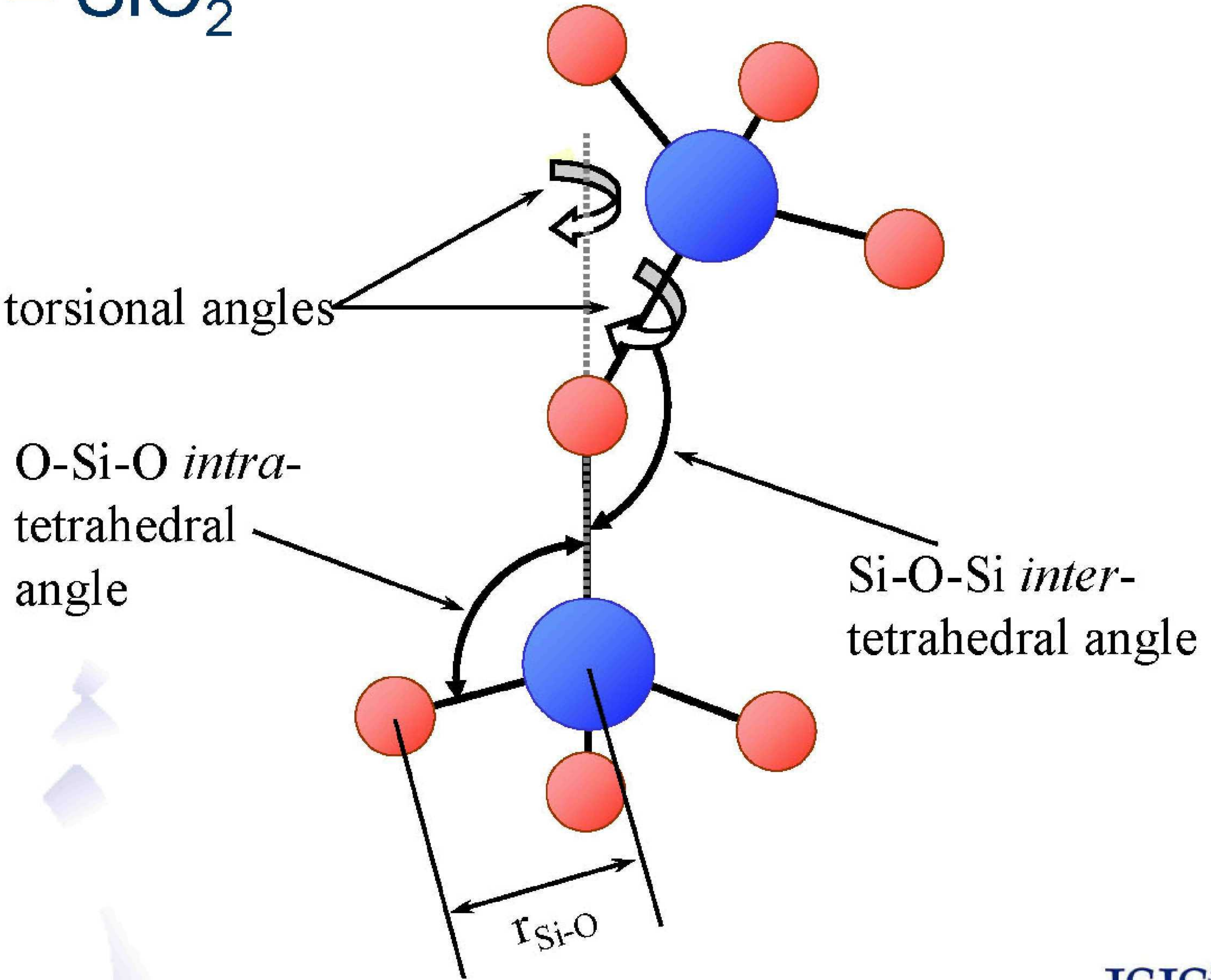


How can you make a Glass?

Rapid cooling of a liquid
Vapor deposition
Chemical vapor deposition
Solvent evaporation
Electrochemical deposition
In-situ liquid polymerisation reaction
Solid state diffusion controlled reaction
Hydrolysis of precursor organics and drying (sol-gel)
Cold compression of crystal
Cold compression of high-P stable crystal
Shock, irradiation or intense grinding of crystals

ISIS

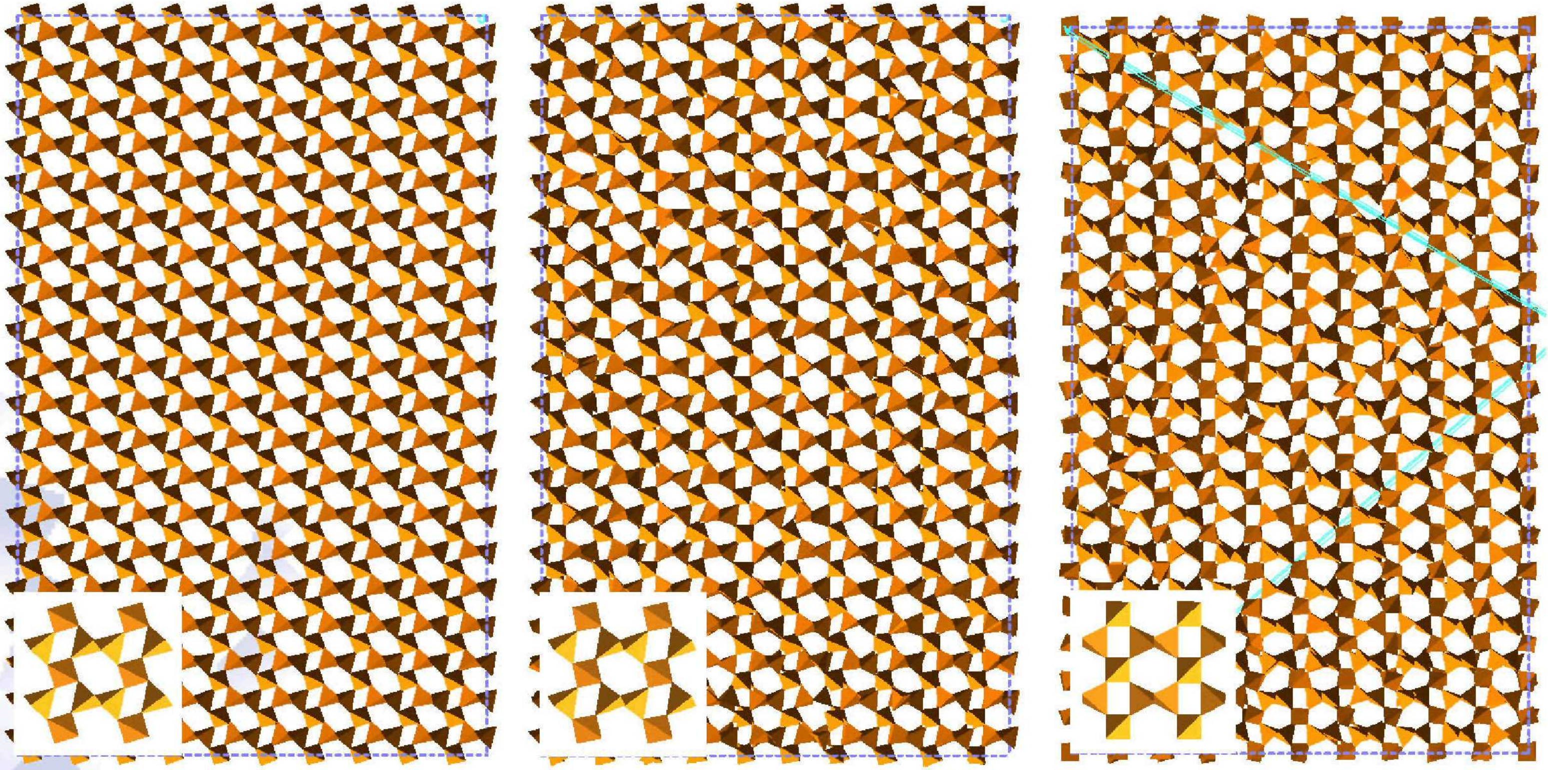
Silica – SiO_2

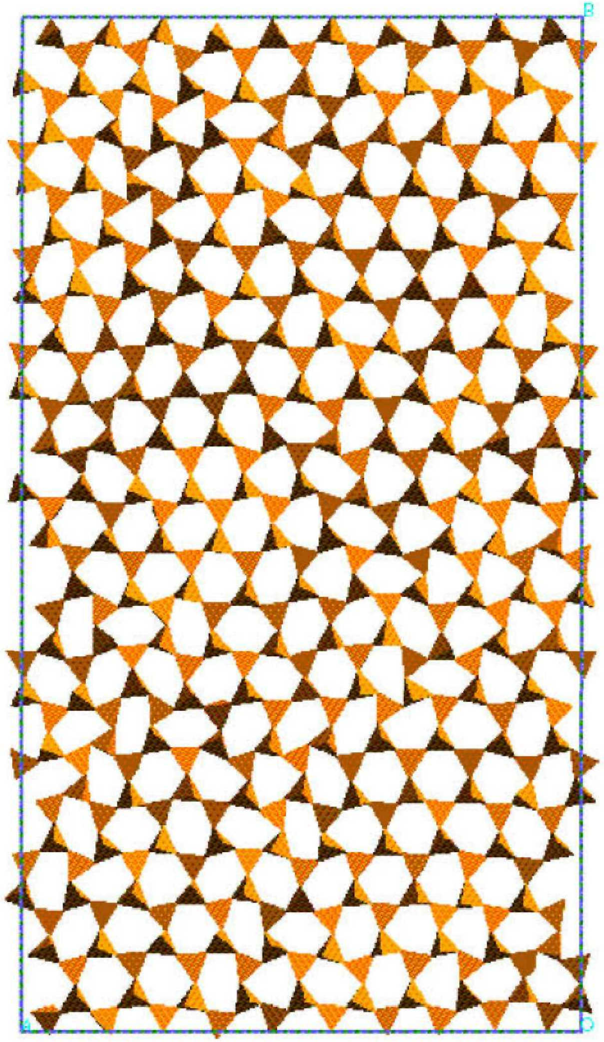


torsional angles
O-Si-O *intra*-
tetrahedral
angle
Si-O-Si *inter*-
tetrahedral angle
$r_{Si\text{-}O}$

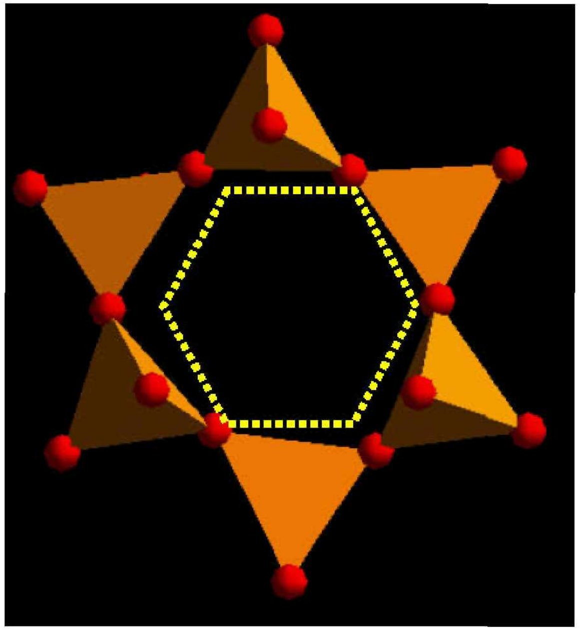
Quartz

20 K, α　　793 K, α　　1073 K, β

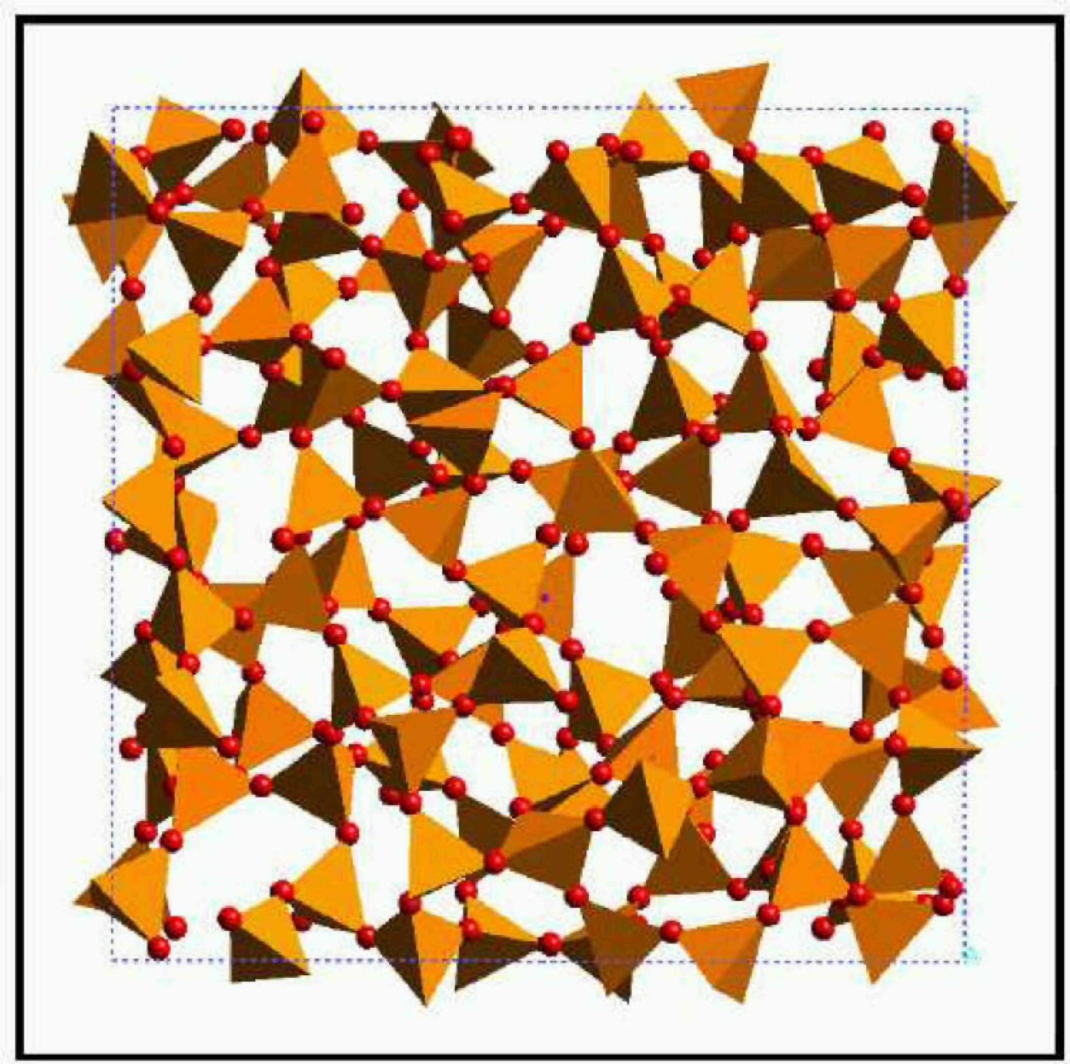


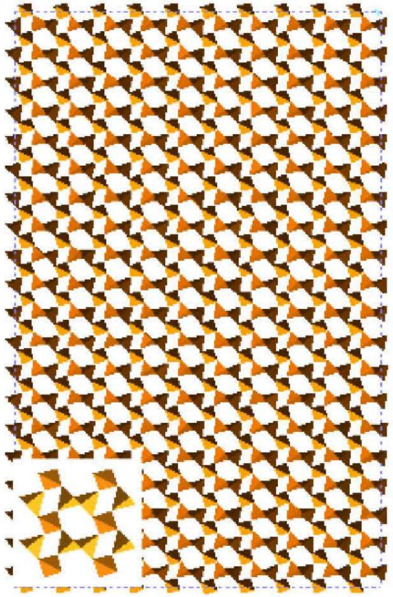


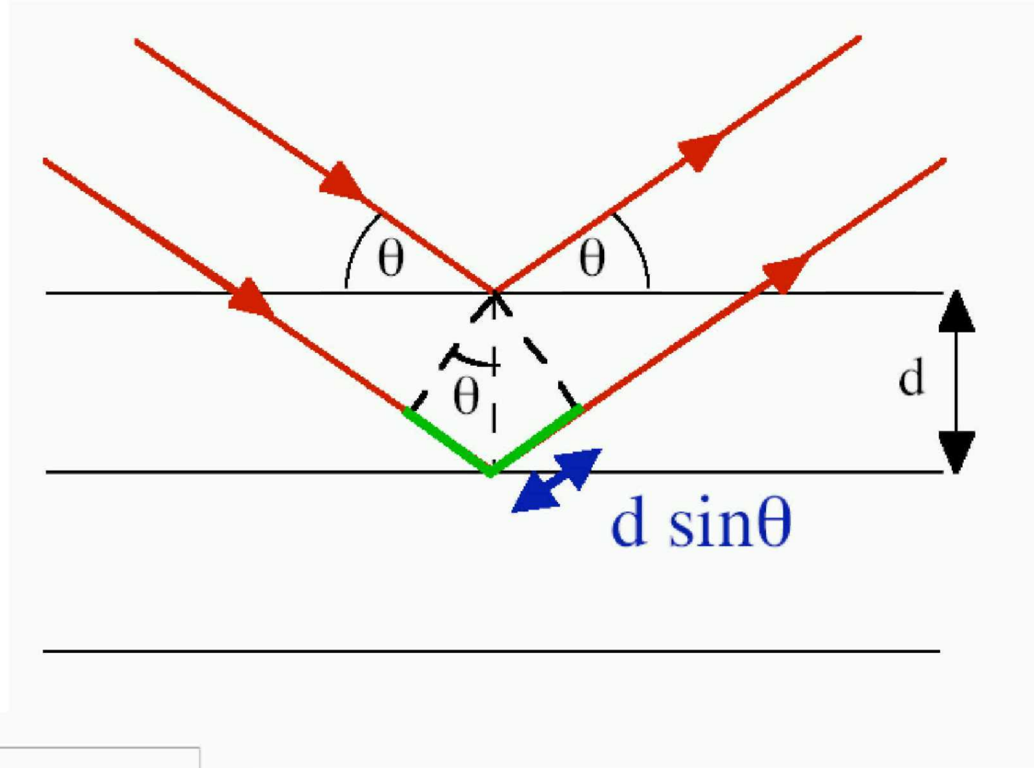
HP Tridymite
MD simulation

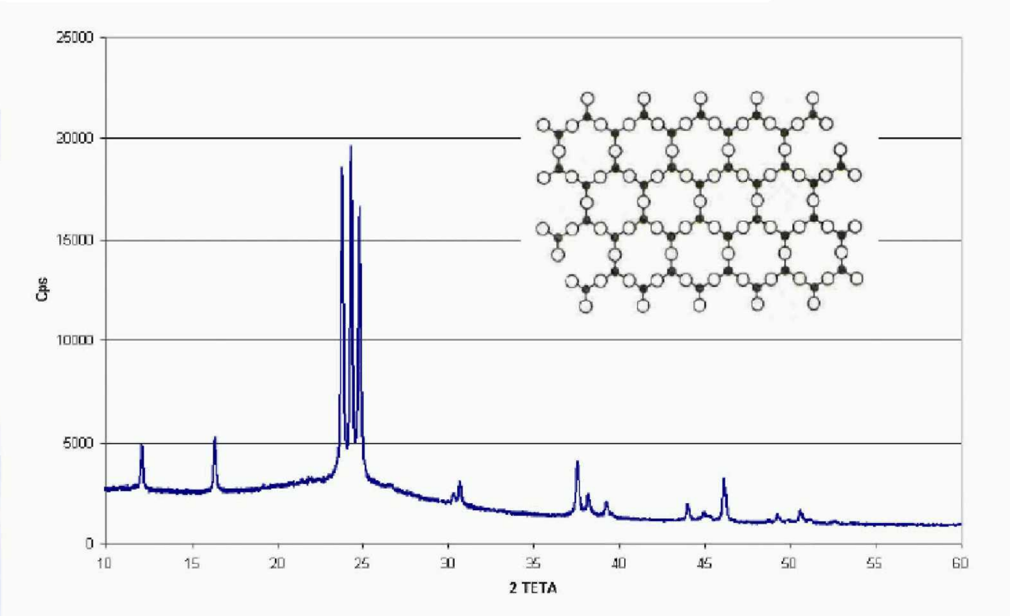


Vitreous silica

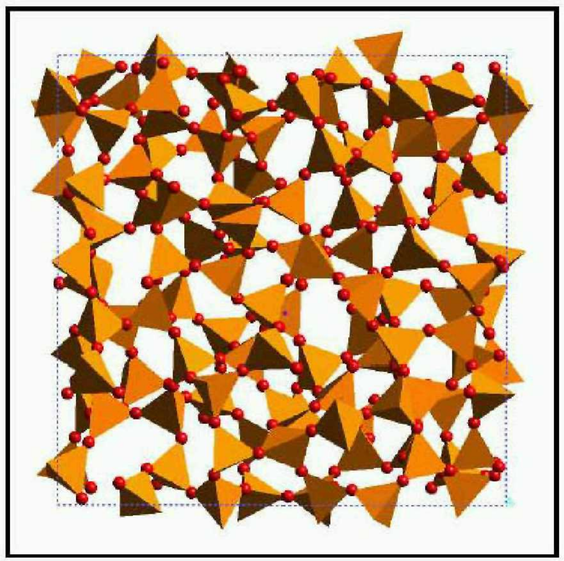


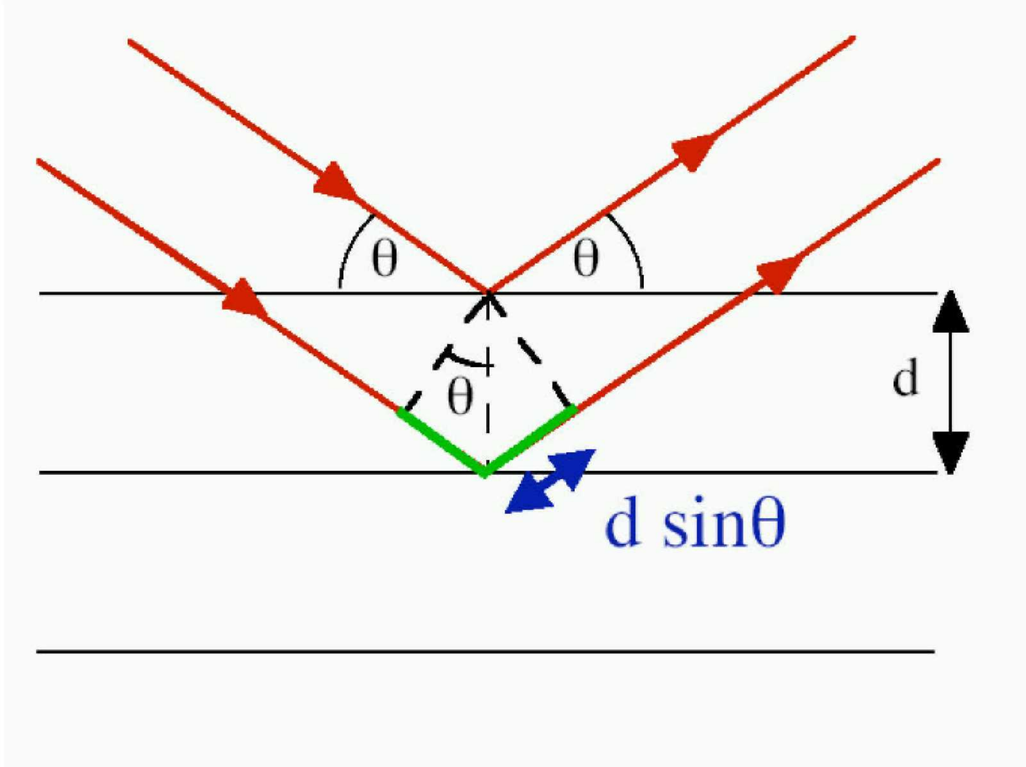




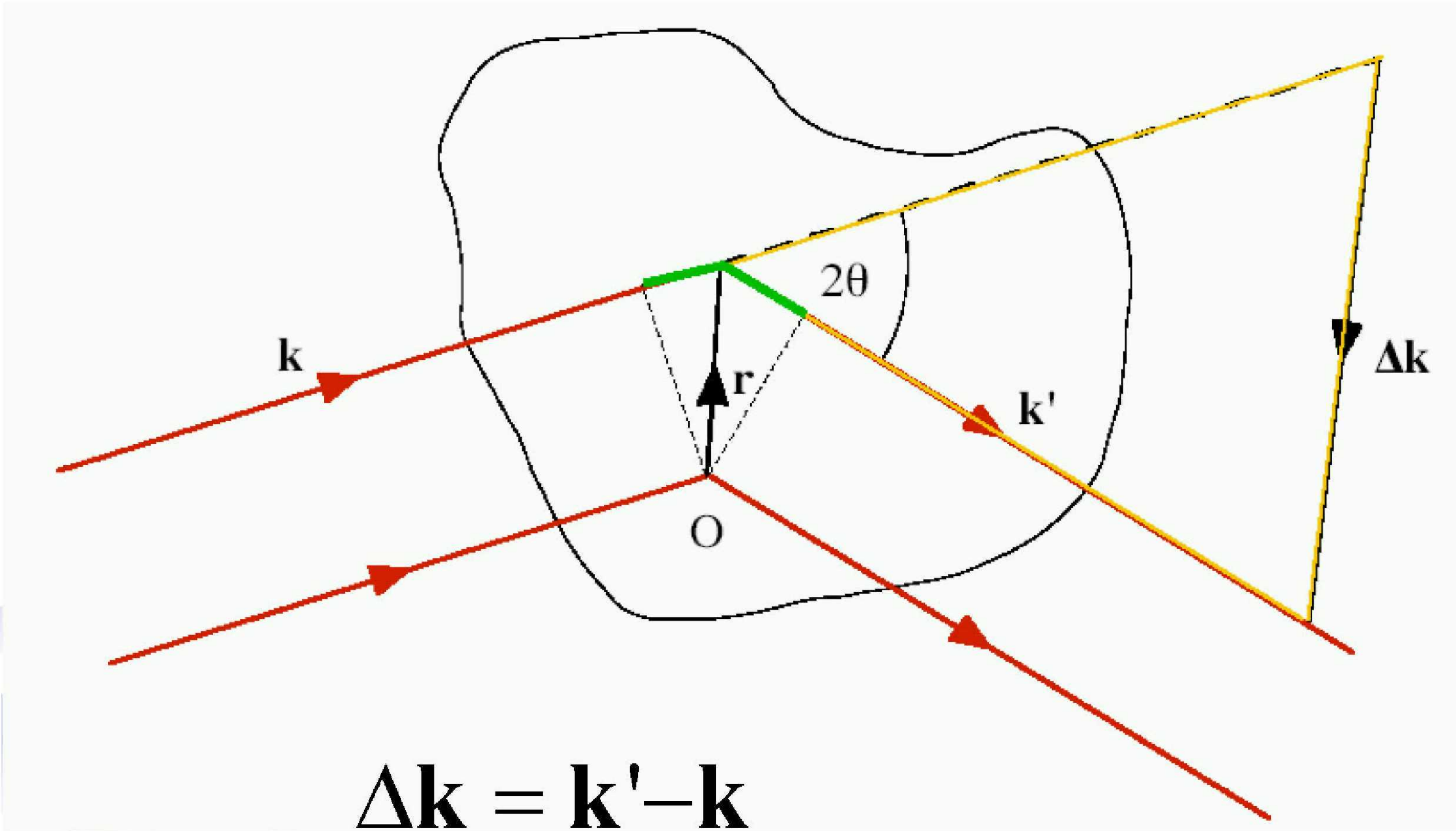


$$2d\sin\theta = n\lambda$$



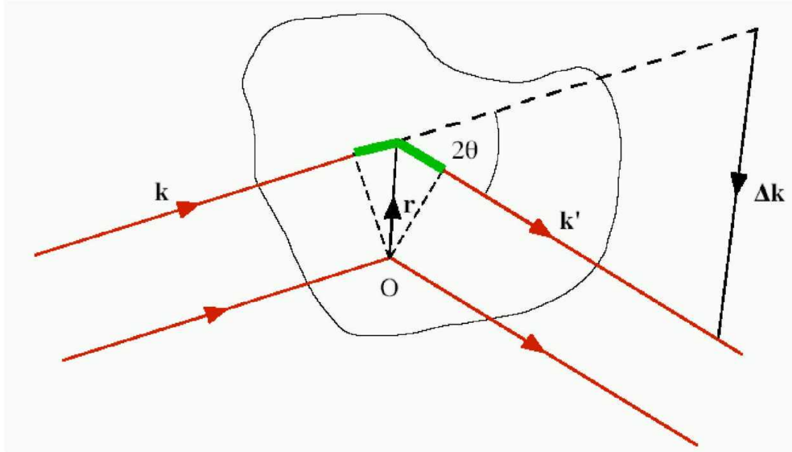

θ
θ
θ
d
d sinθ

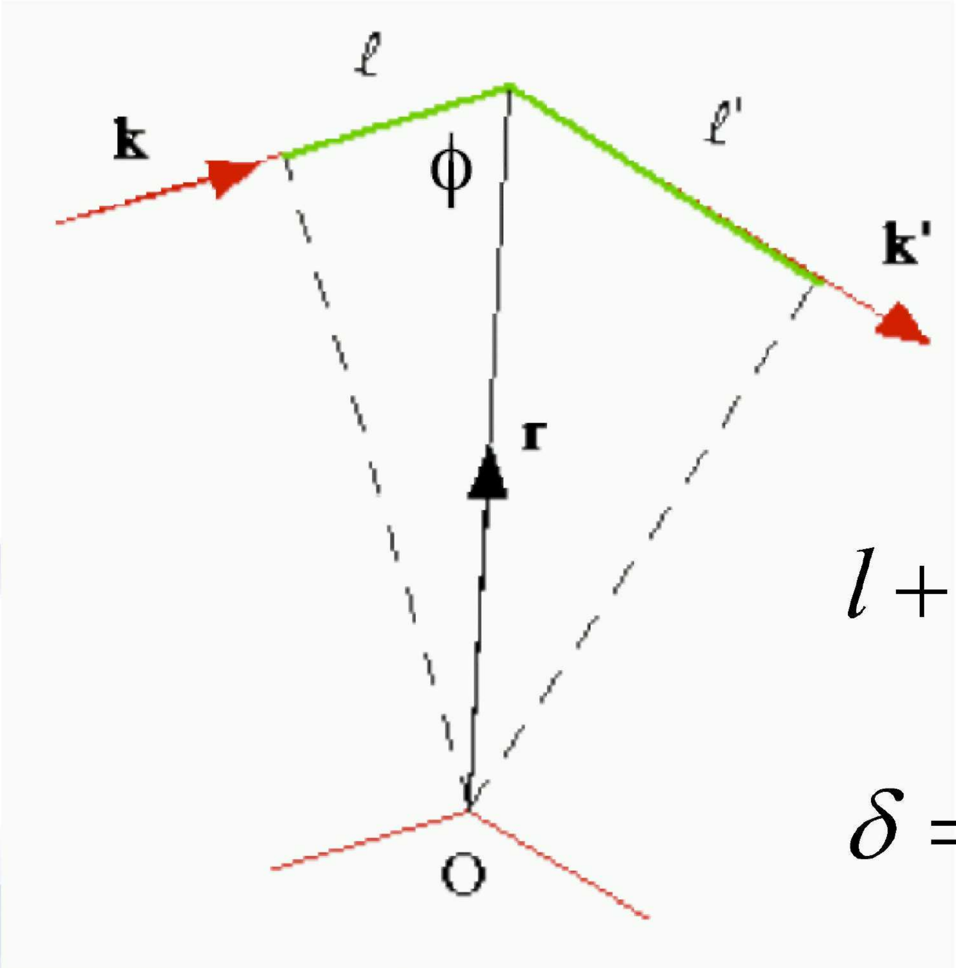
?



$$\Delta \mathbf{k} = \mathbf{k}' - \mathbf{k}$$

$$|\mathbf{k}| = |\mathbf{k}'|$$



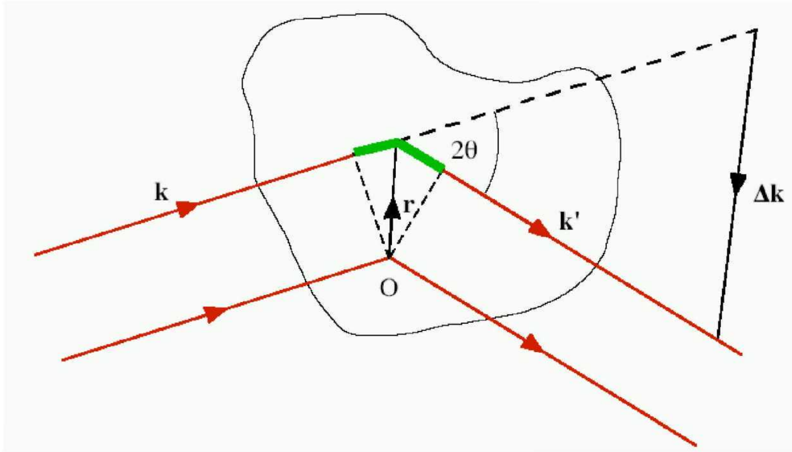


$$l + l' = \frac{\mathbf{k.r}}{|\mathbf{k}|} - \frac{\mathbf{k'.r}}{|\mathbf{k'}|}$$

$$\delta = k \times (l + l') = -\Delta\mathbf{k.r}$$

ISIS

$$A = \int n(\mathbf{r}) \exp(-i\Delta\mathbf{k}.\mathbf{r}) d\mathbf{r}$$



Constructive interference

$$\Delta\mathbf{k}.\mathbf{r} = 2n\pi$$

$$n(\mathbf{r}) = n(\mathbf{r}+\mathbf{T}) \qquad \mathbf{T} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

$$n(\mathbf{r}) = \sum n_{\mathbf{G}} \exp(i\mathbf{G}.\mathbf{r})$$

$$A = \int \sum n_{\mathbf{G}} \exp\big(i(\mathbf{G}-\Delta\mathbf{k}).\mathbf{r}\big) d\mathbf{r}$$

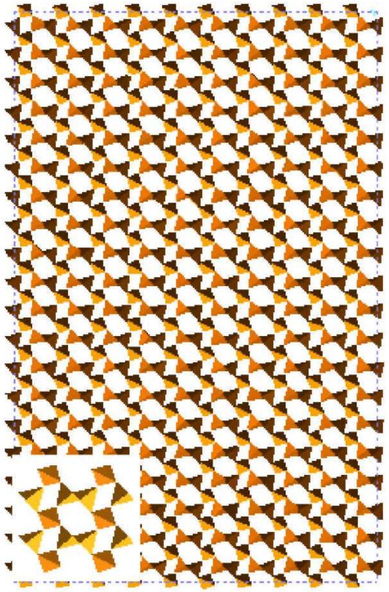
Constructive interference

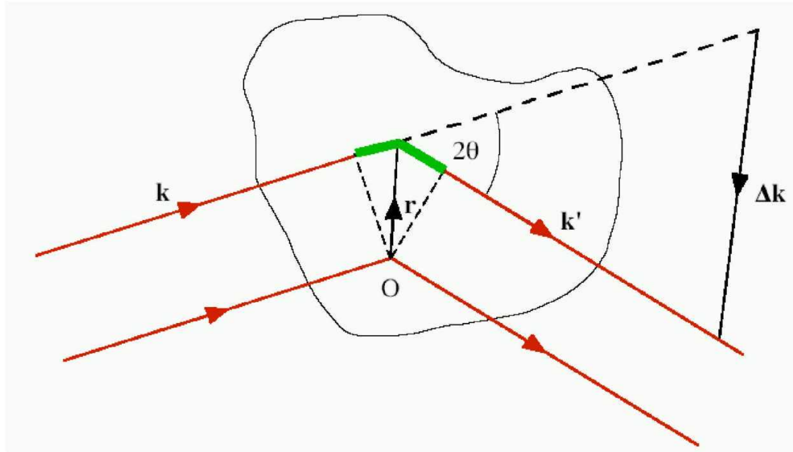
$$(\mathbf{G}-\Delta\mathbf{k}).\mathbf{r} = 2n\pi$$

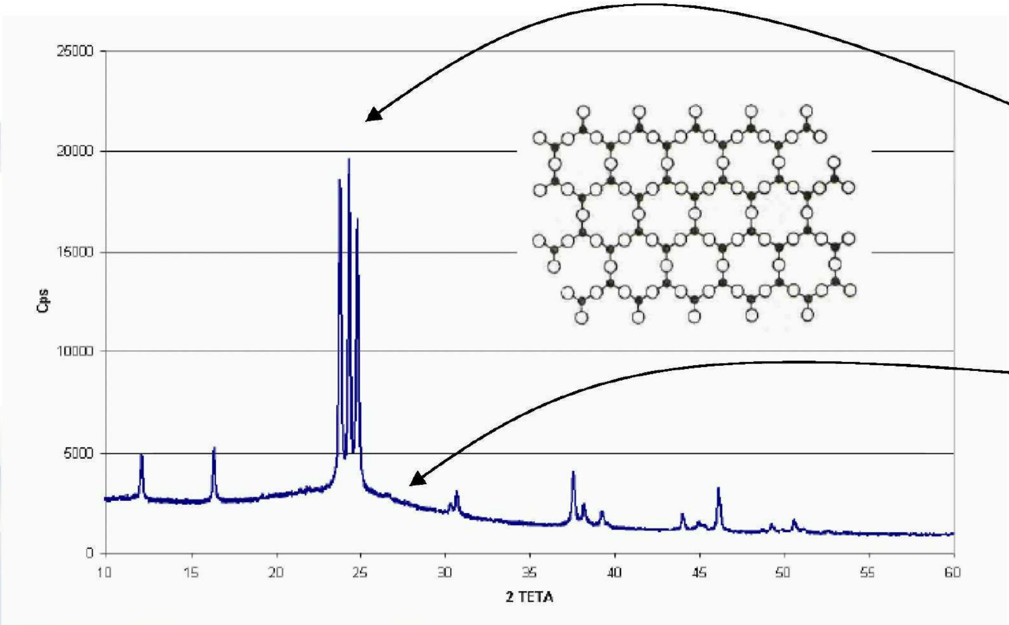
$$\mathbf{G} = \Delta\mathbf{k}$$

$$I = A^* A$$

ISIS

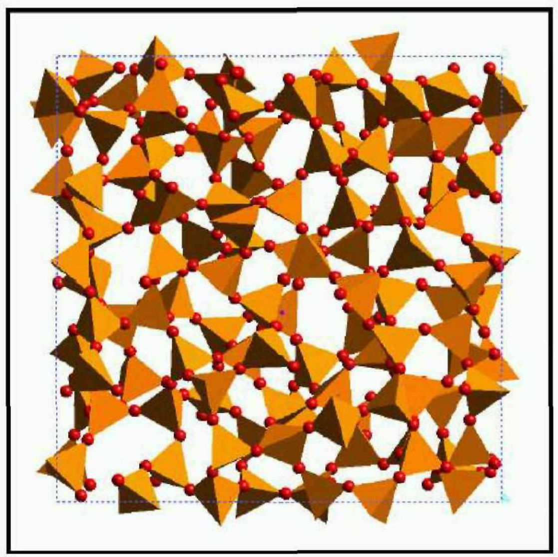


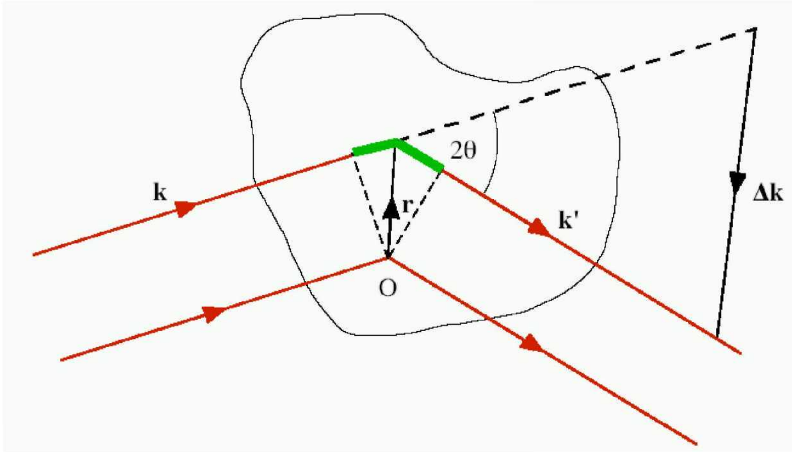




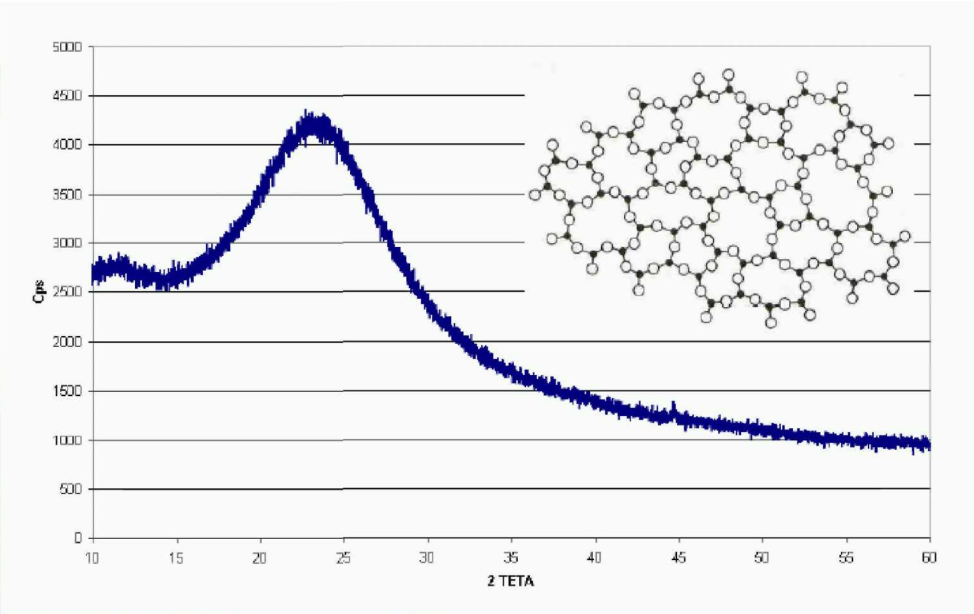
$$\Delta \mathbf{k} = \mathbf{G}$$

$$\Delta \mathbf{k} \neq \mathbf{G}$$



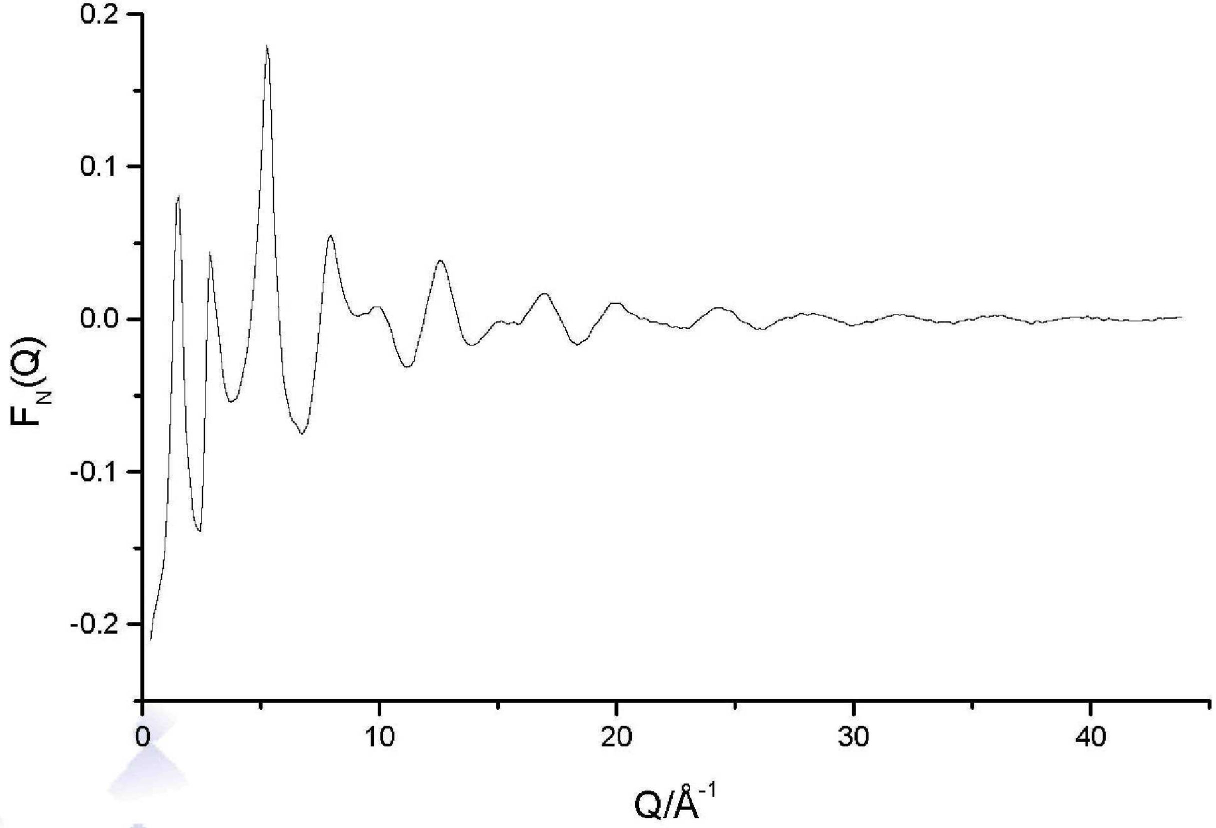


$$A = \int n(\mathbf{r}) \exp(-i\Delta\mathbf{k}.\mathbf{r}) dr$$

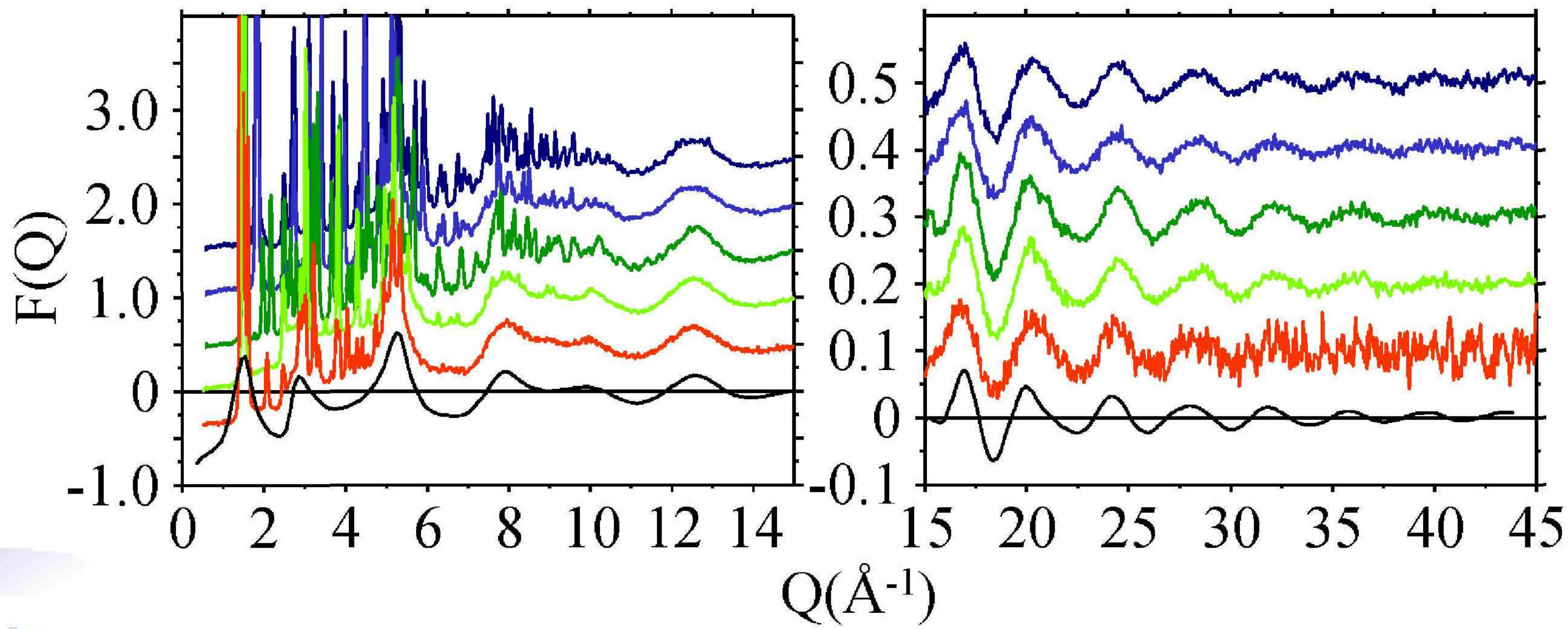


$$\Delta\mathbf{k}.\mathbf{r} \neq 2n\pi \qquad A \neq 0$$

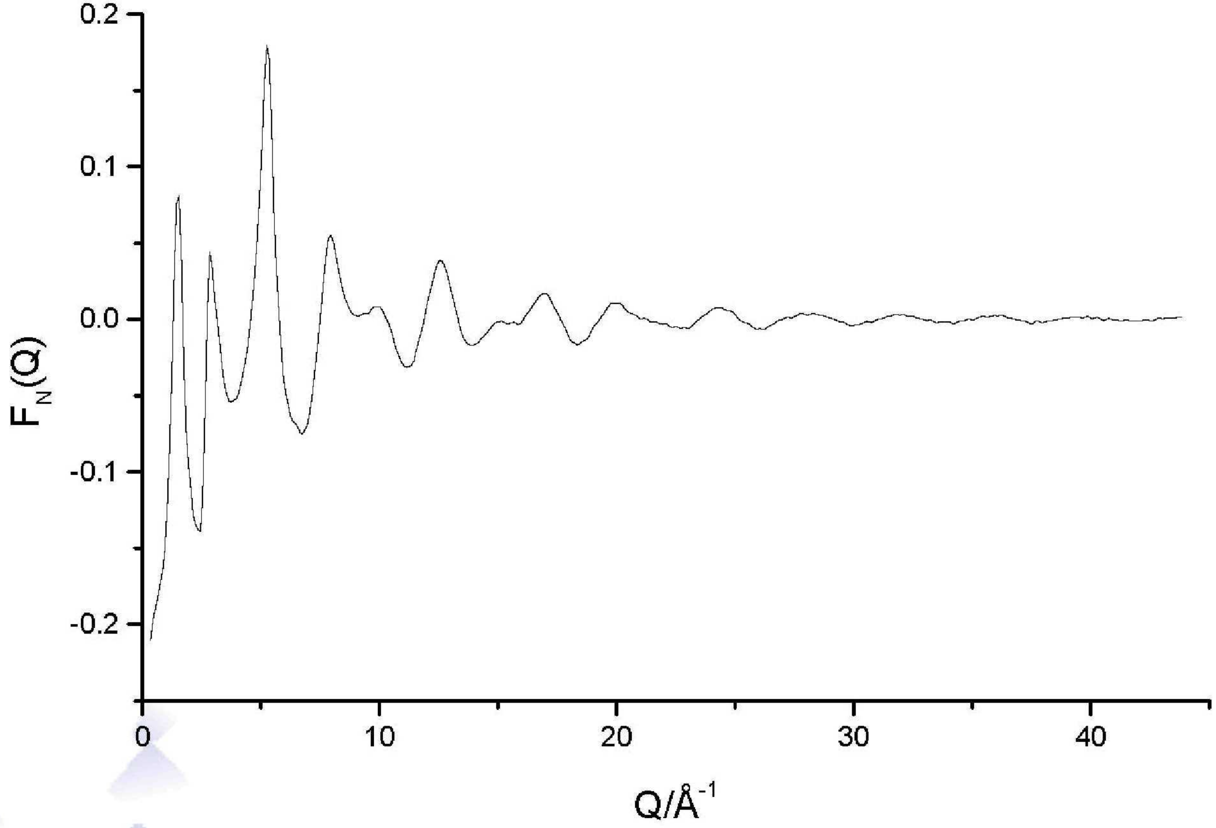
ISIS



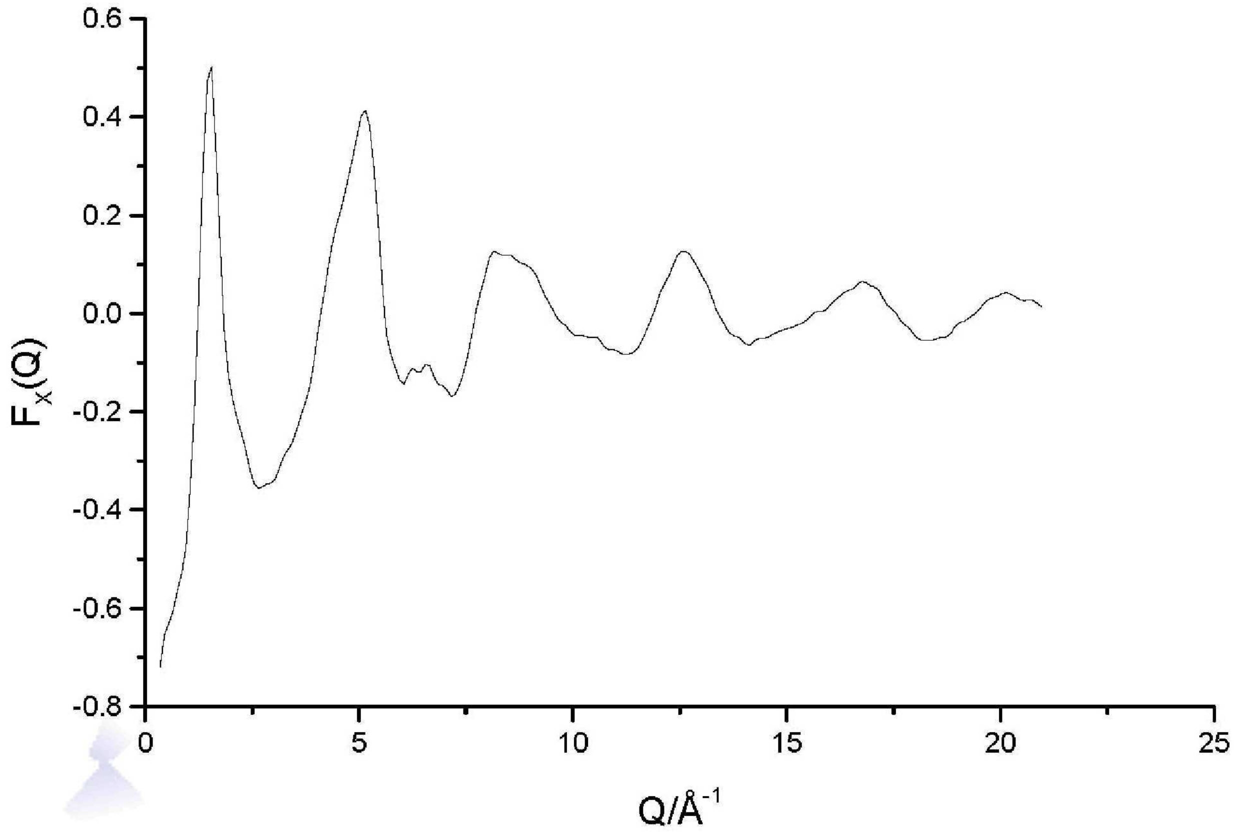
Neutron diffraction from vitreous SiO_2



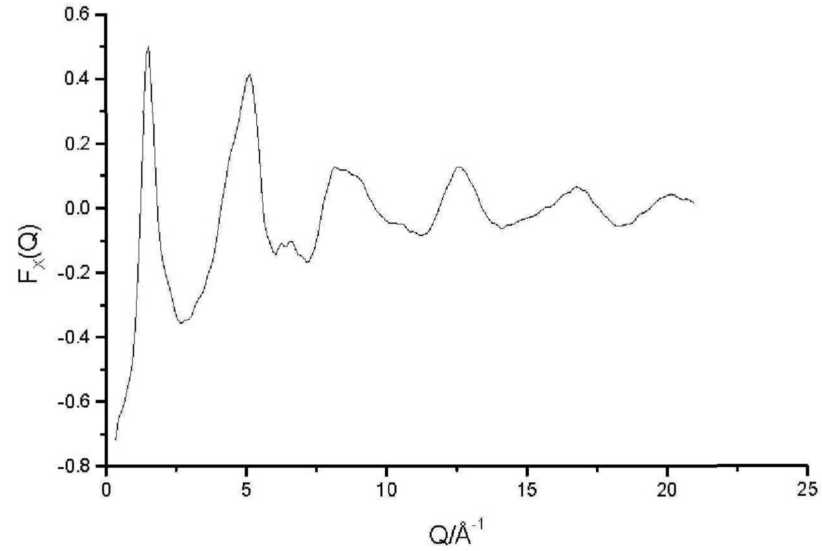
Neutron diffraction from vitreous and crystalline SiO_2

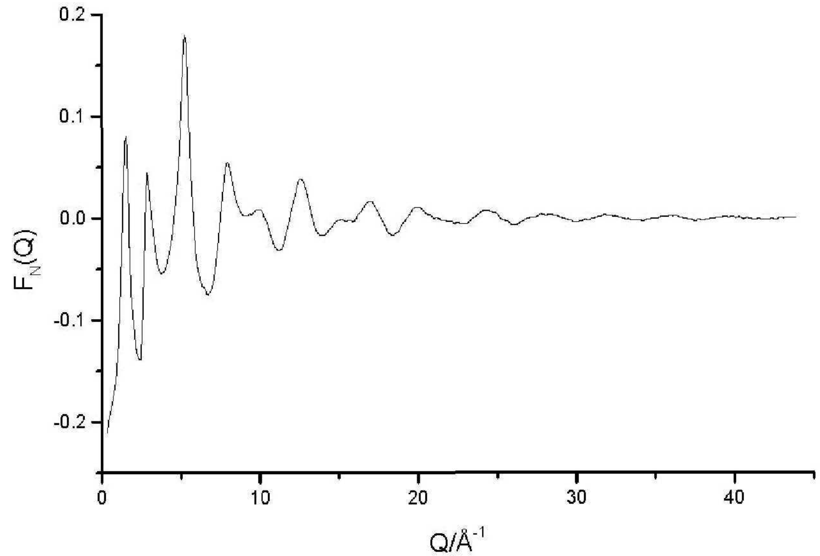


Neutron diffraction from vitreous SiO_2



X-ray diffraction from vitreous SiO_2 (form factor corrected)





$$A = \int n(\mathbf{r}) \exp(-i\mathbf{Q}.\mathbf{r}) d\mathbf{r} \qquad n(\mathbf{r}) = \sum_j f_j(\mathbf{r}_j)$$

X-rays

$$\int f_j(r_j) \propto Z_j$$

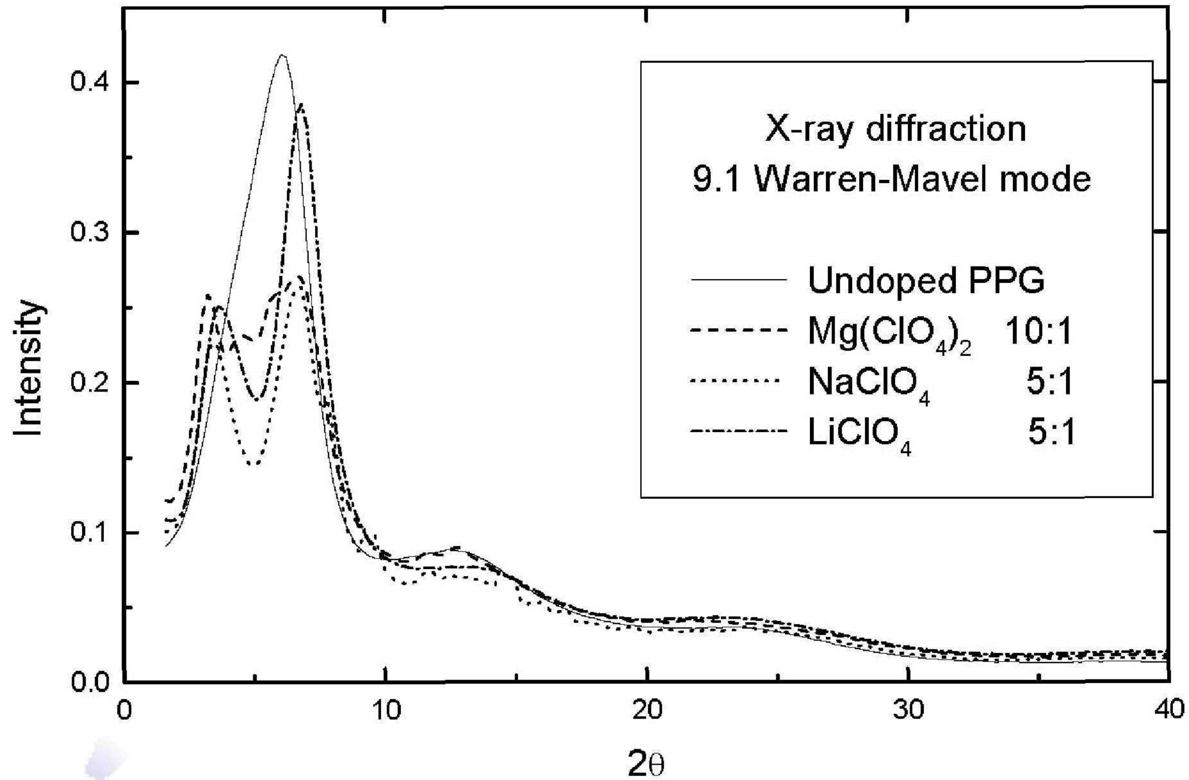
Si – 14; O - 8

Neutrons

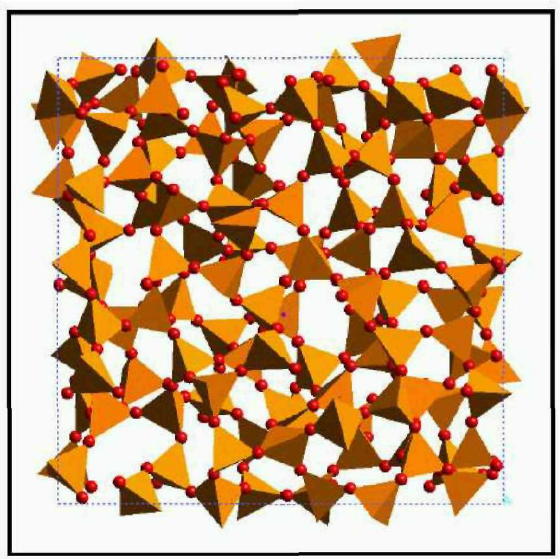
$$f_j(r_j) = b_j$$

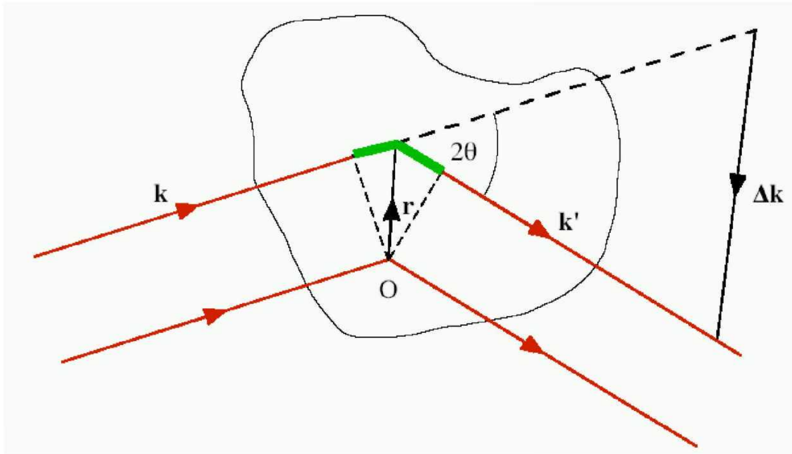
Si – 4.15; O – 5.8

ISIS

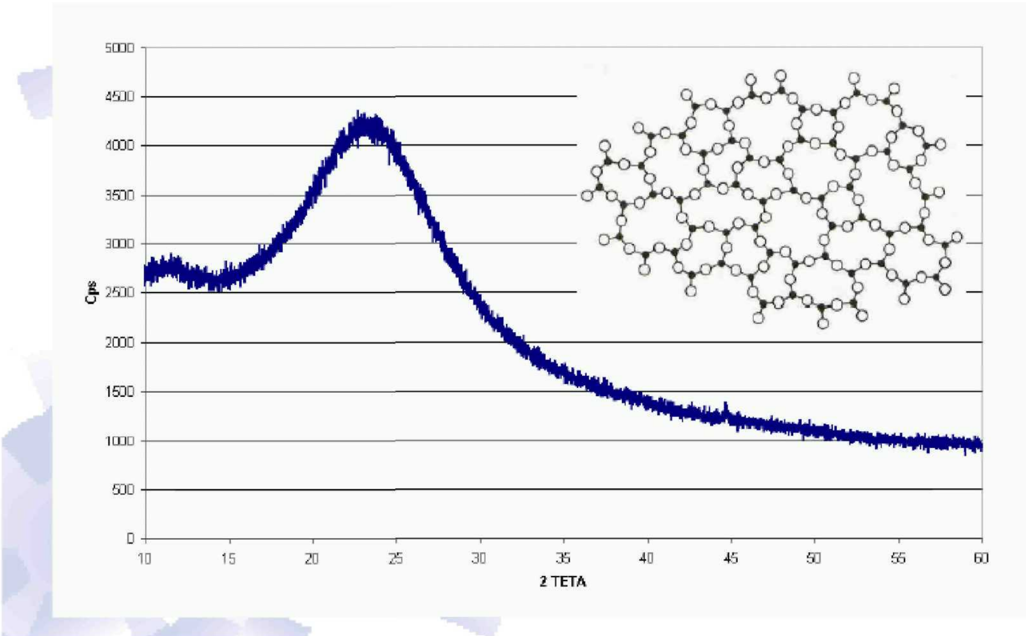


X-ray diffraction from a polymer glass (as measured)





$$A = \int n(\mathbf{r}) \exp(-i\Delta\mathbf{k}.\mathbf{r}) d\mathbf{r}$$



$$\Delta\mathbf{k}.\mathbf{r} \neq 2n\pi \qquad A \neq 0$$

$$n(\mathbf{r}) = \sum_j f_j(\mathbf{r}_j)$$

$$I = A^* A$$

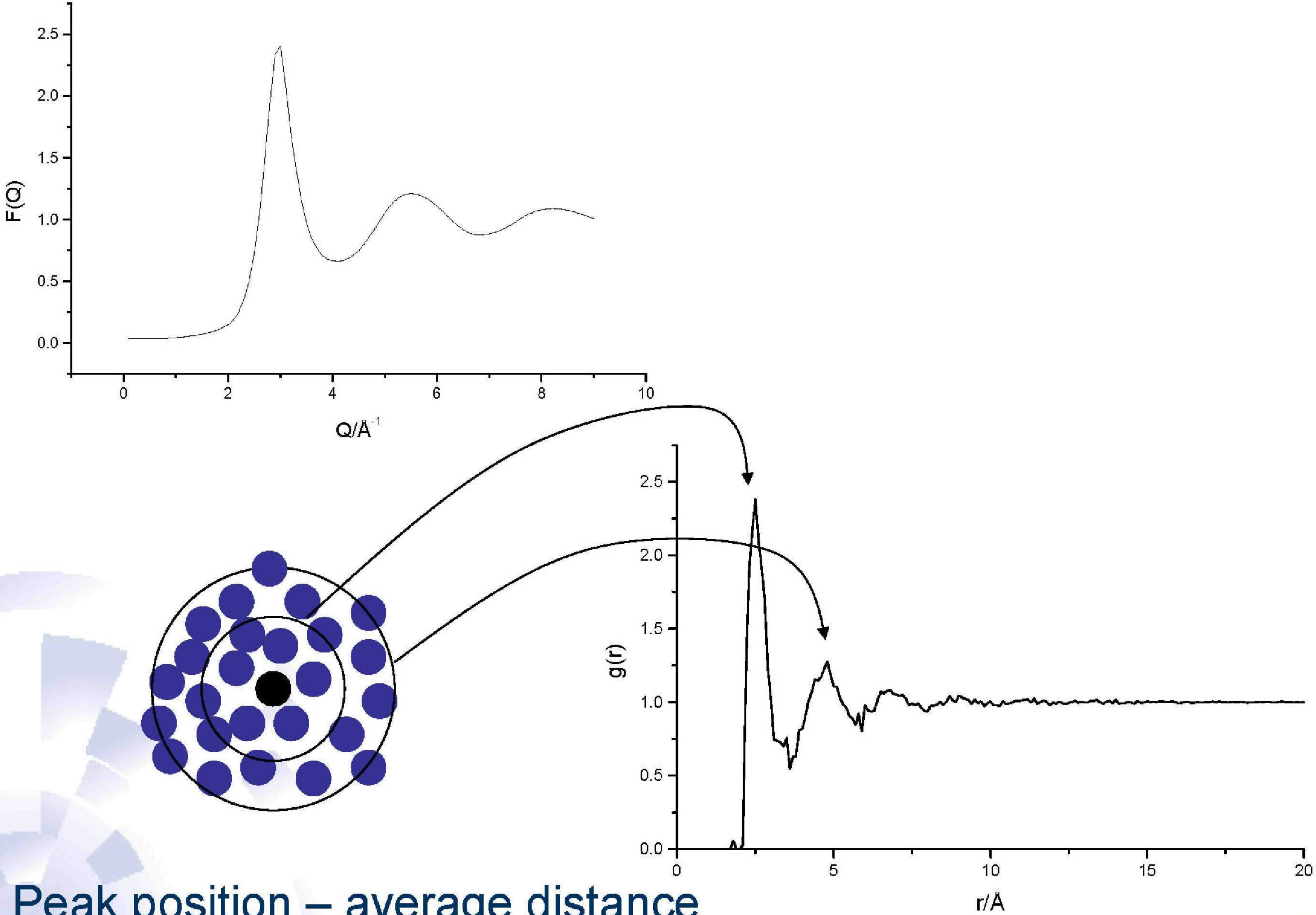
ISIS

$$I \propto F(Q) = \sum_{i,j} c_\alpha c_\beta f_\alpha f_\beta \left(S_{\alpha\beta}(Q) - 1\right)$$

$$S_{\alpha\beta}(Q) - 1 = \rho \int 4\pi r^2 \frac{\sin Qr}{Qr} \left(g_{\alpha\beta}(r) - 1\right) dr$$

$F(Q)$	Structure Factor
$S_{\alpha\beta}(Q)$	Partial Structure Factor
$g_{\alpha\beta}(r)$	Partial radial distribution function

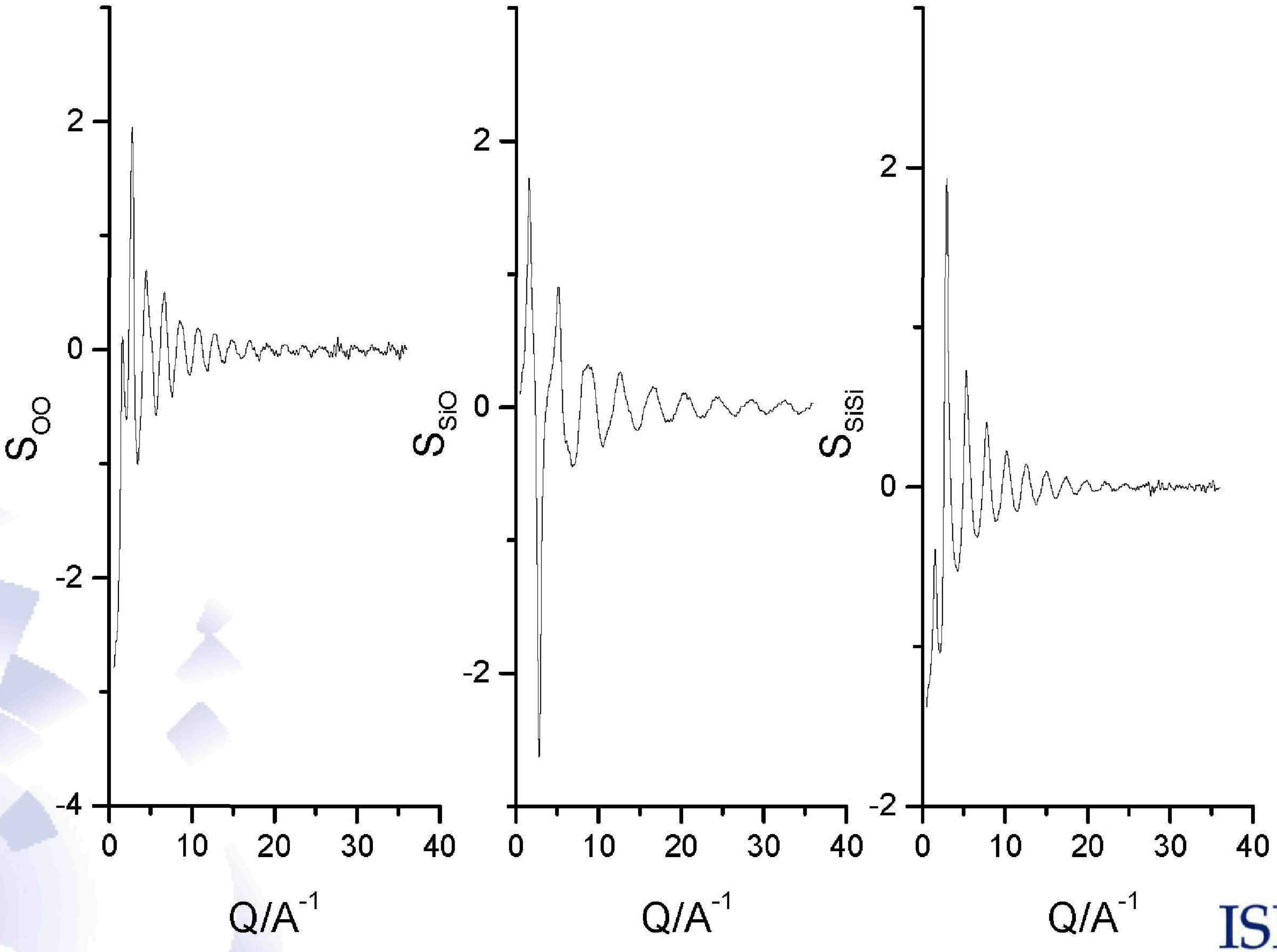
ISIS



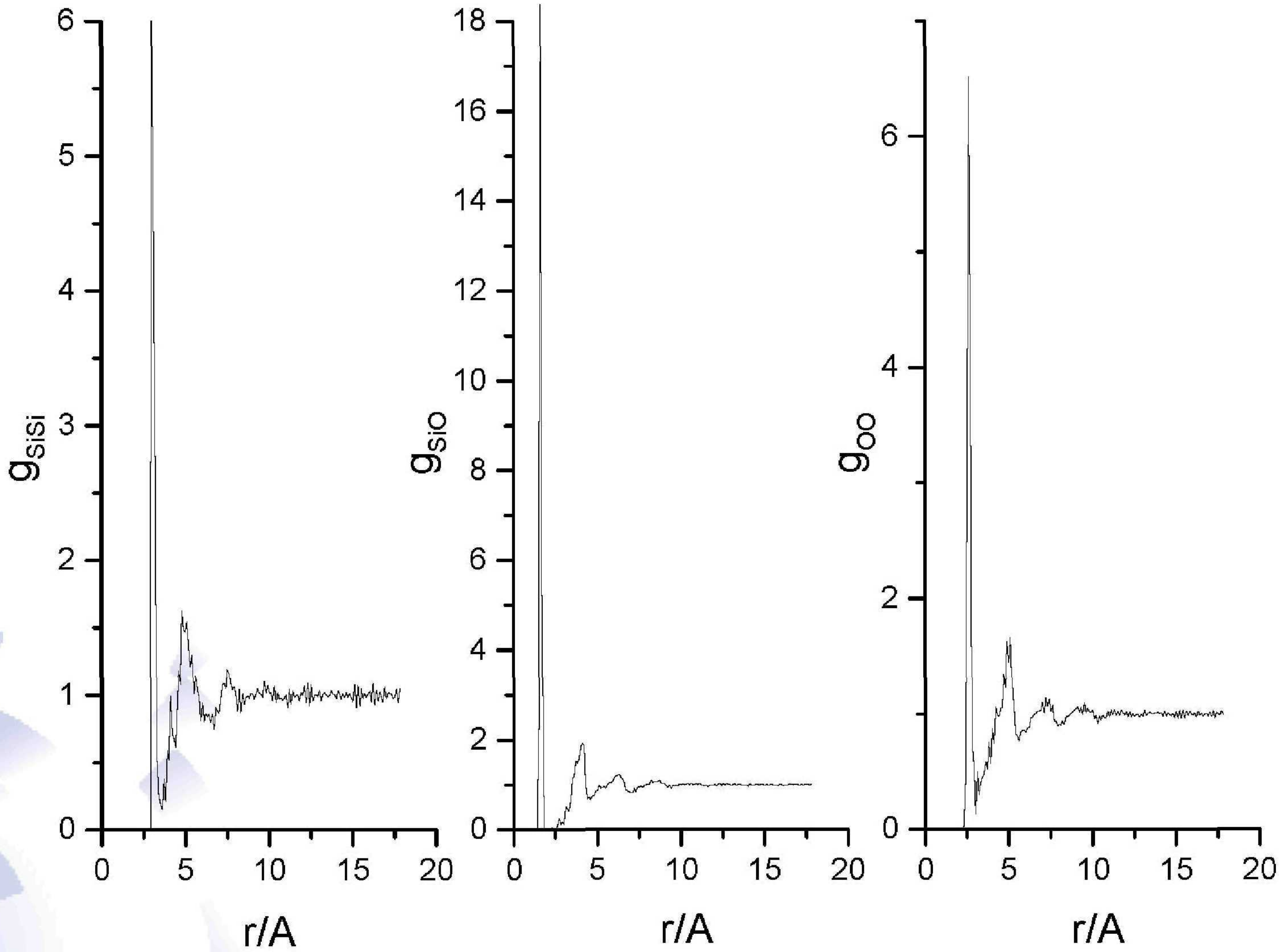
Peak position – average distance

Peak area – coordination number

Vitreous silica



Vitreous silica



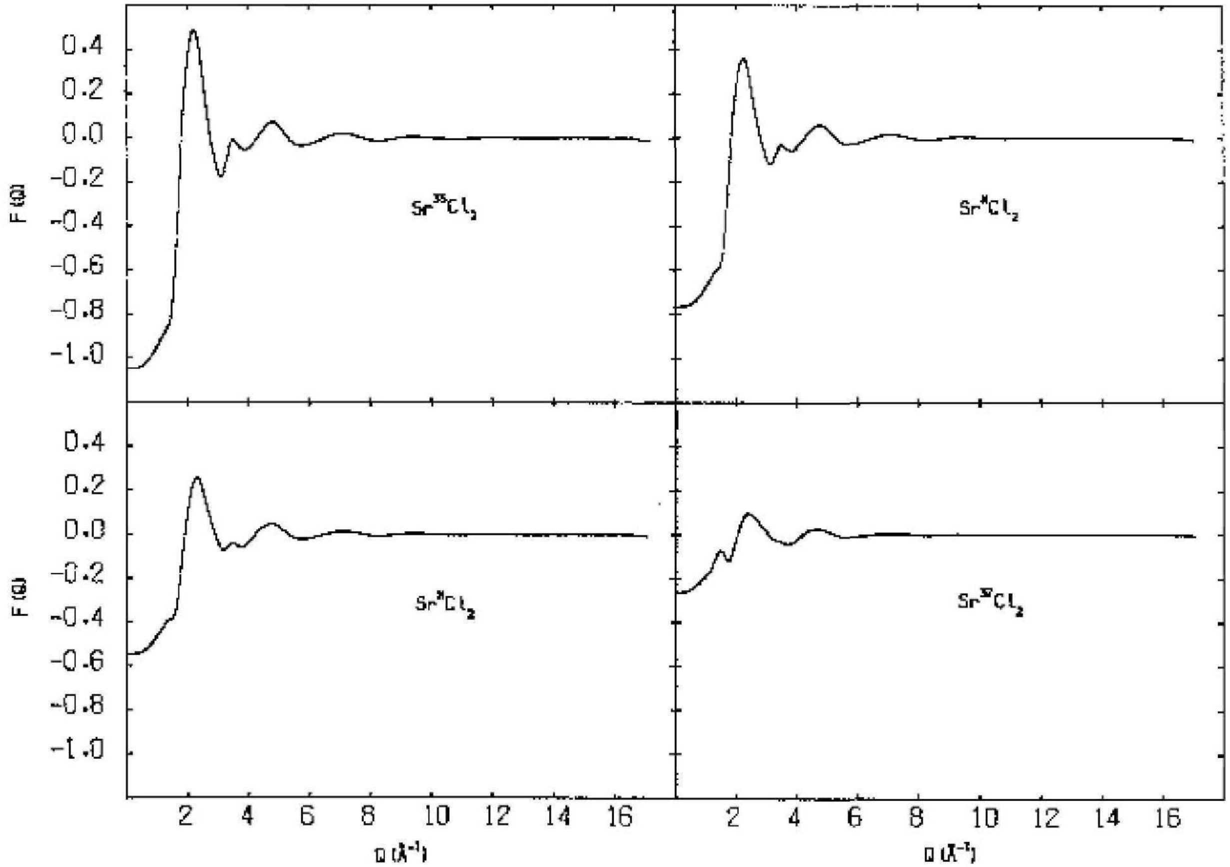
$$I \propto F(Q) = \sum_{i,j} c_\alpha c_\beta f_\alpha f_\beta \left(S_{\alpha\beta}(Q) - 1\right)$$

$$F^{(k)}(Q) = \sum_{i,j} c_\alpha c_\beta f_\alpha^{(k)} f_\beta^{(k)} \left(S_{\alpha\beta}(Q) - 1\right)$$

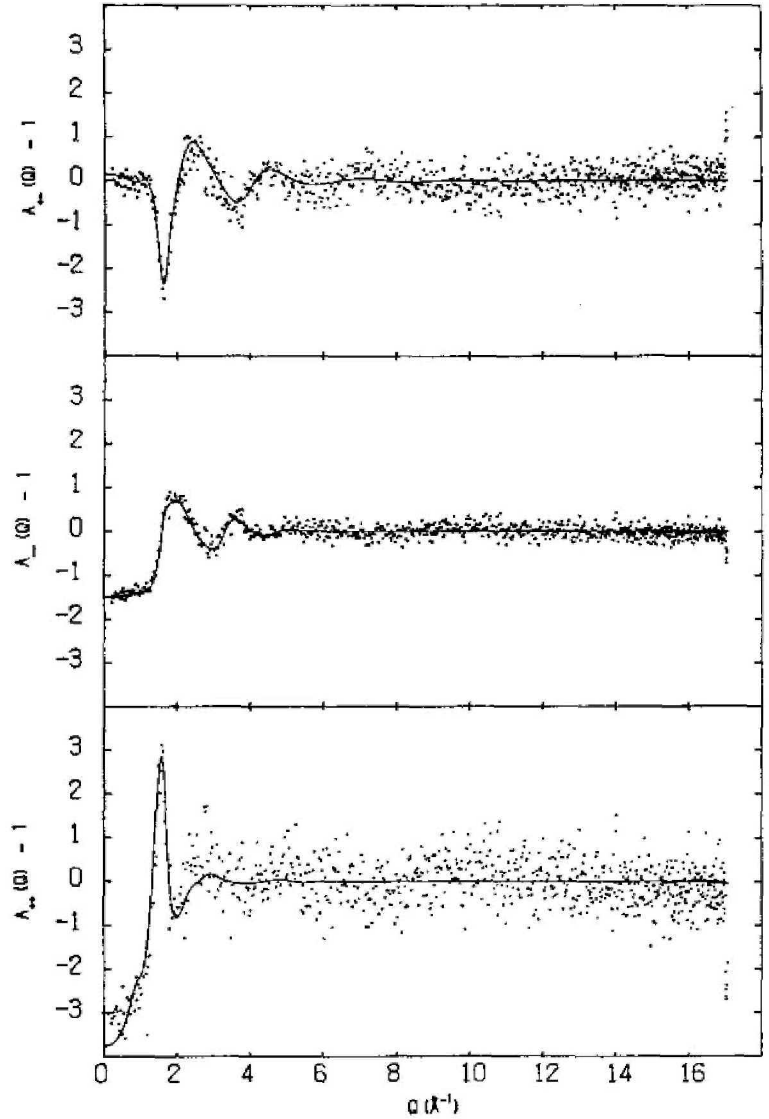
Isotopic subsitution

Total structure factors F(Q) for molten $SrCl_2$

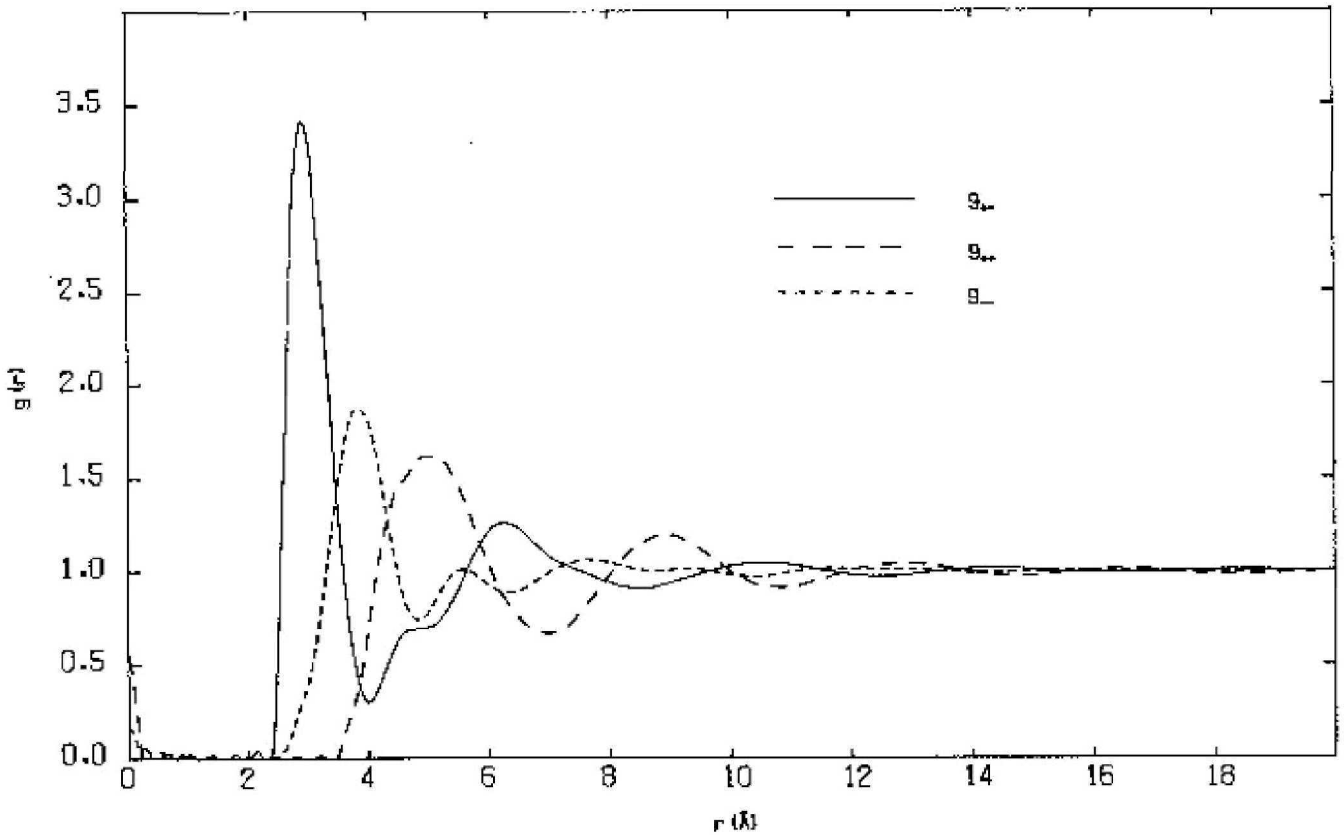
^{37}Cl b = 0.25
^{M}Cl b = 0.75
^{N}Cl b = 1.0
^{35}Cl b = 1.25



Partial structure factors $A_{ij}(Q)$ for molten $SrCl_2$



Partial radial distribution functions $g_{ij}(r)$ for molten $SrCl_2$



$$I \propto F(Q) = \sum_{i,j} c_\alpha c_\beta f_\alpha f_\beta \left(S_{\alpha\beta}(Q) - 1\right)$$

$$F^{(k)}(Q) = \sum_{i,j} c_\alpha c_\beta f_\alpha^{(k)} f_\beta^{(k)} \left(S_{\alpha\beta}(Q) - 1\right)$$

Isotopic subsitution

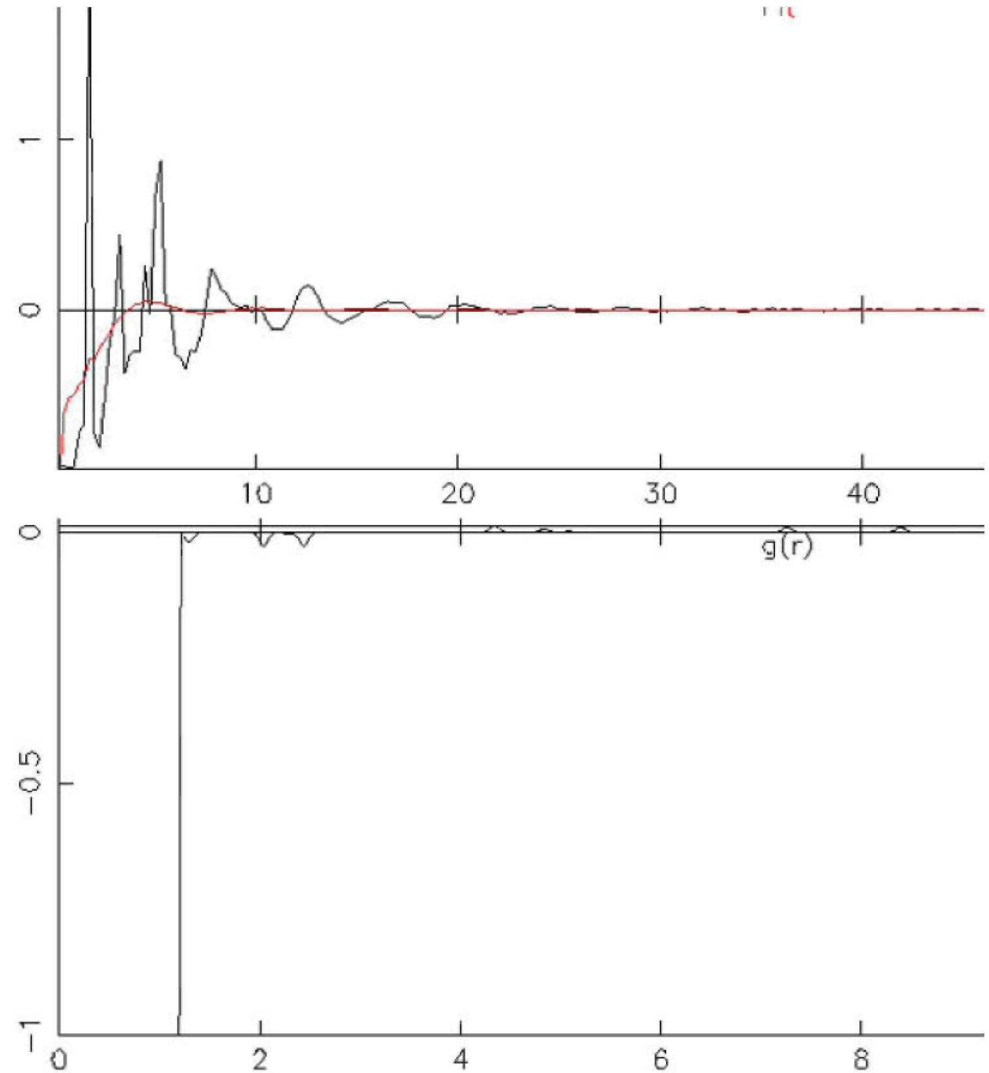
Anomalous scattering

Combine techniques

Modelling

ISIS

$$S_{\alpha\beta}(Q)-1=\rho\int 4\pi r^2\,\frac{\sin Qr}{Qr}\left(g_{\alpha\beta}(r)-1\right)dr$$



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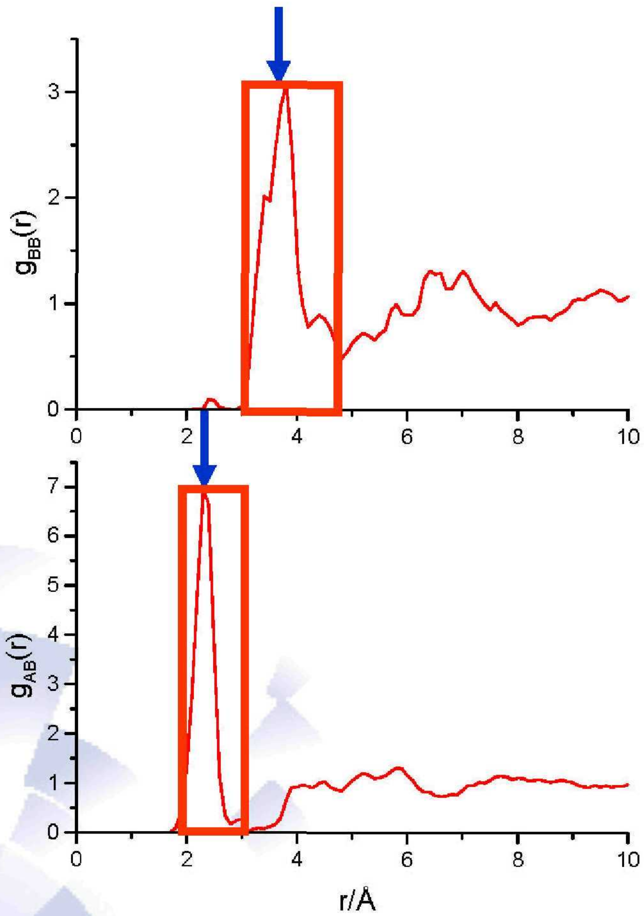
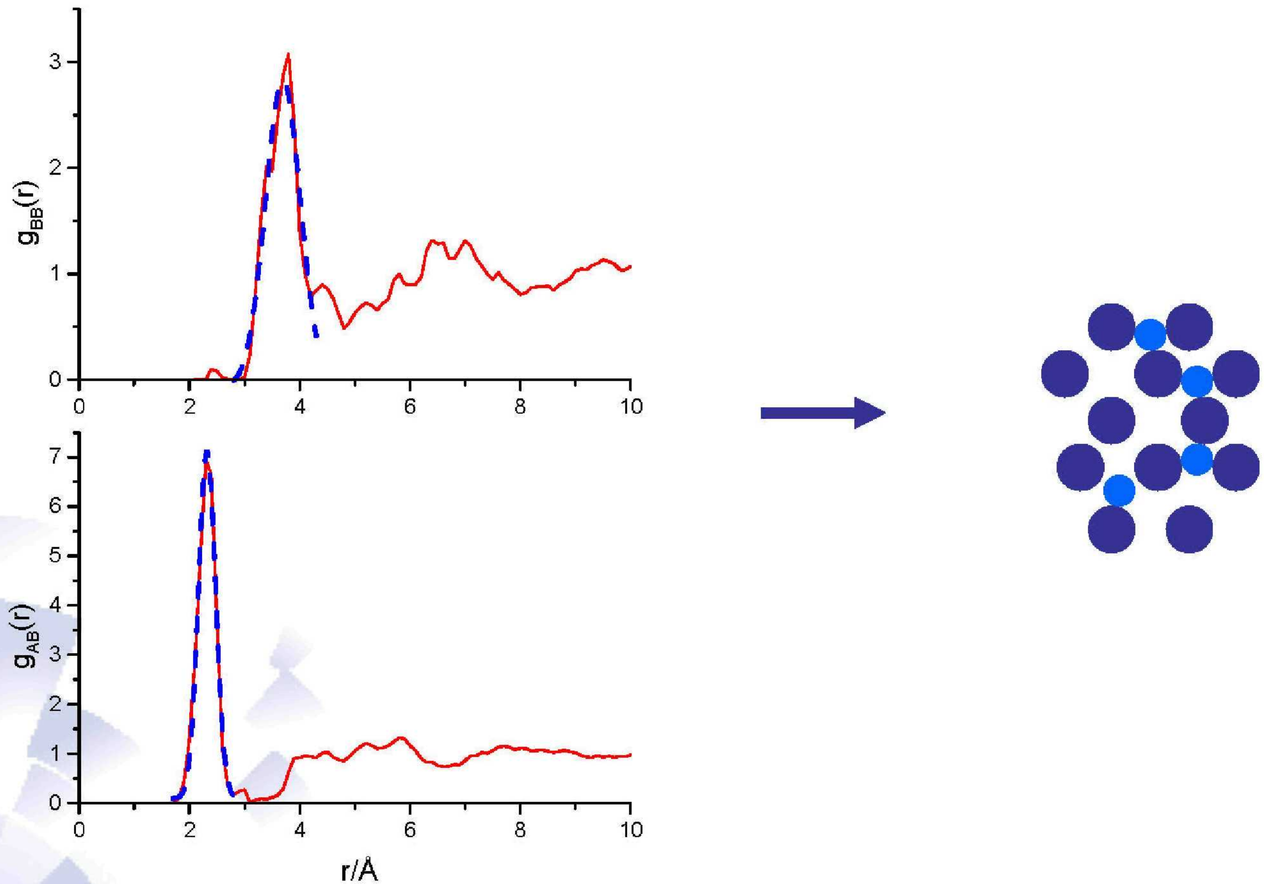


$g_{BB}(r)$
$g_{AB}(r)$
r/Å



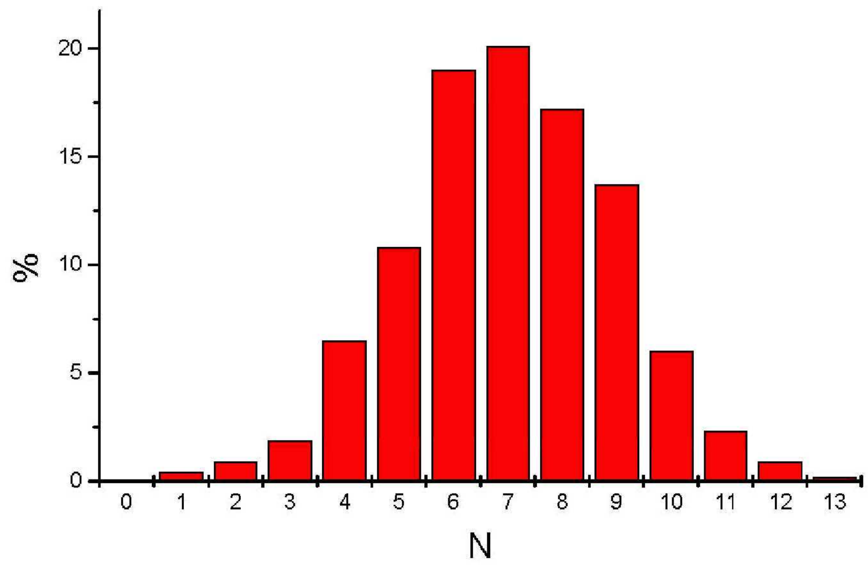
g_BB(r)
g_AB(r)
r/Å

‘Average’ structure models

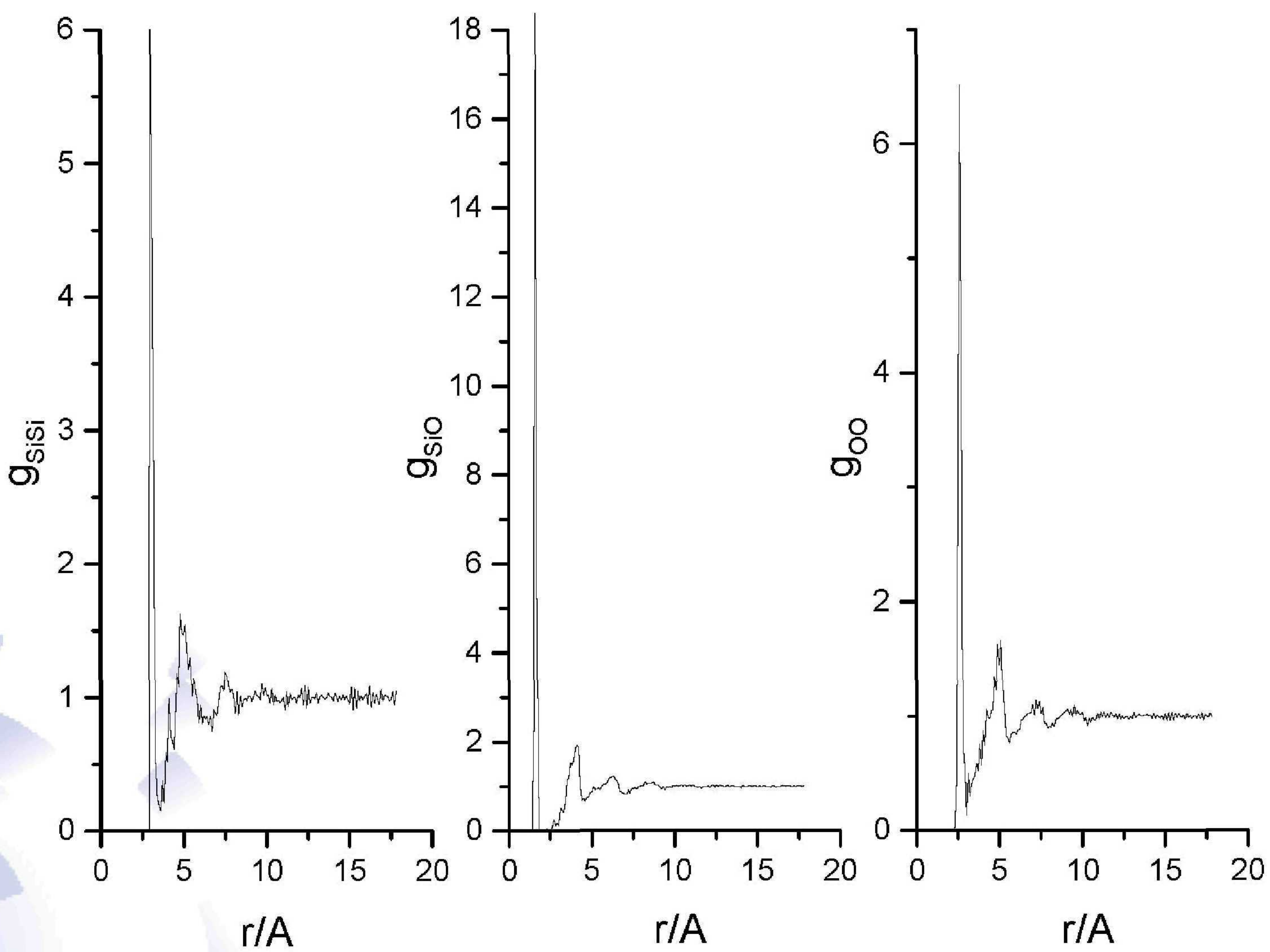
Tend to overestimate the geometrical order

Tend to ignore the variation in local order, coordination etc.

Coordination number distribution for a simple liquid

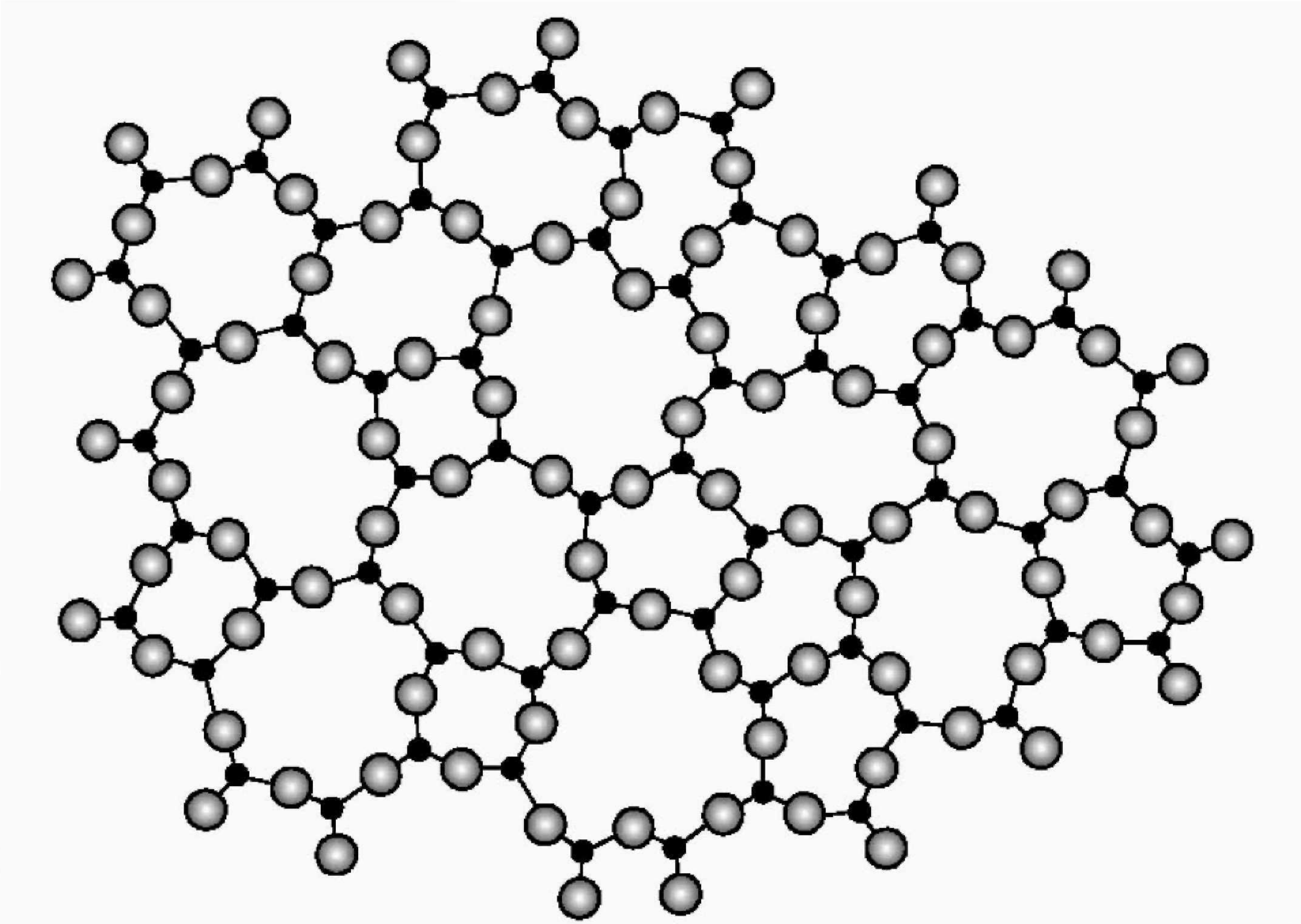


Vitreous silica

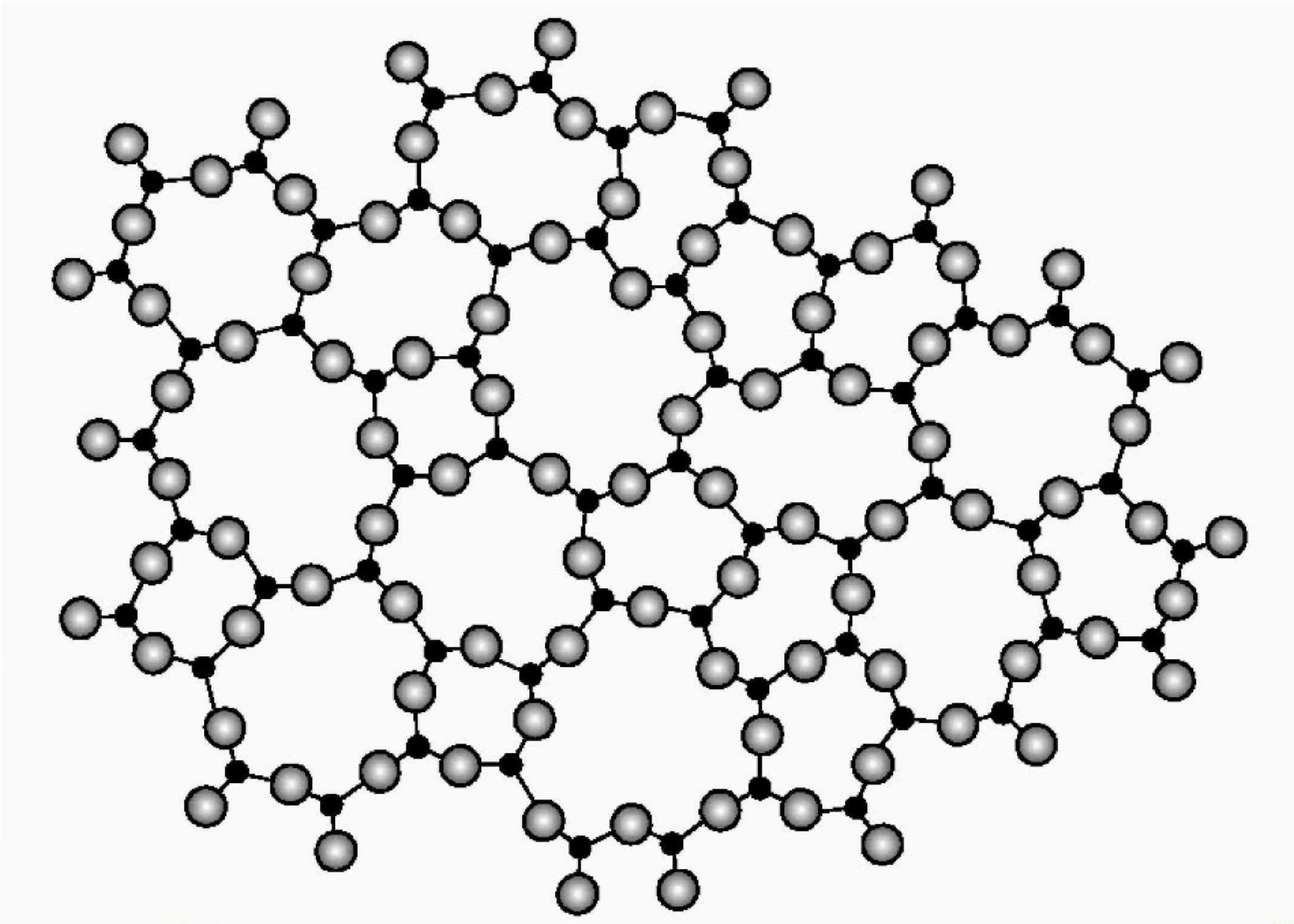


ISIS

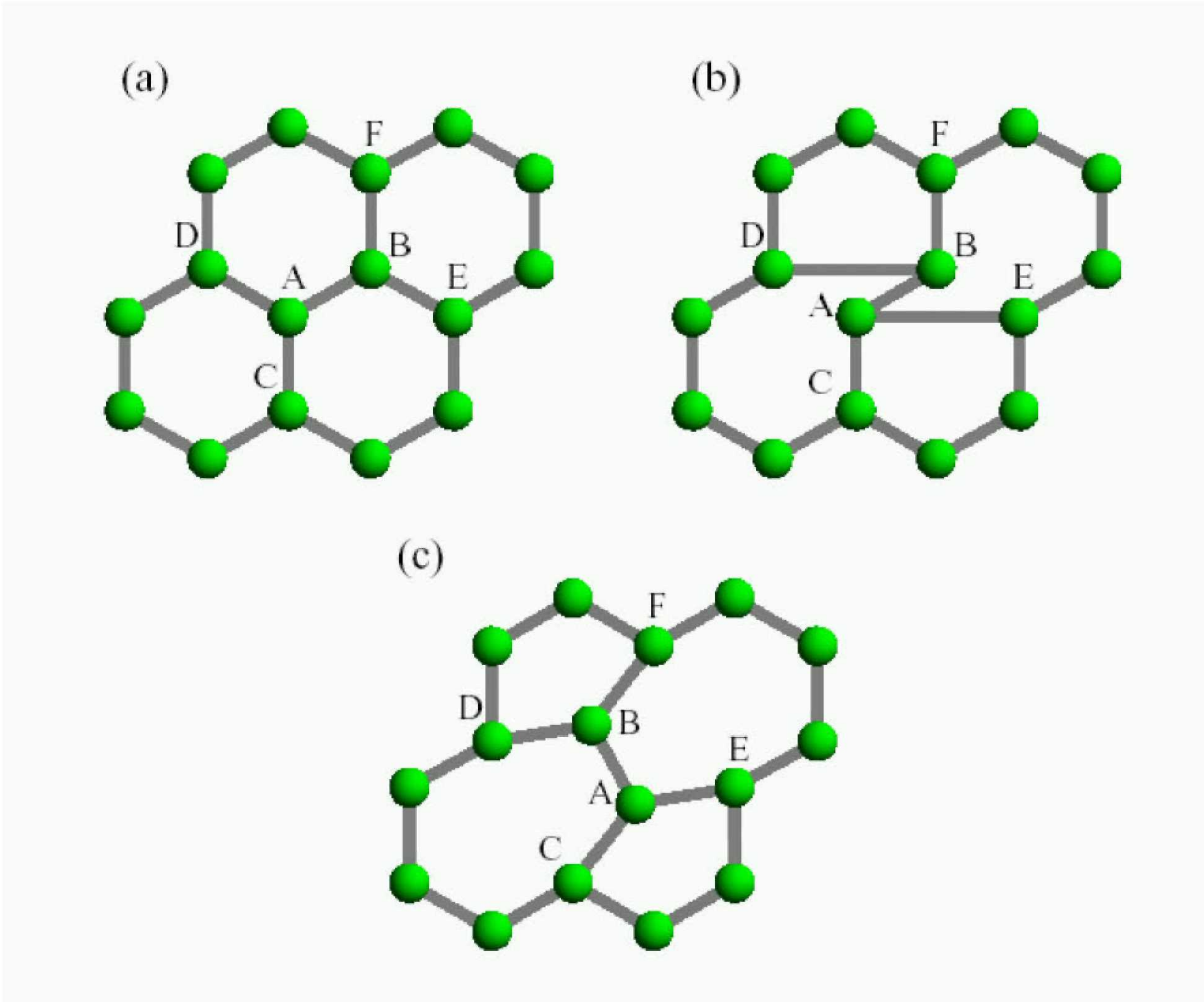
Continuous Random Network (CRN) - Zachariasen

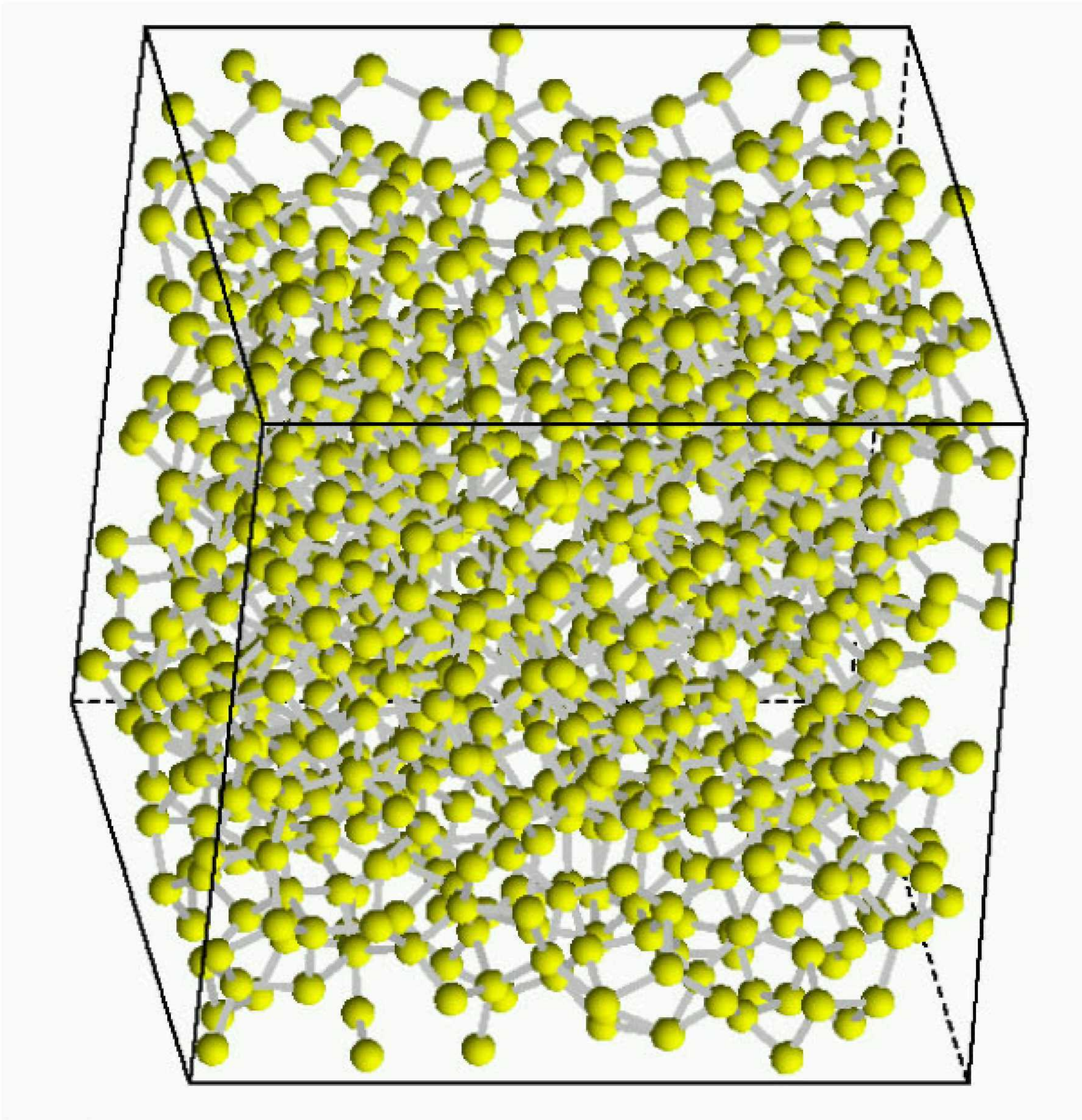


Hand built models

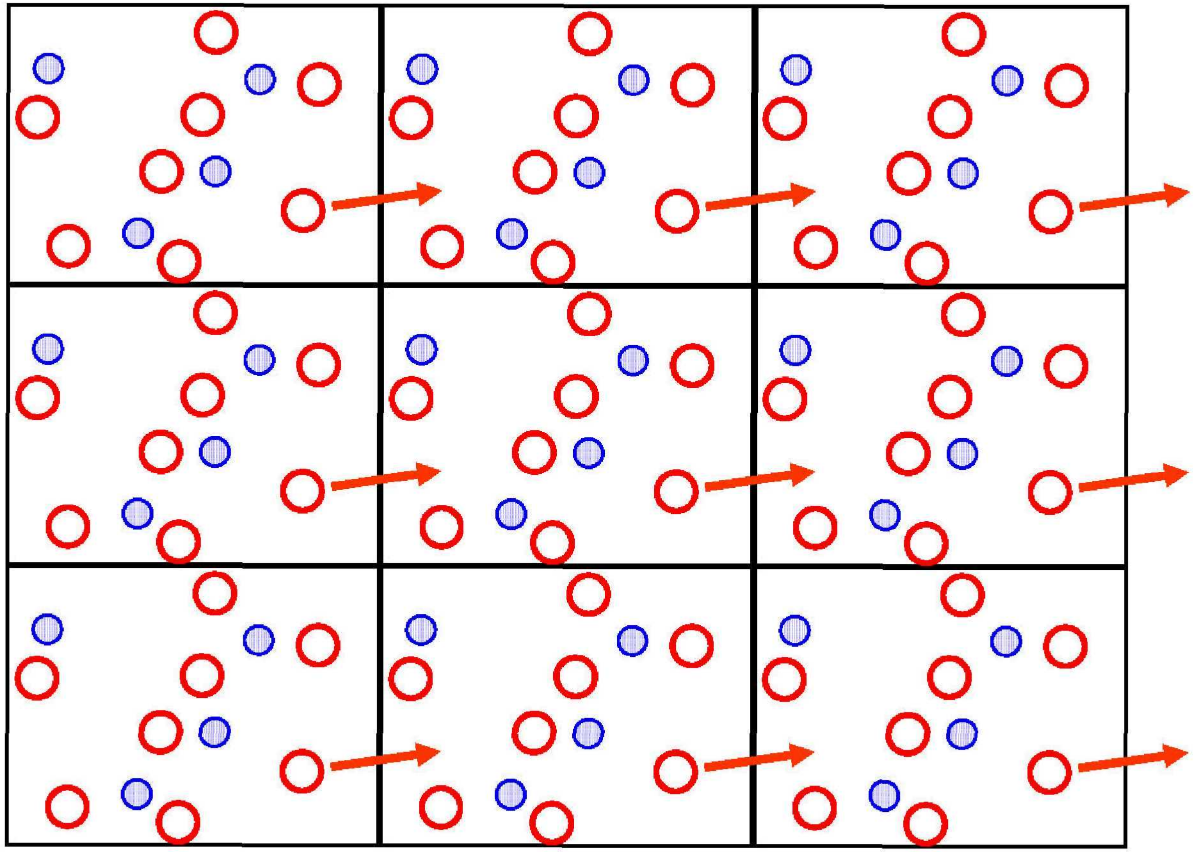


Computer generated models





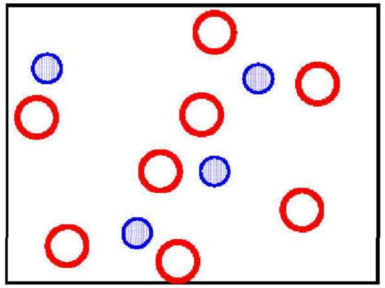
Molecular dynamics - MD



Periodic boundary conditions

Molecular dynamics - MD

$$\left\{ \mathbf{r}_1(t), \ldots, \mathbf{r}_N(t) \right\}$$

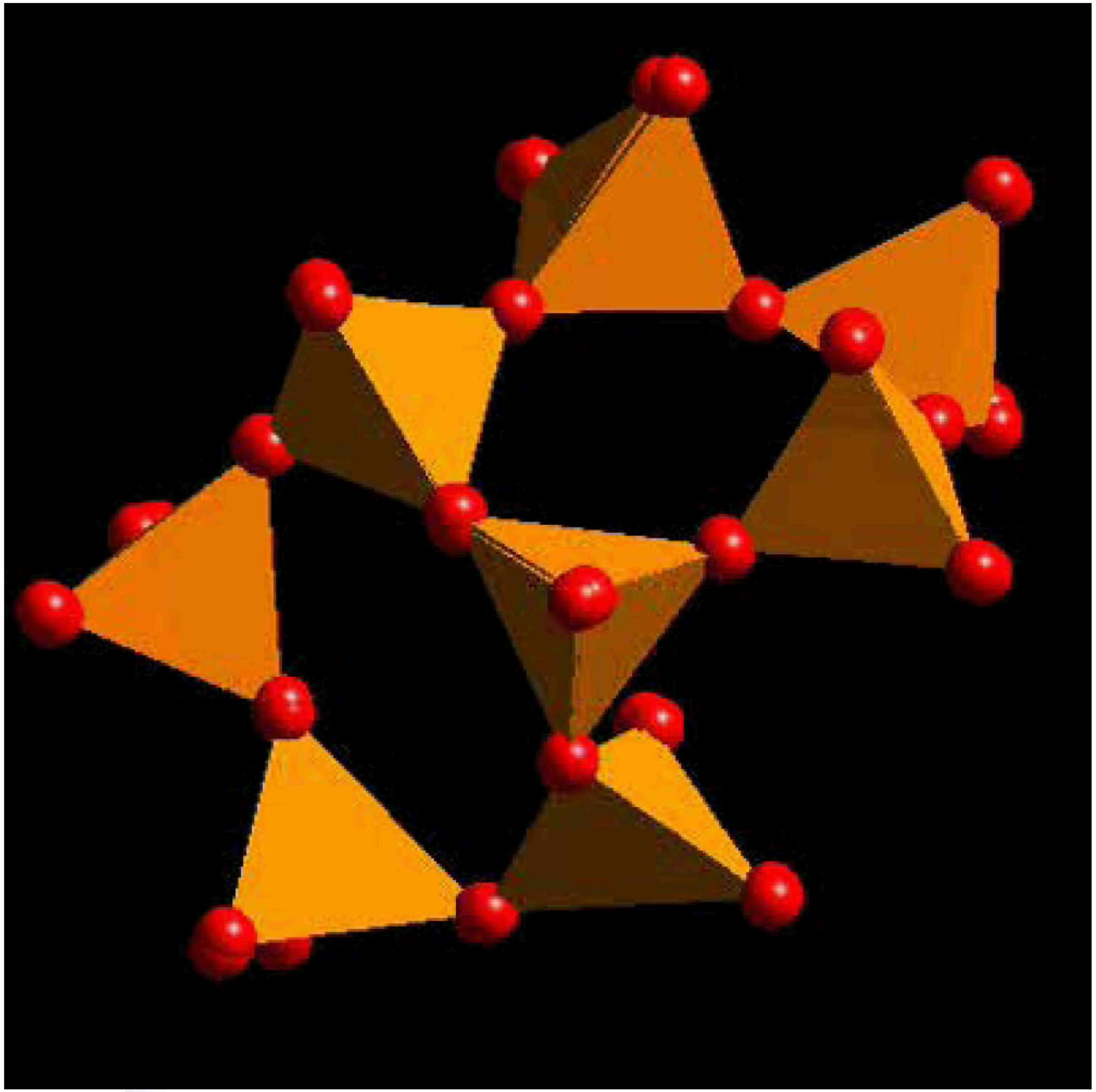


Newton's second law of motion:

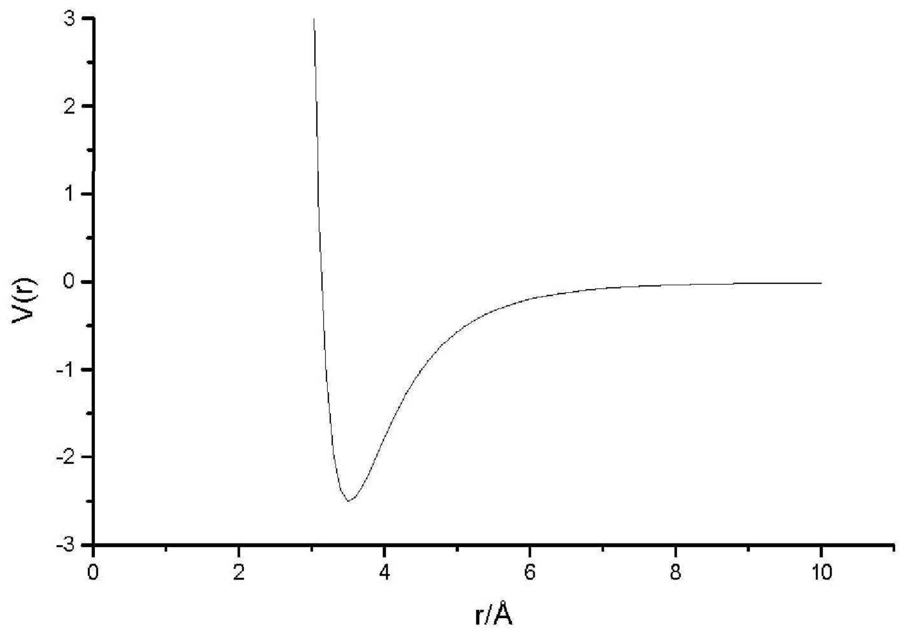
$$m_i \frac{\partial^2 \mathbf{r}_i(t)}{\partial t^2} = -\frac{\delta V}{\delta \mathbf{r}_i}$$

$$V = \sum_{i<j} V_{ij}^{(2)}(\mathbf{r}_{ij}) + \sum_{i,j<k} V_{ijk}^{(3)}(\mathbf{r}_{ij}, \mathbf{r}_{jk})$$

ISIS

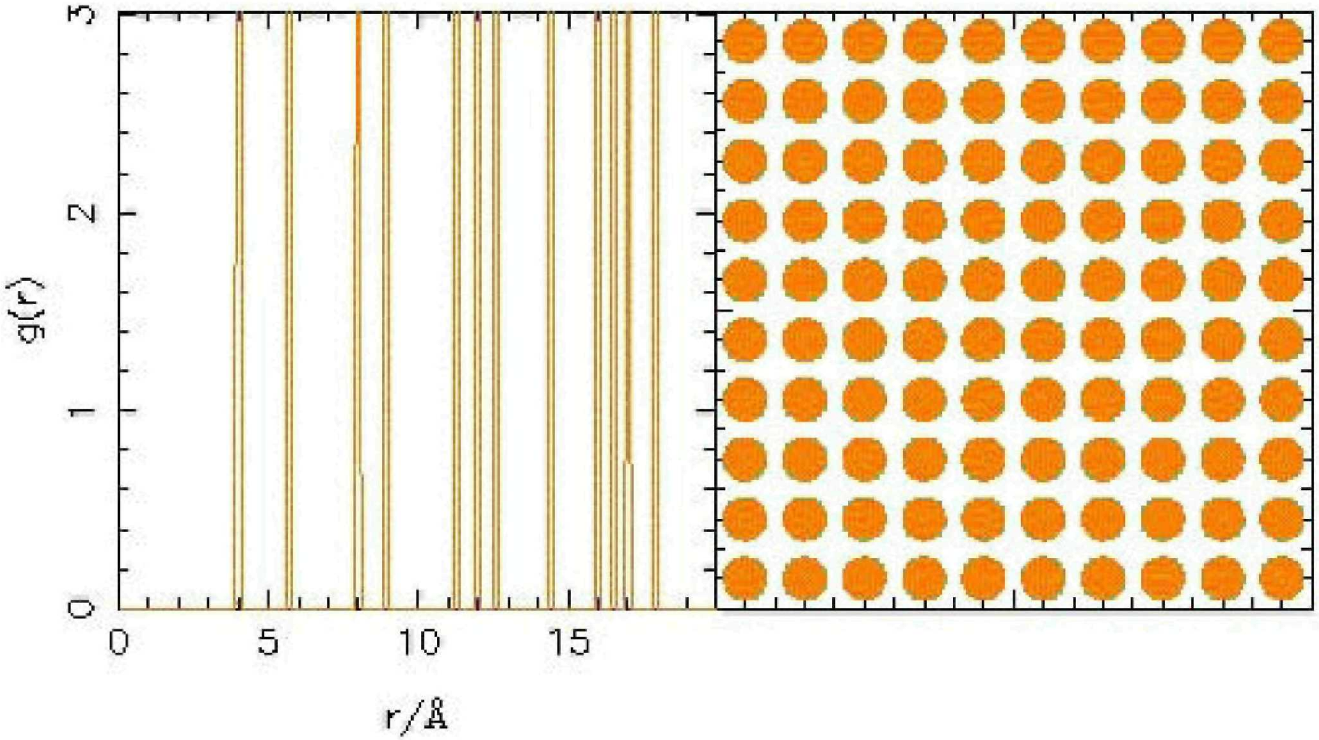


Monte Carlo - MC



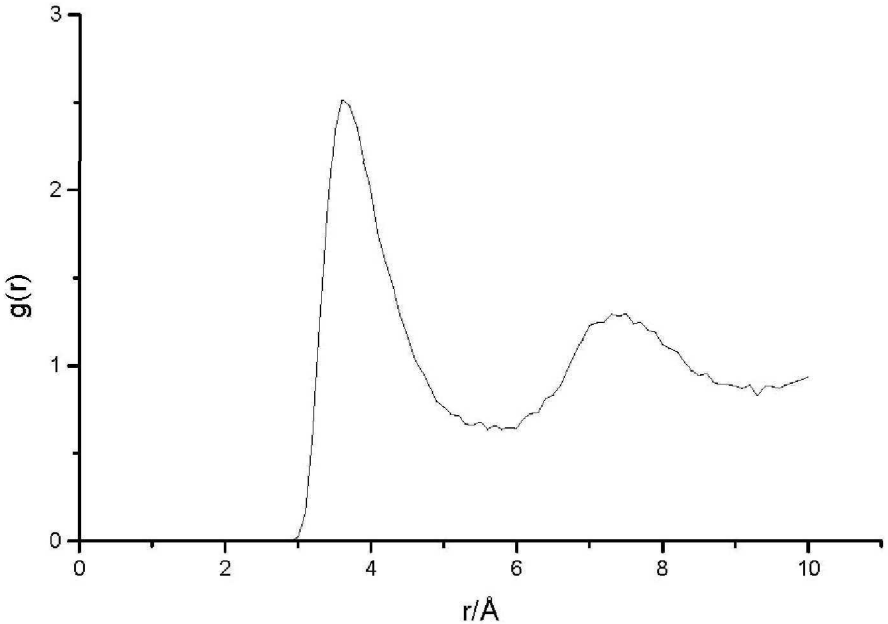
Interatomic potential

Monte Carlo - MC



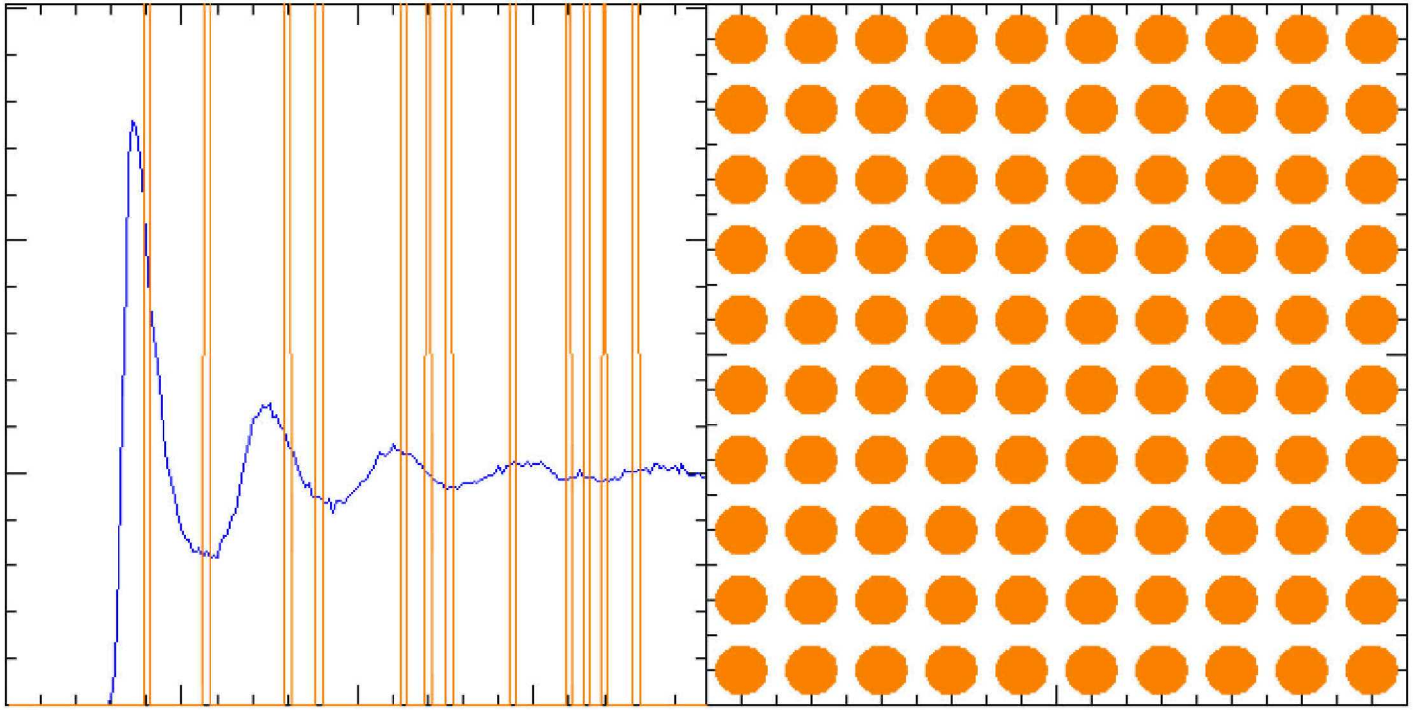
The energy change U_1-U_2/kT 'drives' the simulation

Reverse Monte Carlo - RMC



Experimental data

Reverse Monte Carlo - RMC

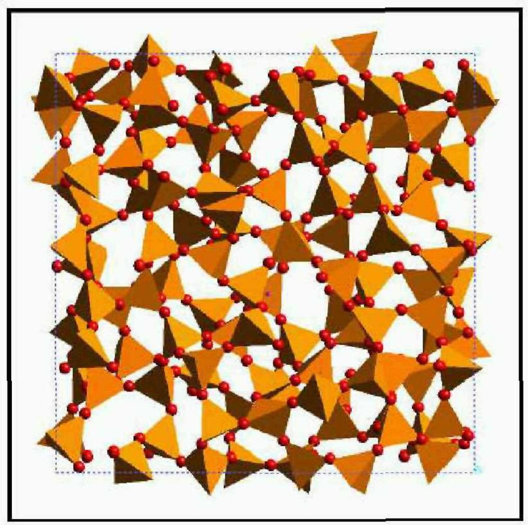


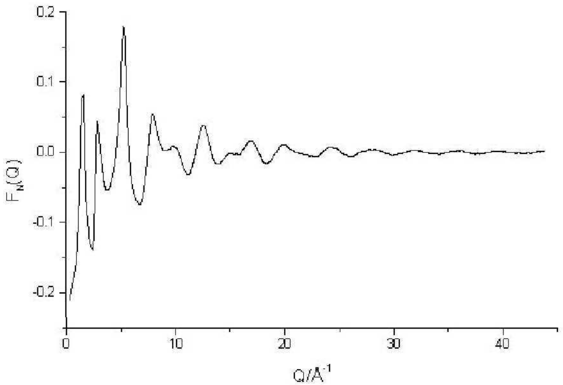
The difference between the data and the model

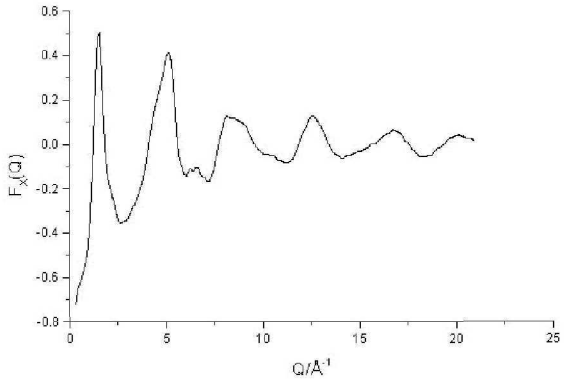
$\chi_1^2 - \chi_2^2 / \sigma^2$

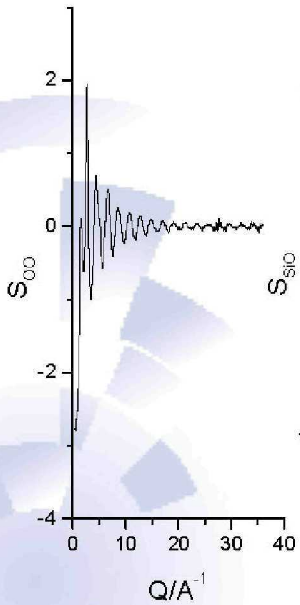
'drives' the simulation

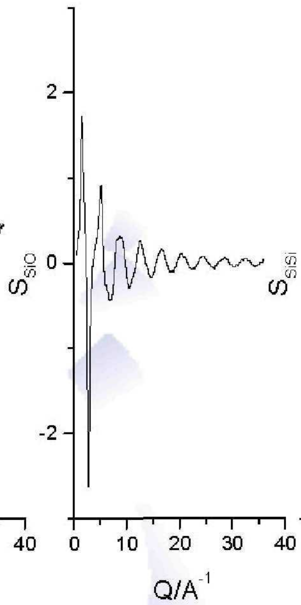
Vitreous silica

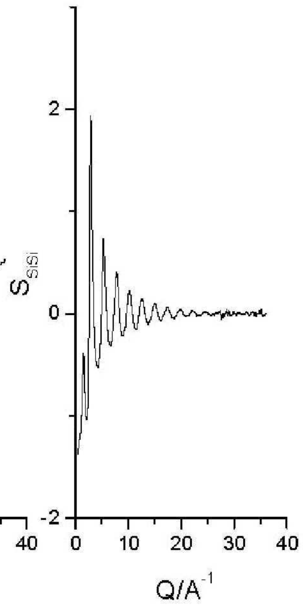


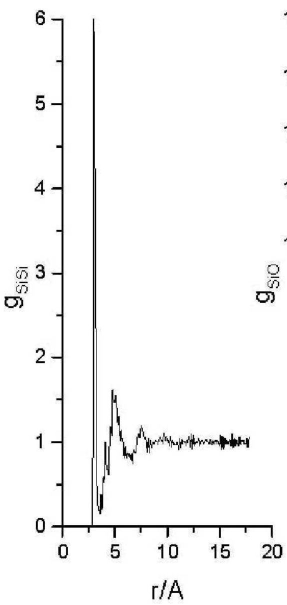


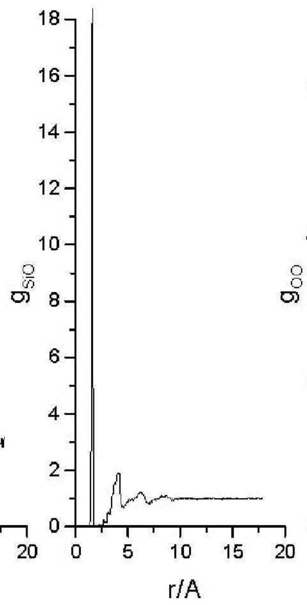


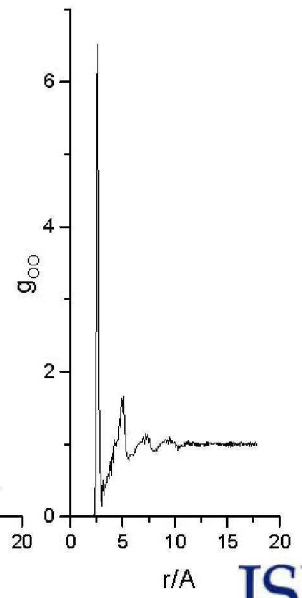




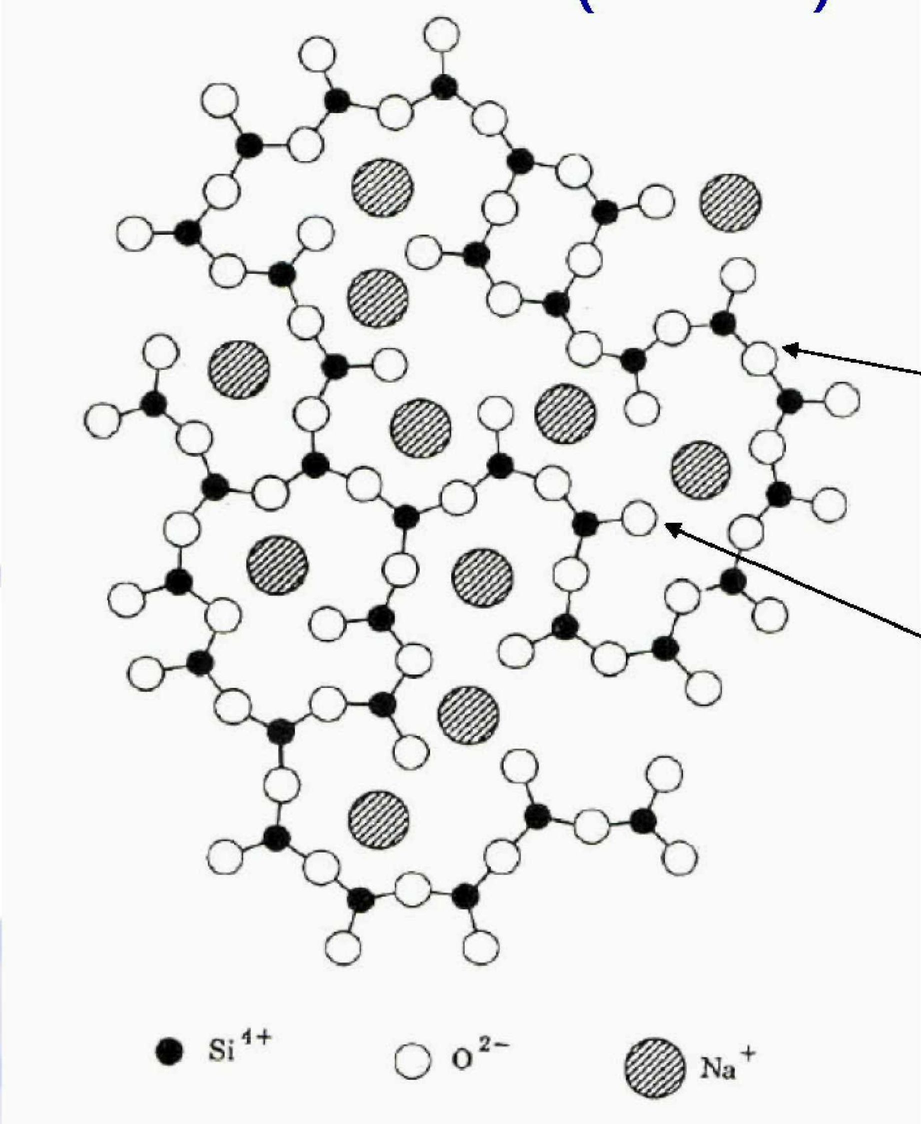








Modified Random Network (MRN) - Greaves

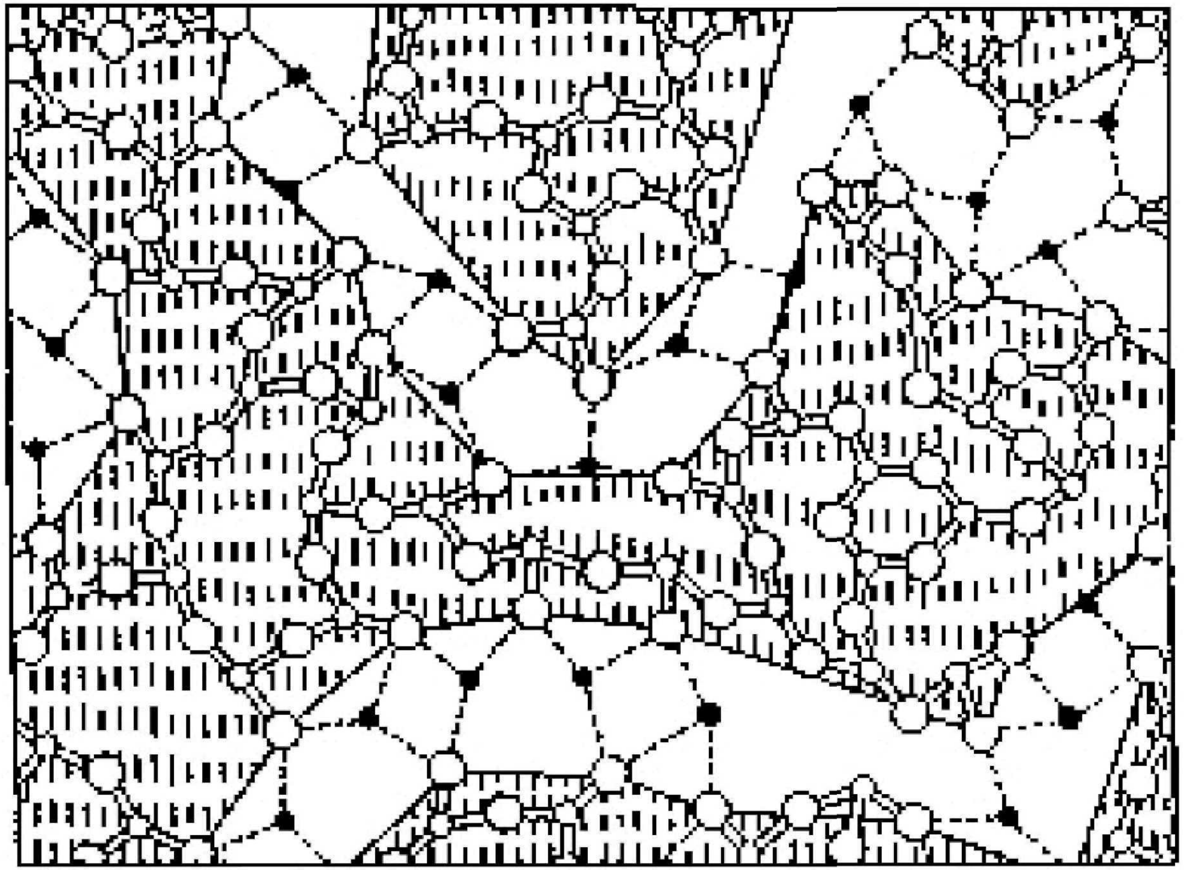


Na_2O-SiO_2

Bridging Oxygen (BO)

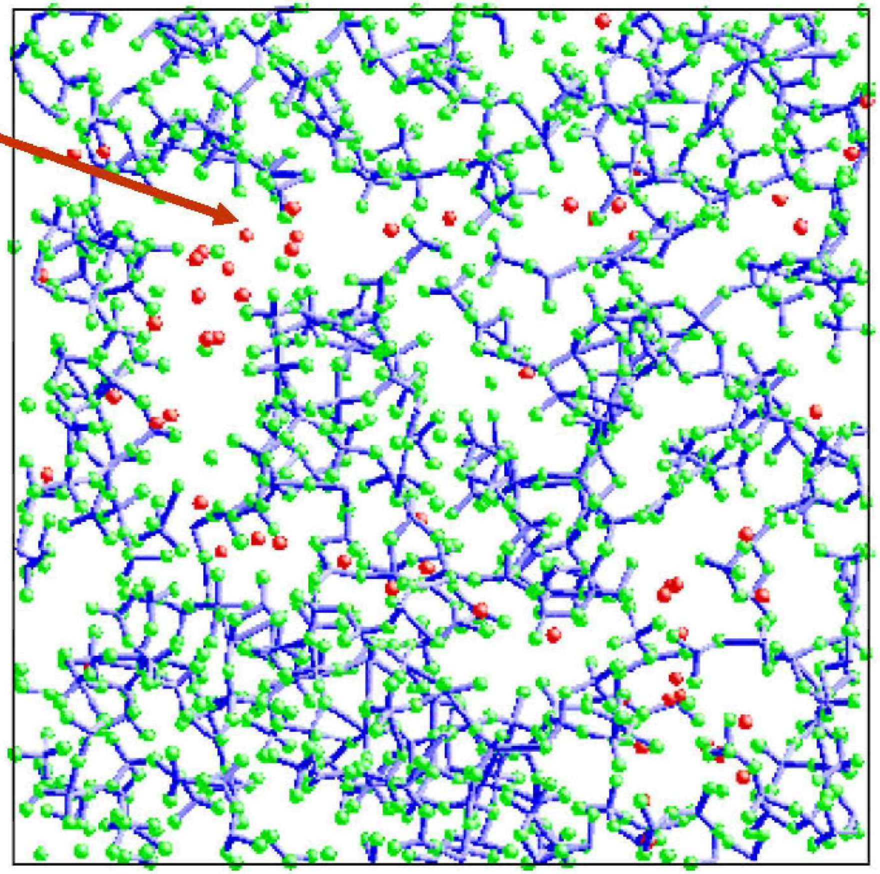
Non-bridging Oxygen (NBO)

Modified Random Network (MRN) - Greaves



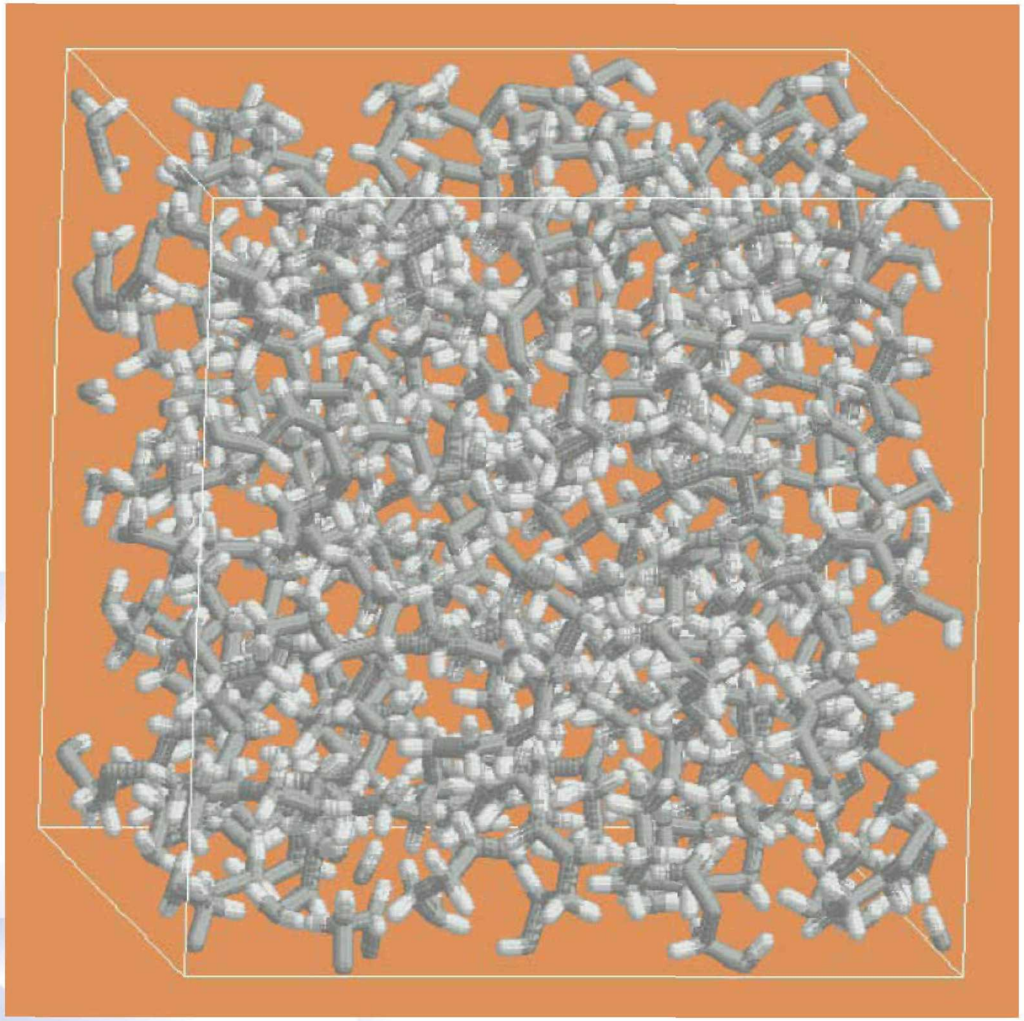
Modified Random Network (MRN) - Greaves

K clusters forming pathways

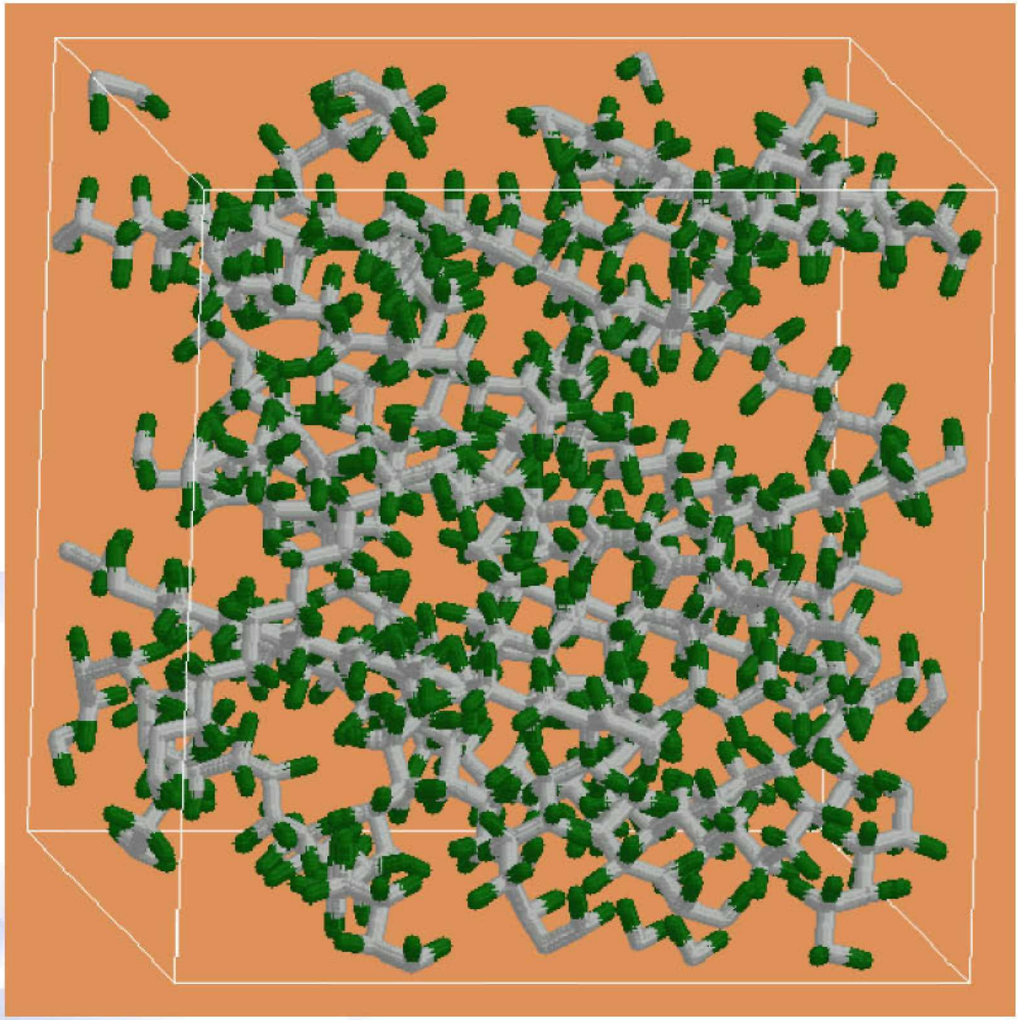


$(K_2O)_{0.45}(SiO_2)_{0.55}$

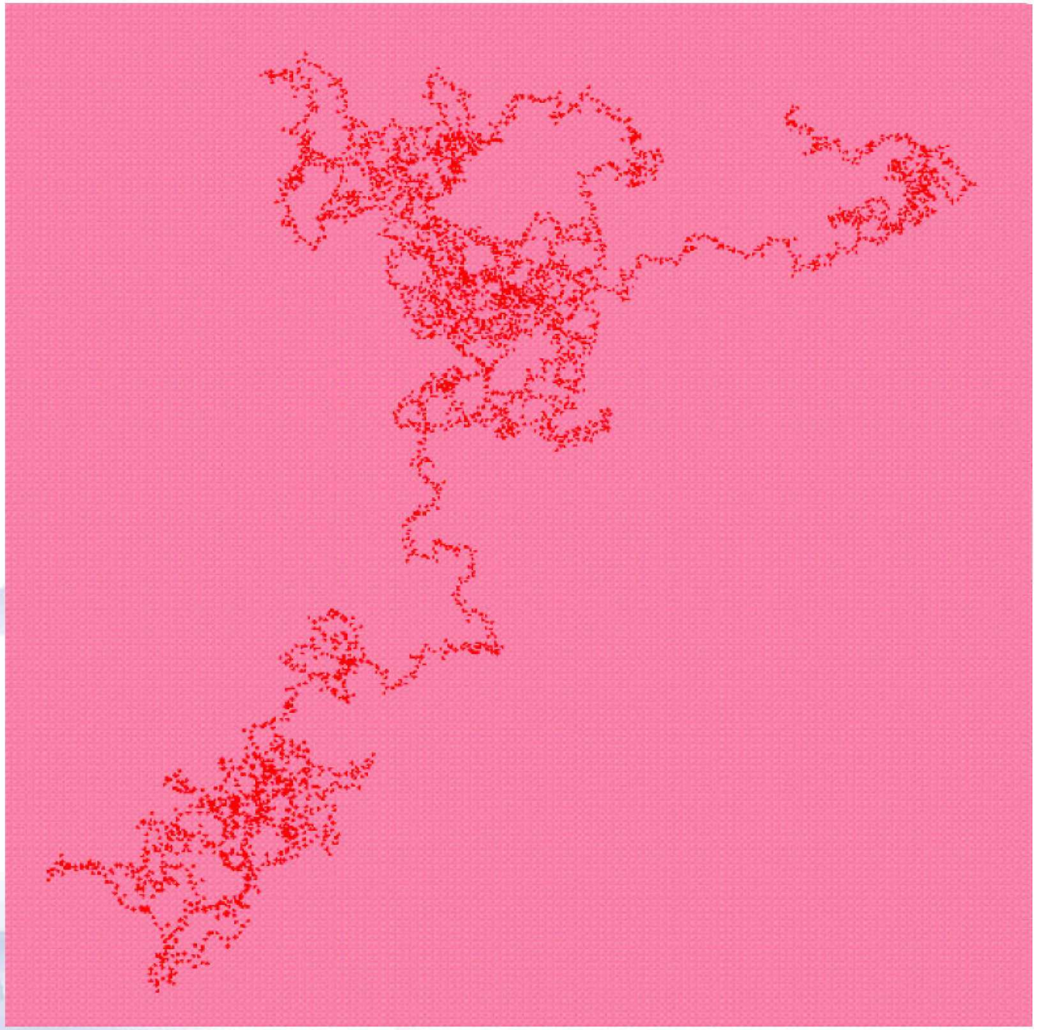
ISIS



$-CH_2-CH_2-$

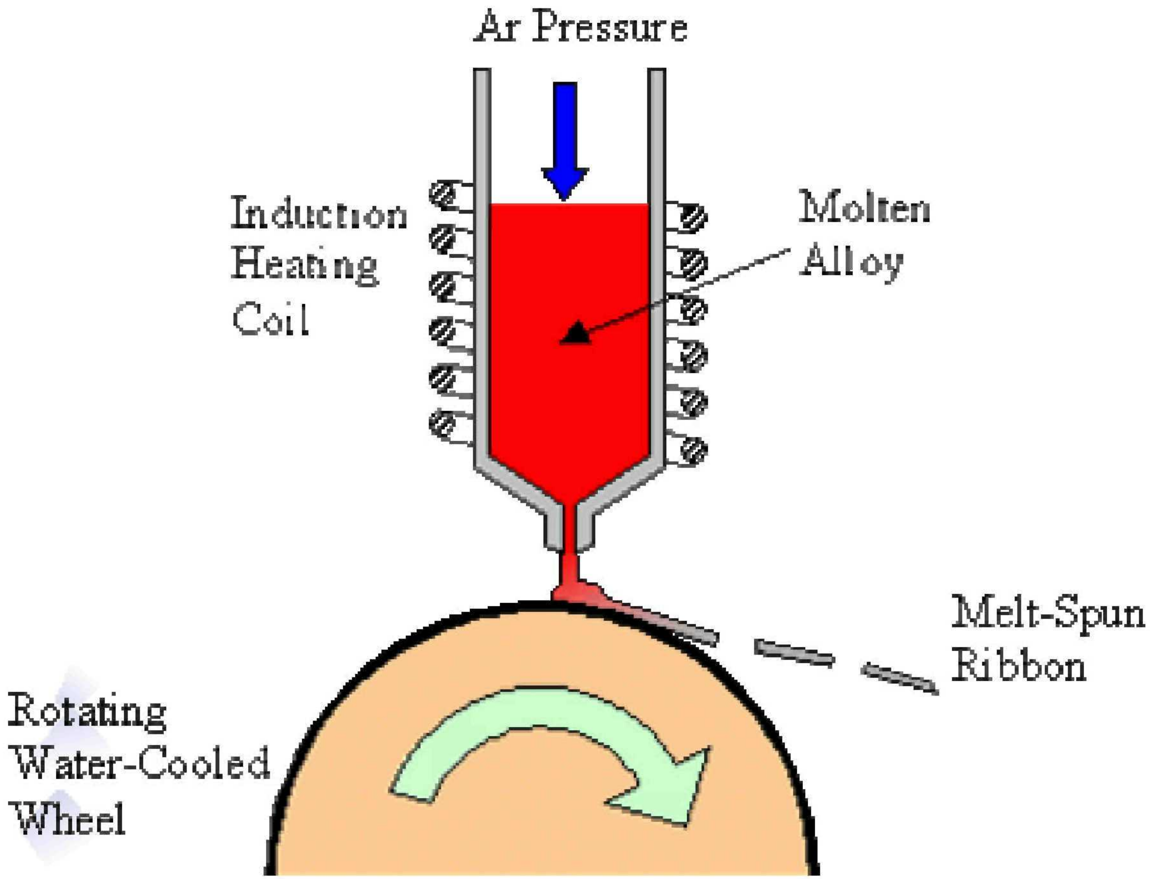


$-CF_2-CF_2-$



$-CH_2-CHCH_3-O-$

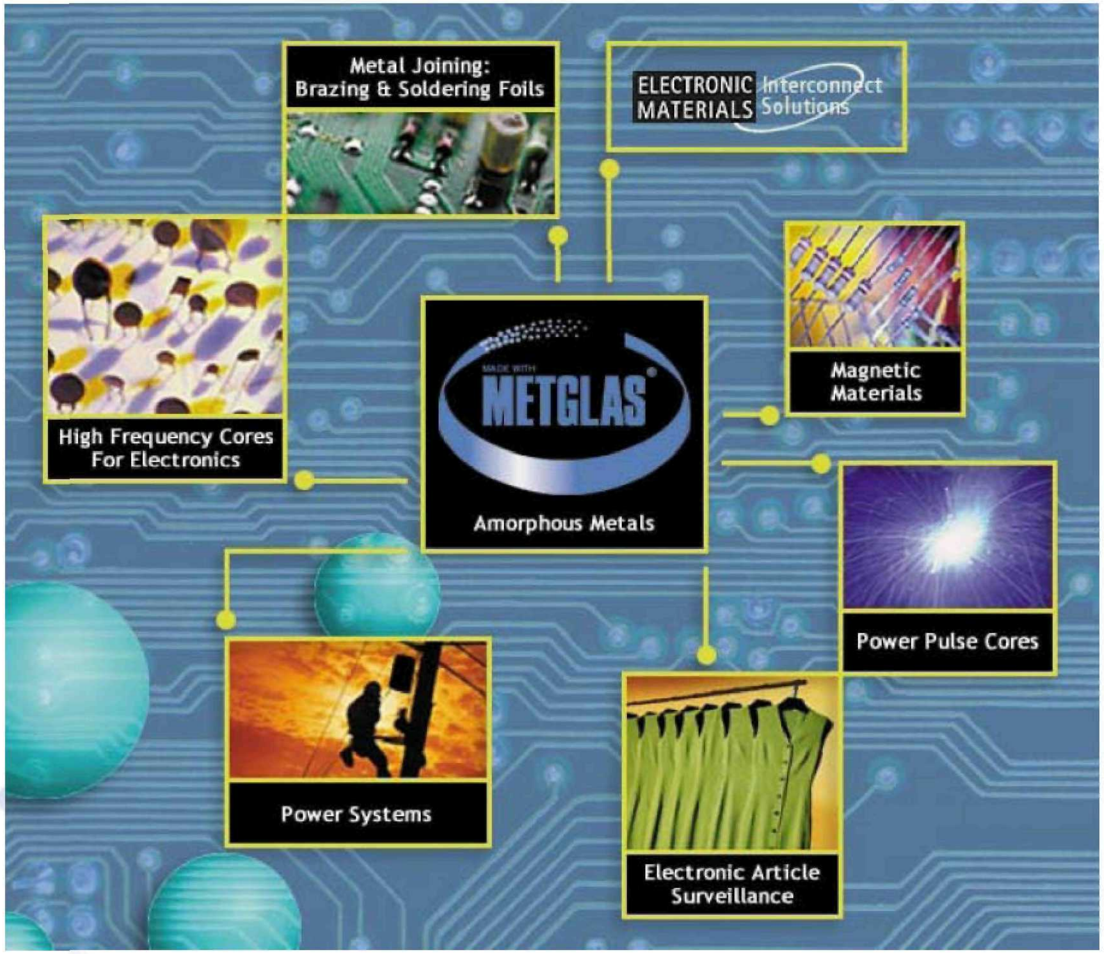
Metallic glasses – melt spinning



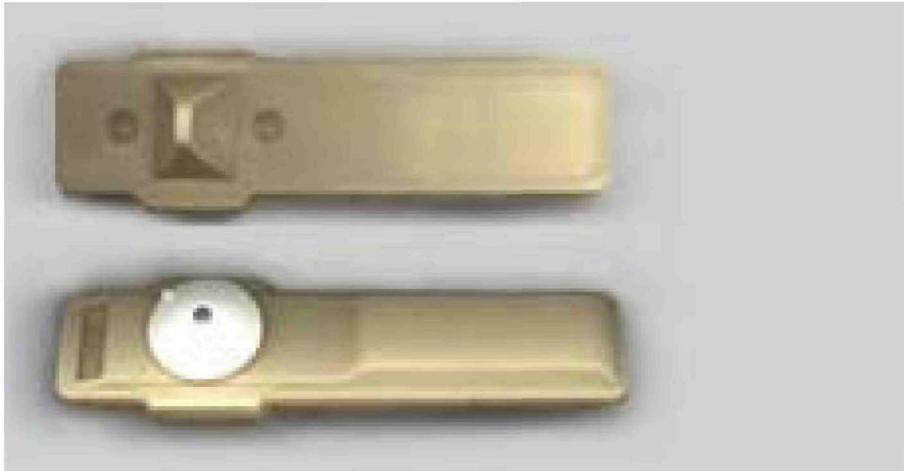
Cooling rate > 10^6 K s^{-1}

Bulk Metallic glasses

Magnetic metallic glasses



Magnetic metallic glasses



ISIS

Magnetic metallic glasses

Amorphous alloys having the formula $Fe_aCo_bNi_cS_xB_yM_z$ are employed as monitoring strips for mechanically oscillating tags, for example for anti-theft protection, together with a source of a pre-magnetization field in which the strip is disposed so as to place the strip in an activated state. In the formula, M denotes one or more elements of groups IV through VII of the periodic table, including C, Ge and P, and the constituents in at % meet the following conditions: a lies between 20 and 74, b lies between 4 and 23, c lies between 5 and 50, with the criterion that b+c>e14, x lies between 0 and 10, y lies between 10 and 20, and z lies between 0 and 5 with the sum x+y+z being between 12 and 21. These alloys have a resonant frequency associated therewith and when passed through an alternating field whose alternation frequency coincides with the resonant frequency, a pulse having a signal amplitude is produced. These alloys can be deactivated by removing the pre-magnetization field, which causes a change in the resonant frequency and the resulting signal amplitude. These alloys exhibit a change in resonant frequency and signal amplitude due to changes in the orientation of the tag in the earth's magnetic field which is smaller than the change occurring upon removal of the pre-magnetization field, so that the tag can be reliably deactivated.

An inexpensive multibit magnetic tag is described which uses an array of amorphous wires in conjunction with a magnetic bias field. The tag is interrogated by the use of a ramped field or an ac field or a combination of the two. The magnetic bias is supplied either by coating each wire with a hard magnetic material which is magnetized or by using magnetized hard magnetic wires or foil strips in proximity to the amorphous wires. Each wire switches at a different value of the external interrogation field due to the difference in the magnetic bias field acting on each wire.

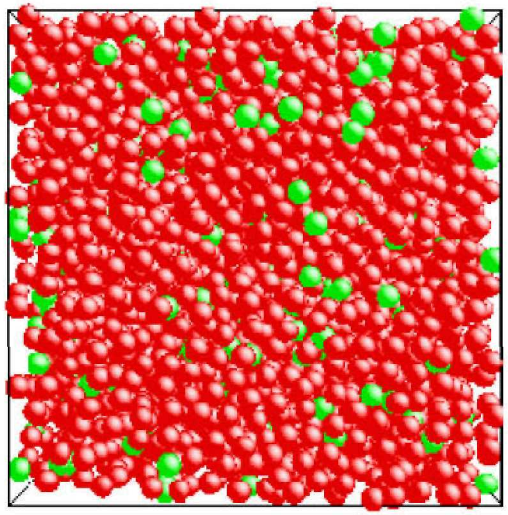
$$Fe_aCo_bNi_cS_xB_yM_z$$

Magnetic metallic glasses

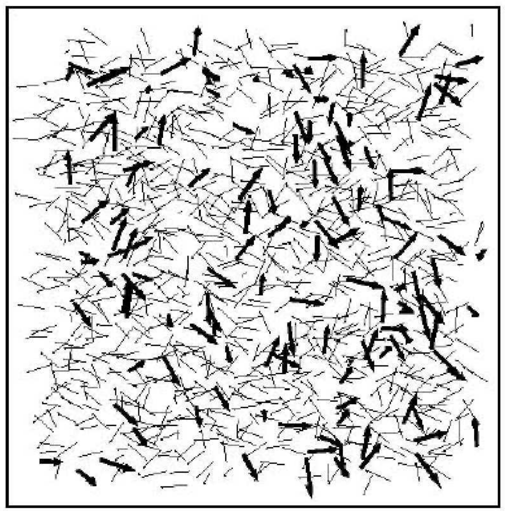
Neutron scattering
+
X-ray scattering
+
EXAFS

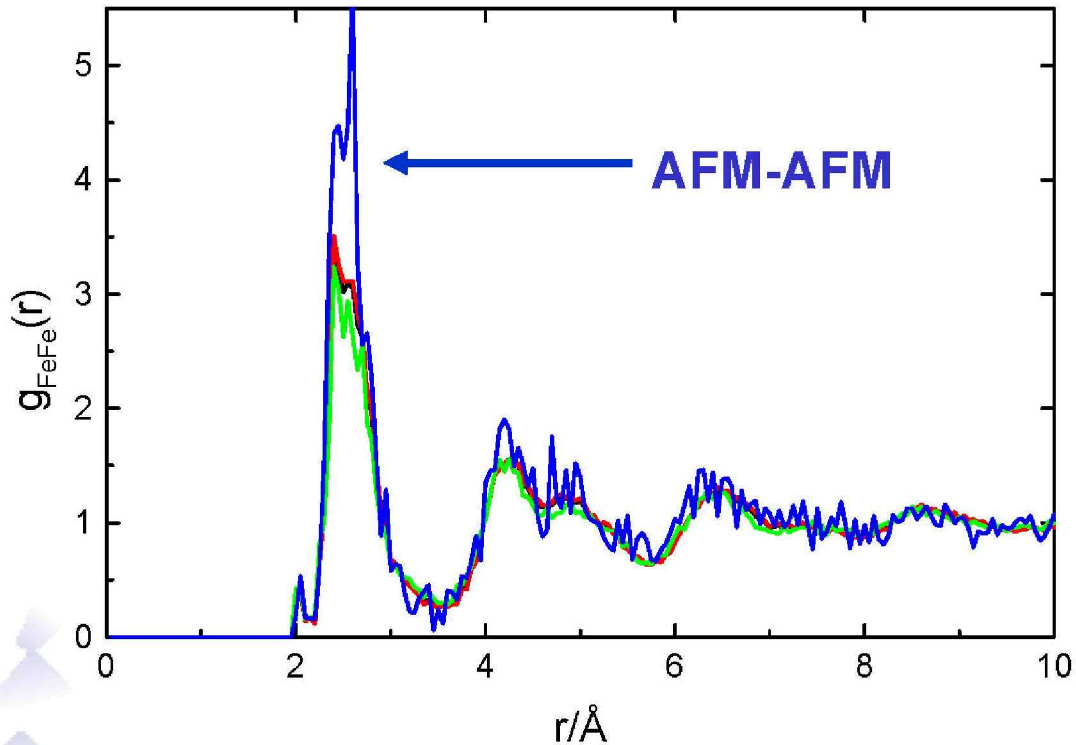
Computer modelling

Neutron scattering

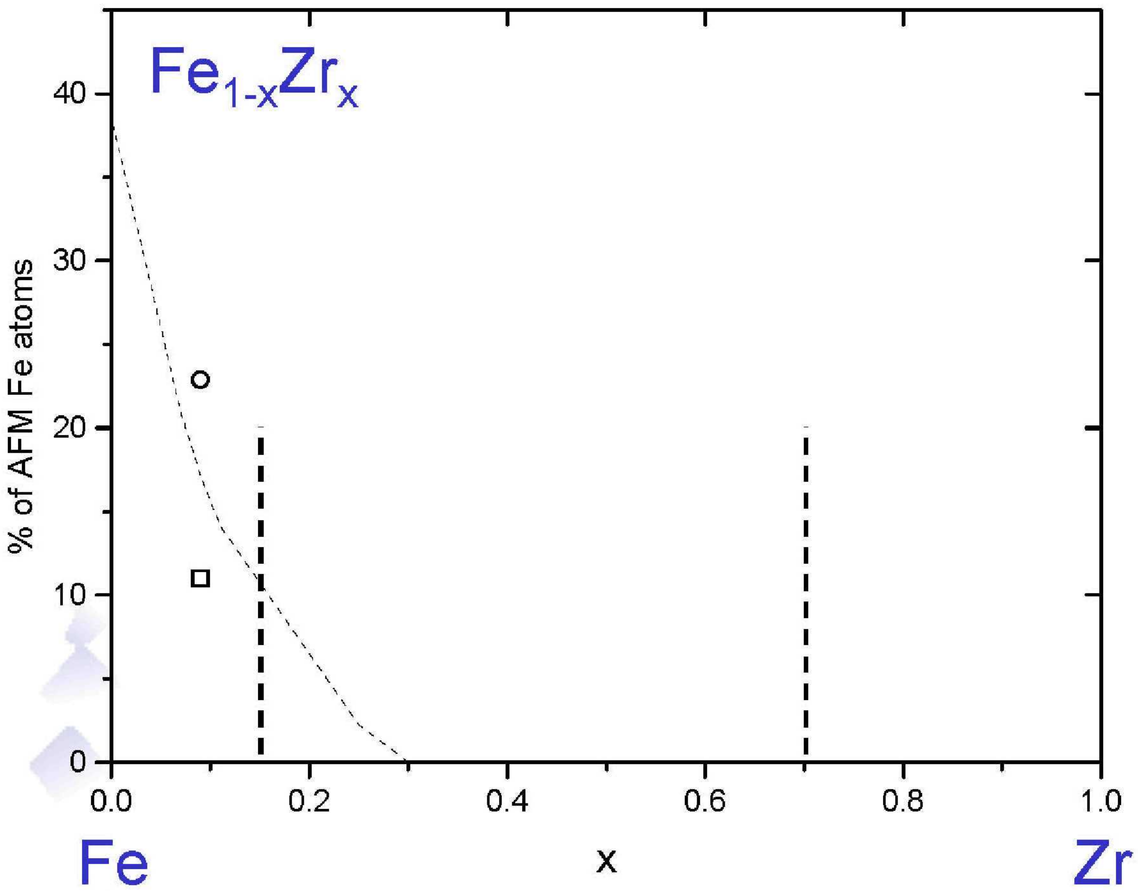


$Fe_{0.91}Zr_{0.09}$

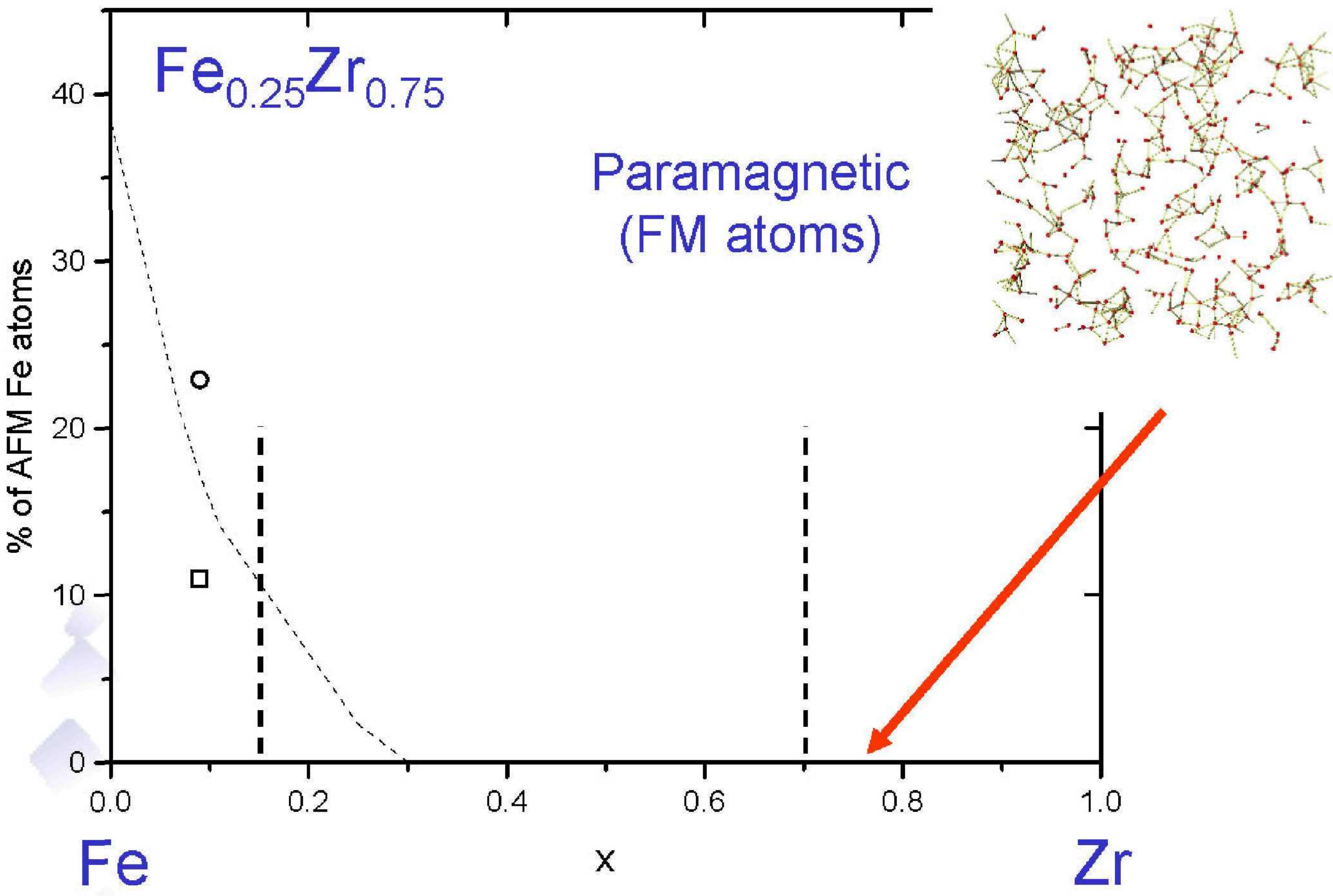


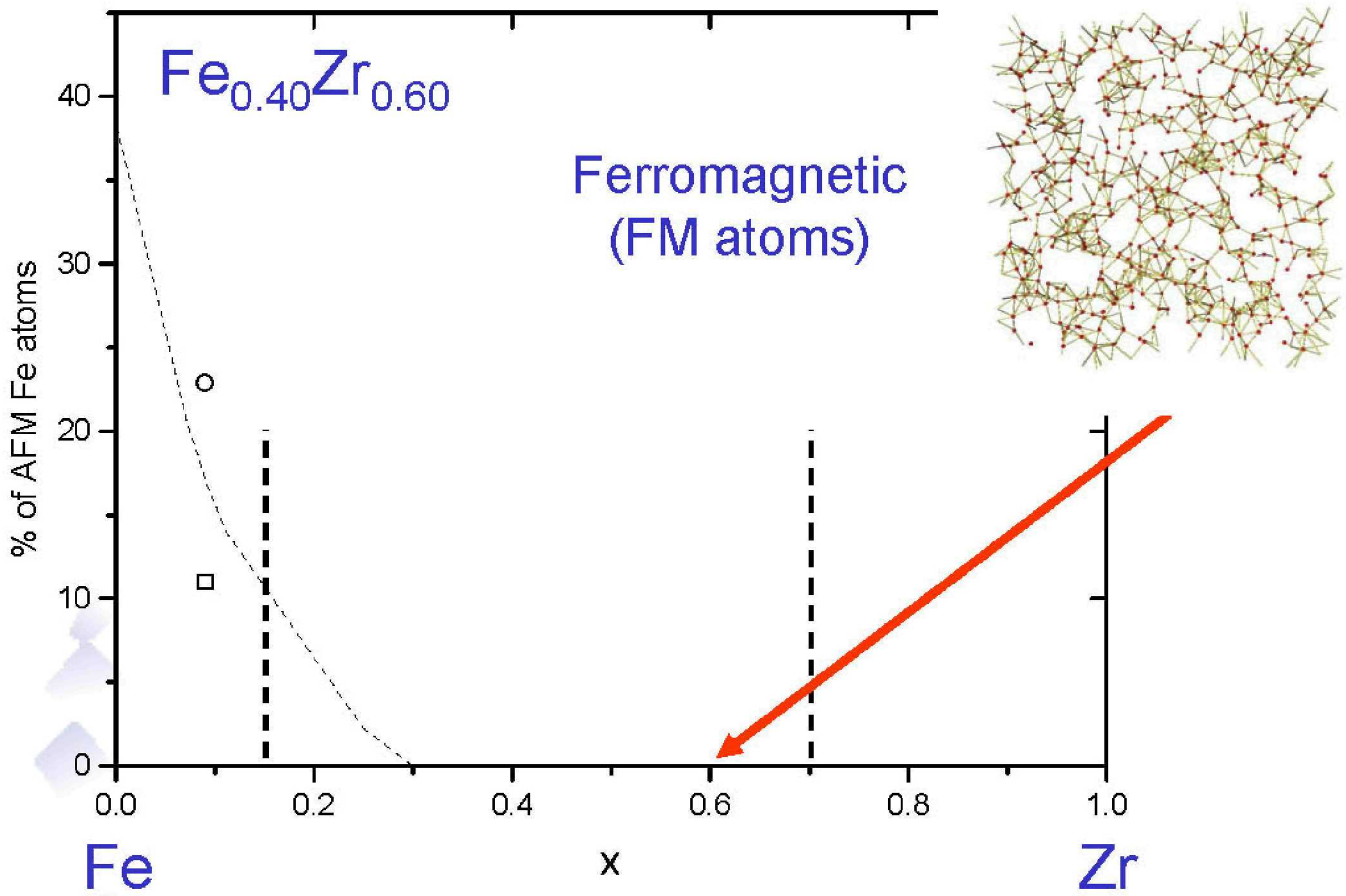


ISIS

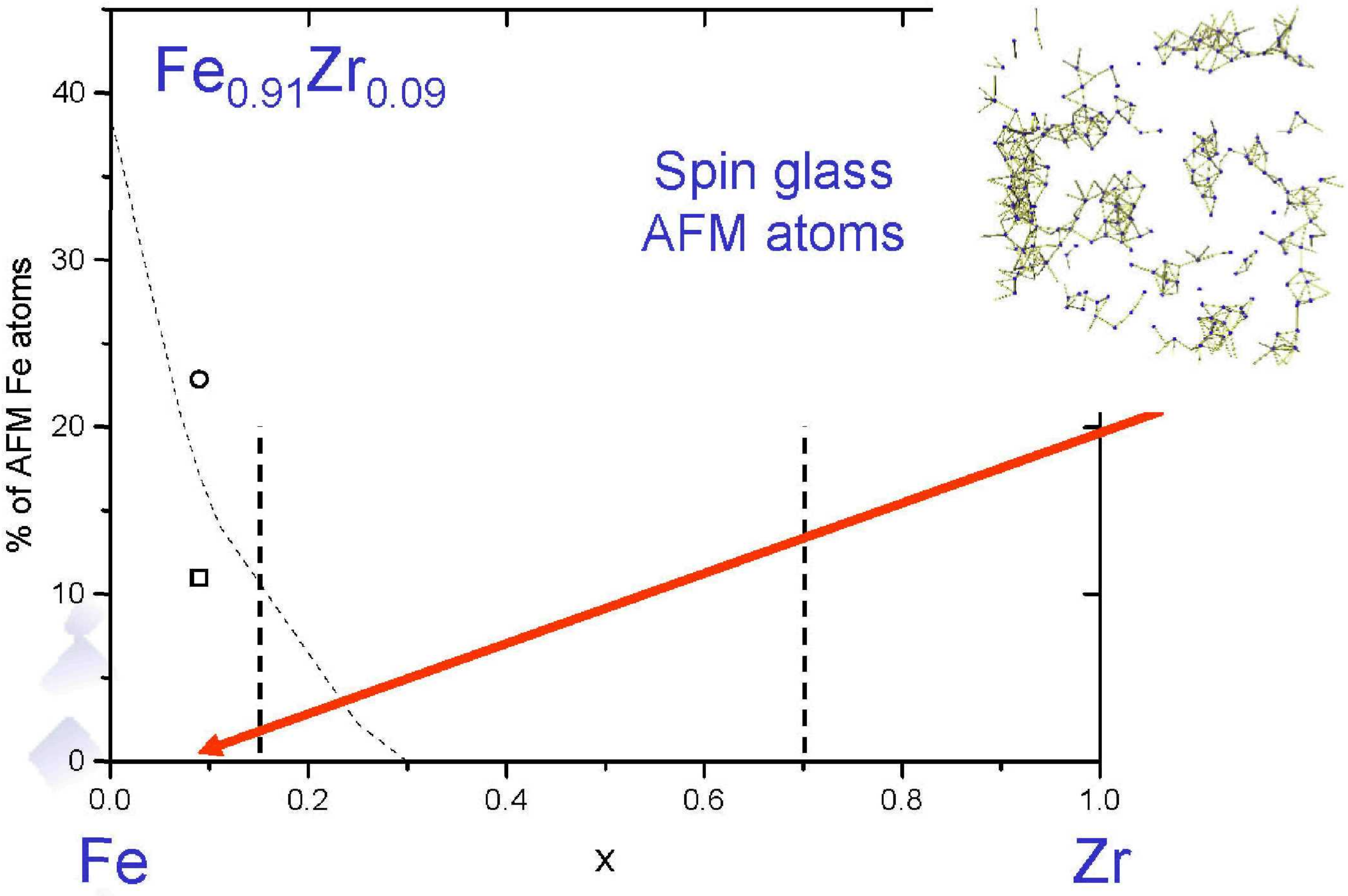


Fe1-xZr x
% of AFM Fe atoms
40
30
20
10
0
0.0
0.2
0.4
0.6
0.8
1.0
x
Fe
Zr


Fe0.25Zr0.75
Paramagnetic
(FM atoms)
% of AFM Fe atoms
0
10
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
Fe
x
Zr



$Fe_{0.40}Zr_{0.60}$
Ferromagnetic
(FM atoms)
% of AFM Fe atoms
0
10
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
x
Fe
Zr



$Fe_{0.91}Zr_{0.09}$
Spin glass
AFM atoms
% of AFM Fe atoms
0
10
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0
x
Fe
Zr

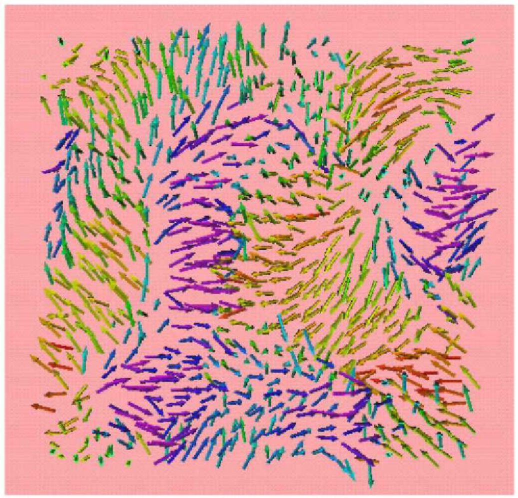
Magnetic metallic glasses

Neutron scattering
+
X-ray scattering
+
EXAFS

Atomic structure

Computer modelling

$Dy_{0.7}Fe_{0.3}$



Neutron scattering

What is a Glass?

A glass is a non-ergodic state of matter which has become non-ergodic by virtue of the continuous slow-down of one or more of its degrees of freedom

A structural glass is an amorphous solid which is capable of passing into the viscous liquid state, usually, but not necessarily, accompanied by an abrupt increase in heat capacity (the glass transition)

An amorphous solid is a solid which lacks long range (crystalline) order

ISIS