#### 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 breaktbrough in

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]



### What is a Glass?

















## 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 shit 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)





### 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























### 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





Quartz





#### HP Tridymite MD simulation





#### Vitreous silica











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















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

Constructive interference

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



$$n(\mathbf{r}) = n(\mathbf{r} + \mathbf{T}) \qquad \mathbf{T} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$
$$n(\mathbf{r}) = \sum n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$$
$$A = \int \sum n_{\mathbf{G}} \exp(i(\mathbf{G} - \Delta \mathbf{k}) \cdot \mathbf{r}) d\mathbf{r}$$

Constructive interference

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

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











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



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







Neutron diffraction from vitreous and crystalline SiO<sub>2</sub>







X-ray diffraction from vitreous SiO<sub>2</sub> (form factor corrected)







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







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



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

 $n(\mathbf{r}) = \sum_{j} f_{j}(\mathbf{r}_{j})$  $I = A^{*}A$ 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

 $S_{\alpha\beta}(Q)$ 

 $g_{\alpha\beta}(r)$ 

**Partial Structure Factor** 

Partial radial distribution function




#### 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<sub>2</sub>



#### 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



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

















# 'Average' structure models

Tend to overestimate the geometrical order

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



## Vitreous silica



# 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:









#### Monte Carlo - MC





10



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





# Modified Random Network (MRN) - Greaves





# Modified Random Network (MRN) - Greaves

K clusters forming – pathways



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





## $-CH_2-CH_2-$





# $-CF_2-CF_2-$





# -CH<sub>2</sub>-CHCH<sub>3</sub>-O-



#### Metallic glasses – melt spinning



## Bulk Metallic glasses

















Amorphous alloys having the formuld  $Fe_aCo_bNi_cS_xB_yM_z$  are employed as monitoring strips for mechanically oscillating tags, for example for anti-theft protection, tigether 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.

 $Fe_aCo_bNi_cS_xB_vM_z$ 


















## Magnetic metallic glasses



## What is a Glass?

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