MSE-238
Structure of Materials

Week 9 – amorphous structures I: glasses

Spring 2025

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General Outline

- introduction and reminder of atomic bonds, crystals – week 1

Part I: crystallography - weeks 2-6

- packing of spheres, constructing crystal structure week 2
- crystal lattice and symmetry operations week 3
- mathematical description of the lattice, Miller indices week 4
- reciprocal space (&diffraction) week 6
- characterization I: diffraction week 7
- diffraction & recap of crystallography week 8

BREAK 18.4. & 25.4.

Part III: amorphous & hierarchical structures – week 9-12

- **glasses**
- polymers
- Characterization II: scattering
- biological and hybrid materials

Recap – week 13

Overview

- amorphous vs. crystalline materials
- order and disorder
- structural parameters for amorphous materials
- Pair distribution function and how it is measured
- glass transition temperature
- atomic scale structure
- continous random-network model
- properties of crystal and amorphous structure
- application of amorphous structures

Amorphous vs crystalline materials

- Amorphous

Silica and other oxides
short-range order

- Cristalline

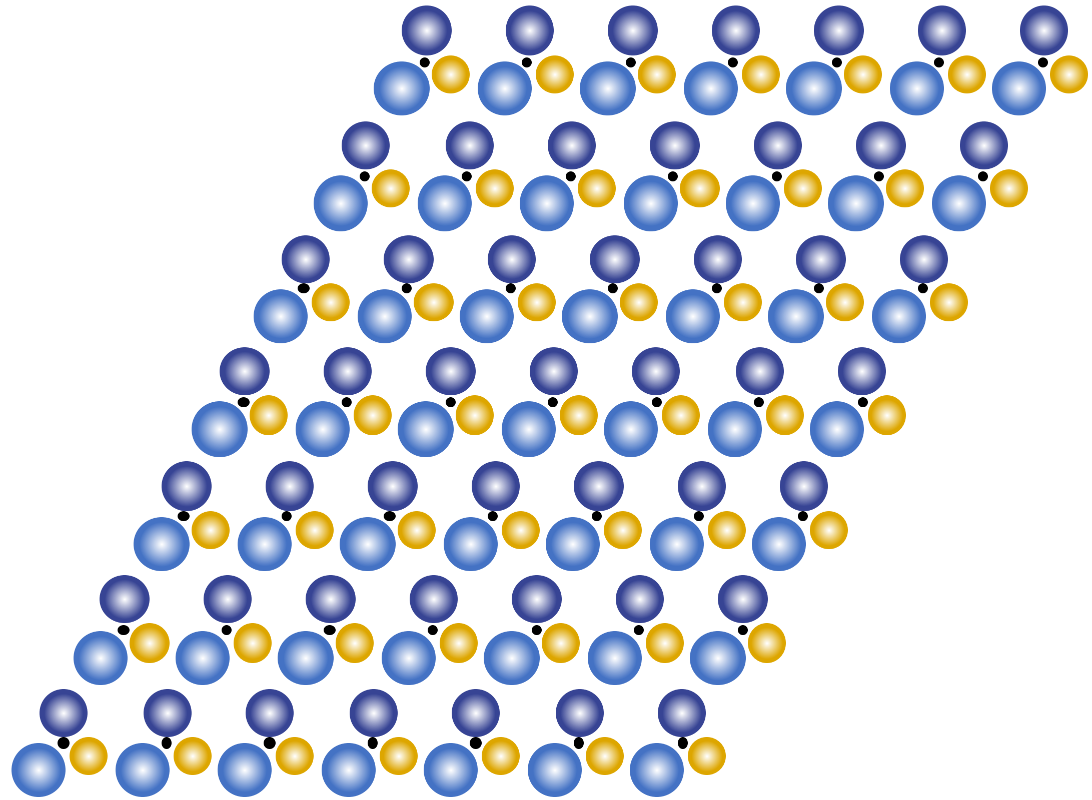
Quartz resonator, quartz and spoon in stainless steel
long range order

How to describe the structure?

Bravais lattice

⊗ Basis

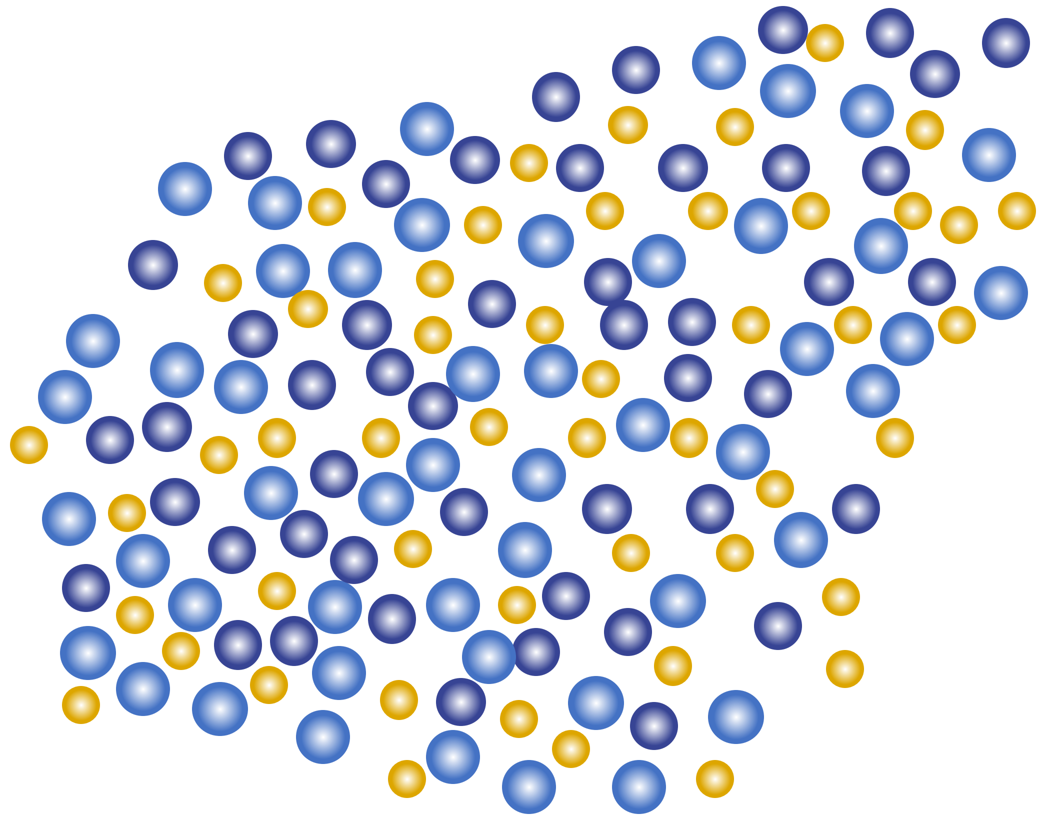
= Crystal



crystal: describe atomic structure with just one unit cell!

animation: Phil Willmott

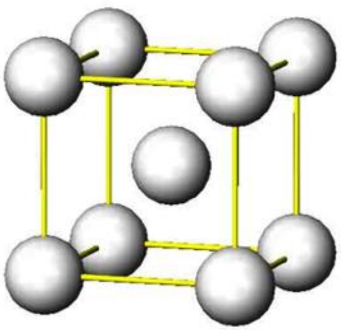
How to describe the structure?

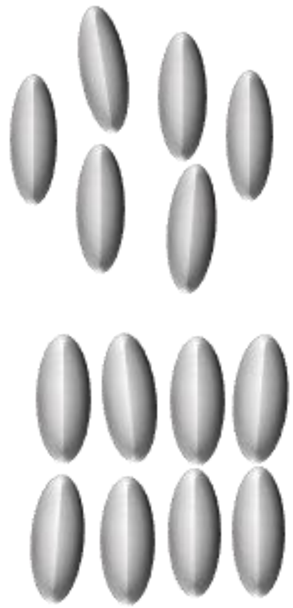


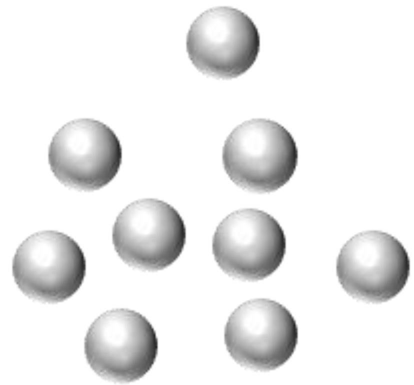
amorphous material: the atomic arrangement of two amorphous samples are never identical

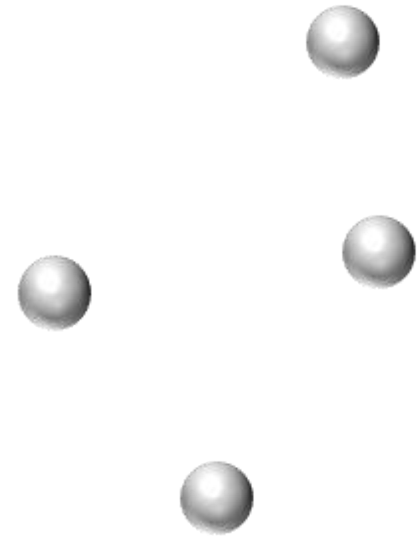
we have to look at **average** structural features

Order and disorder





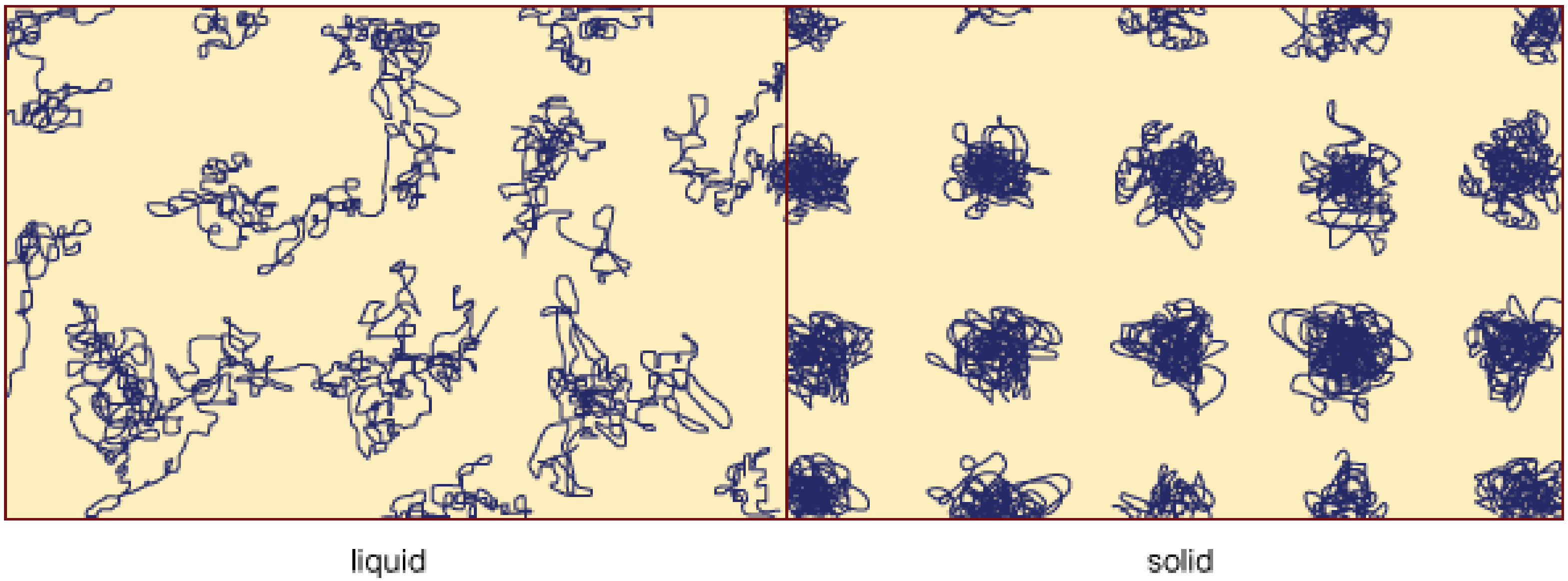




long-range order	long-range order	short-range order	disordered
translational symmetry	orientational symmetry (nematic)	some correlation	no correlation
	orient. & transl. sym. (smectic)	no symmetry	no symmetry
solid	liquid (2D or 3D)	liquid or solid	gas
densly packed	densly packed	densly packed	compressable
crystalline	liquid-crystalline	amorphous solid/glass, liquid	gas

solid vs. liquid

on atomic scale:



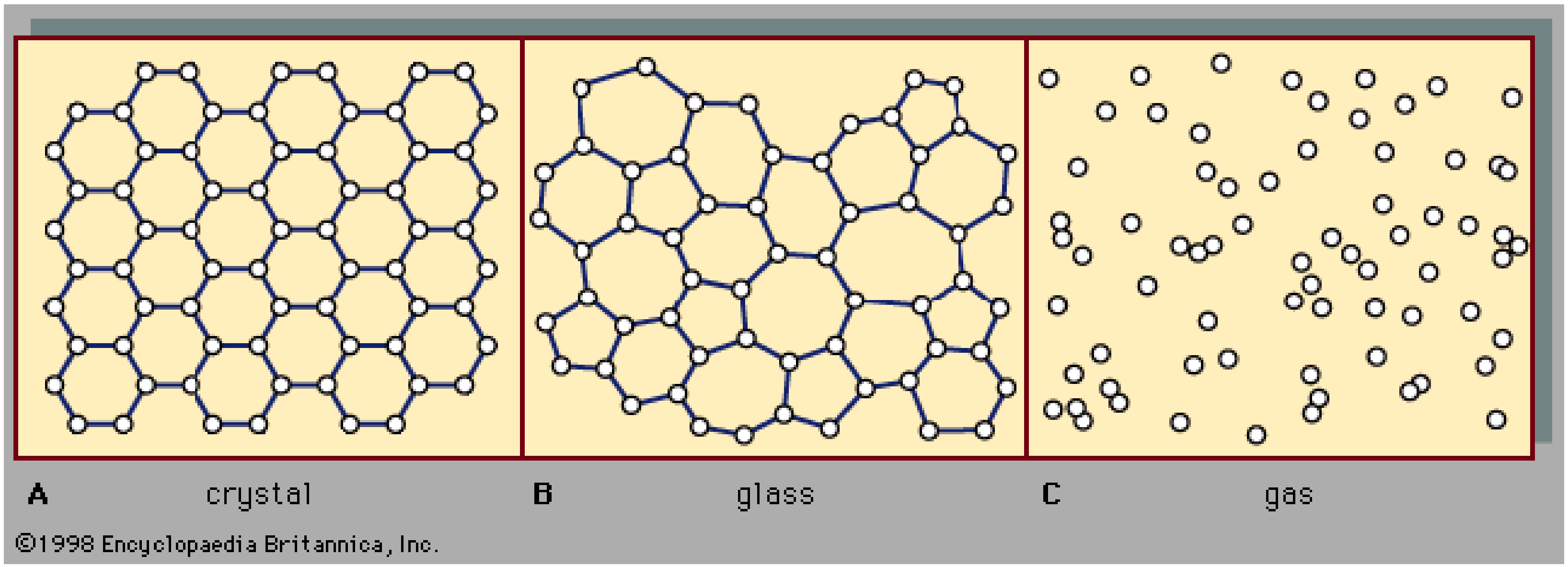
in liquids atoms are **mobile** and continually wander throughout the material

in solid atoms are not mobile, they oscillate rapidly about **fixed points** in space
→ arrangement with long-range order: crystal
→ arrangment without long-range order: solid amorphous structure

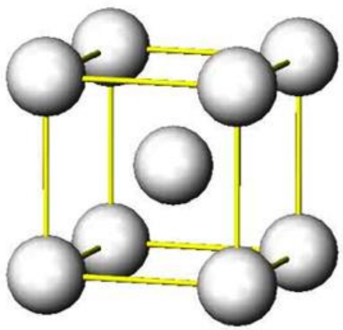
solid: crystal and amorphous solids

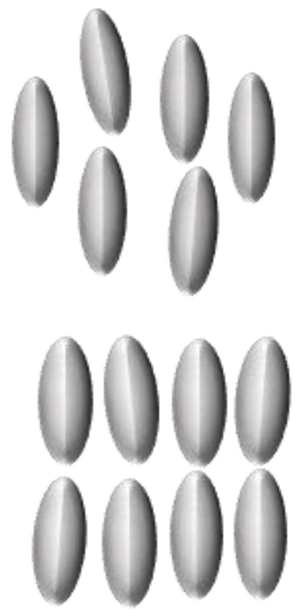
solid dots: only one snap shot of one configuration of atomic positions

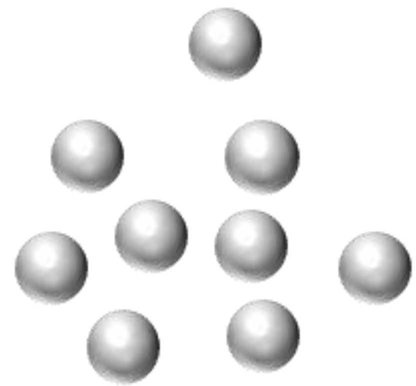
solid dots: fixed position



Order and disorder







→ how to describe structure of amorphous materials?

long-range order: periodic distribtuion of atoms ordered over large distances

exact location from an atom can be inferred relative to a chosen atom at the origin
→ **atomistic**

short-range order: over short distances (some atomic diameters) a certain periodicity in the distribution of atoms still exists.

some randomness in the position of the atoms: structural order can only be described **statistical**

Structural parameters

- density/packing efficiency: overall mass per unit volume
- free volume: the unoccupied space within the structure
- coordination number
- bond length (distribution)
- bond angle distribution: variability in bond angles
- pair distribution function, or radial distribution functions: how atomic density varies as a function of distance from a reference atom

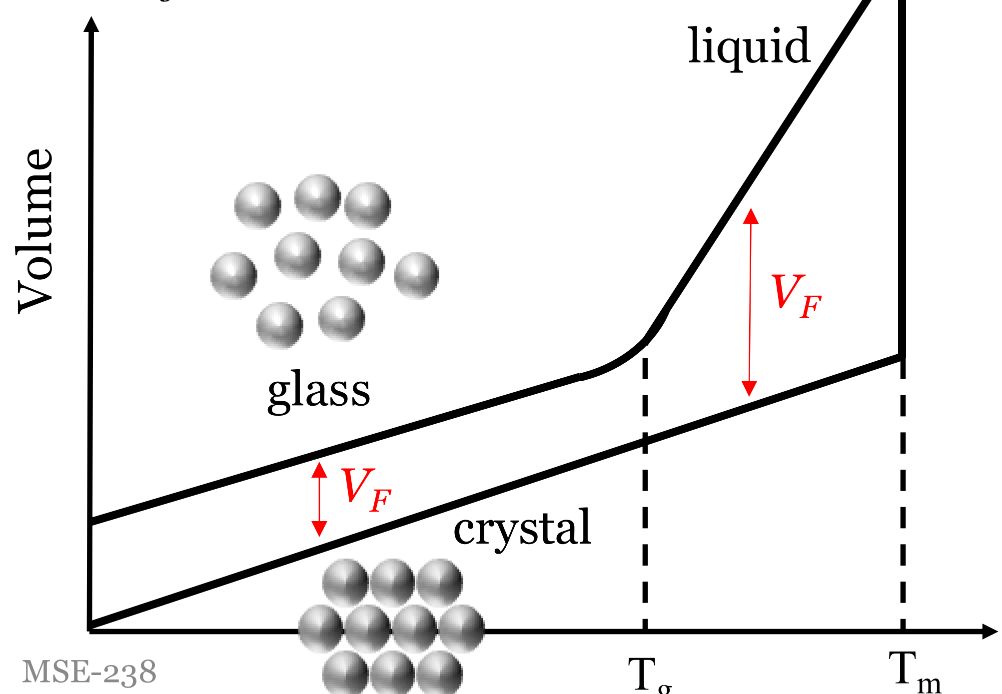
Free volume

- space in the material not occupied by atoms/molecules
- a temperature dependent property!
- the free volume V_F is the difference between the total sample specific volume (volume per unit mass) and the occupied specific volume V_o
- V_o can be approximated as the specific volume in the crystalline state

$$V_F\,(\mathrm{T}) = \mathrm{V(T)} - V_o\,(\mathrm{T}) \simeq \mathrm{V(T)} - V_{cryst}\,(\mathrm{T})$$

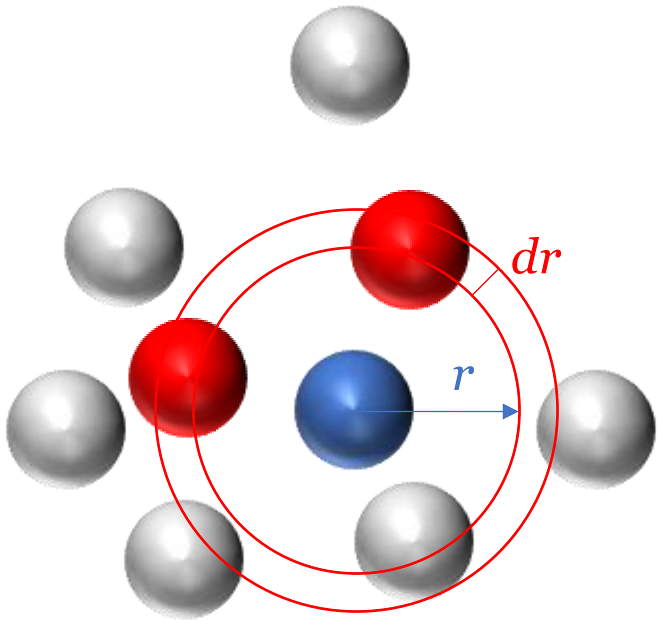
melting temperature T_m with an abrupt change in the specific volume

glass transition T_g thermal expansion coefficient changes (different slope) but no abrupt change in specific volume

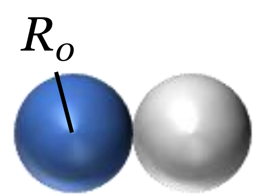


Pair distribution function (PDF)

- probability of finding an atom/molecule at a certain distance normalized over the overall density → local density in the structure surrounding a typical atom



$$g(r) = \frac{dn(r,r+dr)}{dv(r,r+dr)}\frac{1}{\rho_0} = 4\pi r[\rho(r) - \rho_0]$$



$$g(r < 2R_o) = 0$$

dn : number of atoms in a spherical shell

dv : spherical shell volume

r : distance of the shell from an arbitary atom selected as the origin

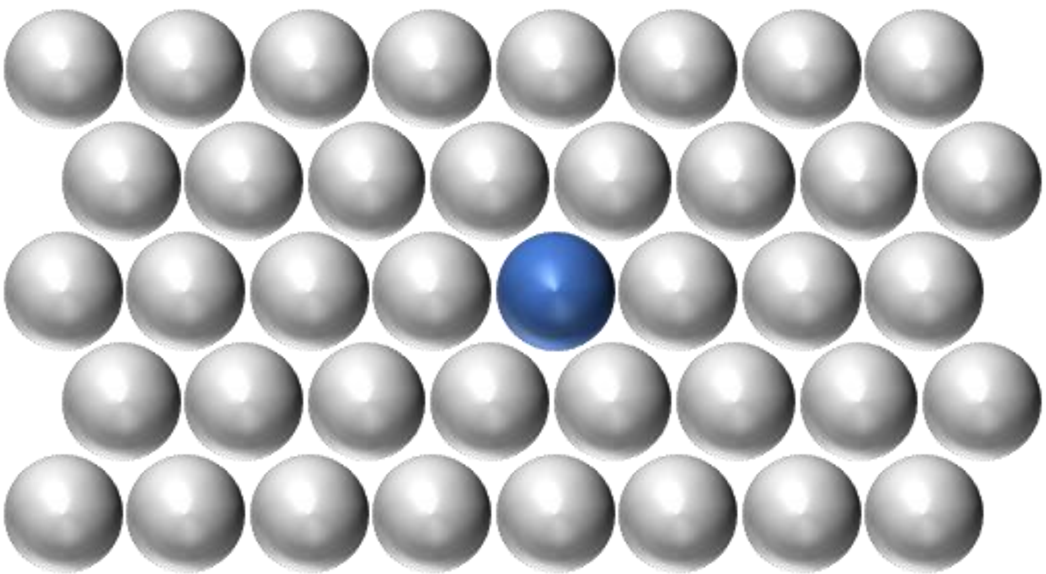
ρ_0: average particle density

$\rho(r)$: atomic pair density

R_o = radius of atom (solid sphere model)

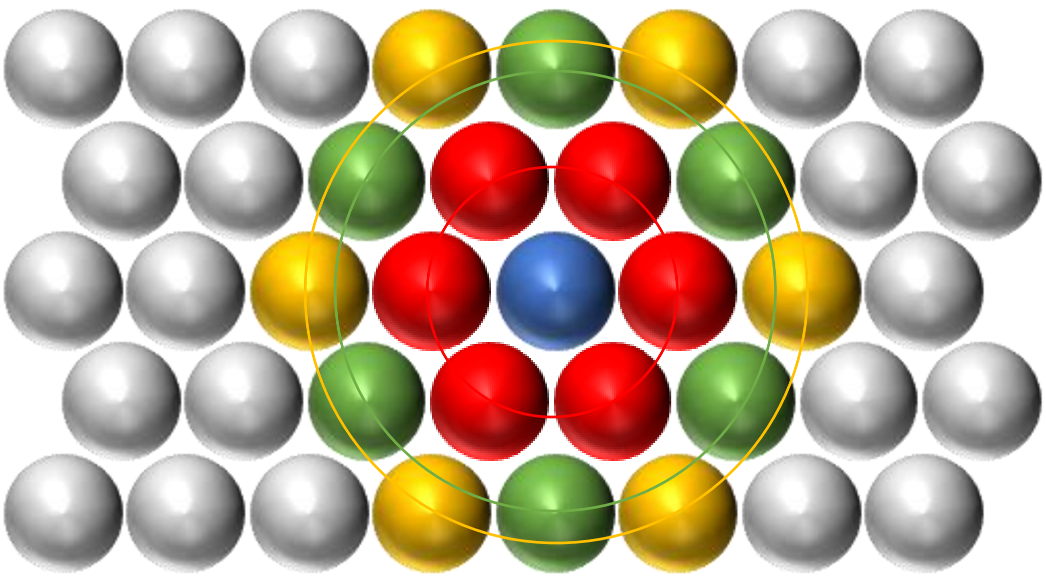
Pair distribution function for crystals

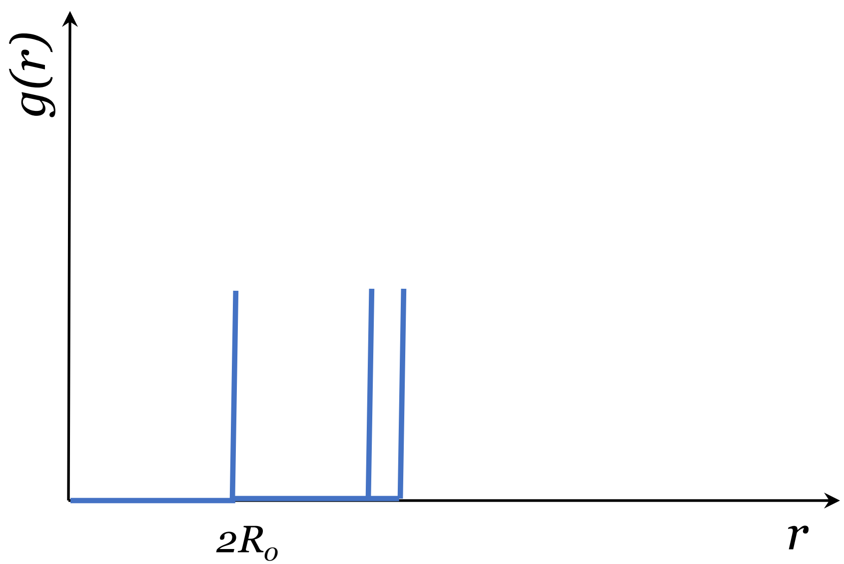
- long-range order



Pair distribution function for crystals

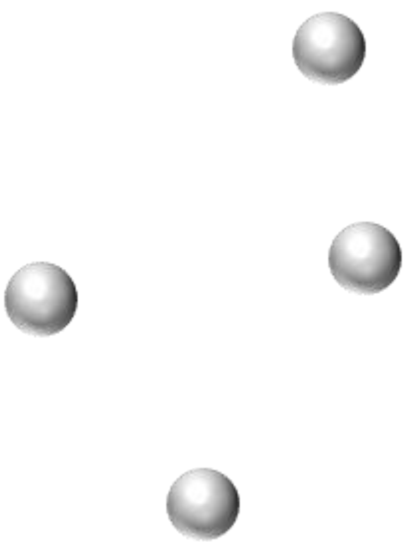
- long-range order
- *g(r)* infinite series of discrete peaks (delta functions) at the values of interatomic separation
- depends on particular crystal structure

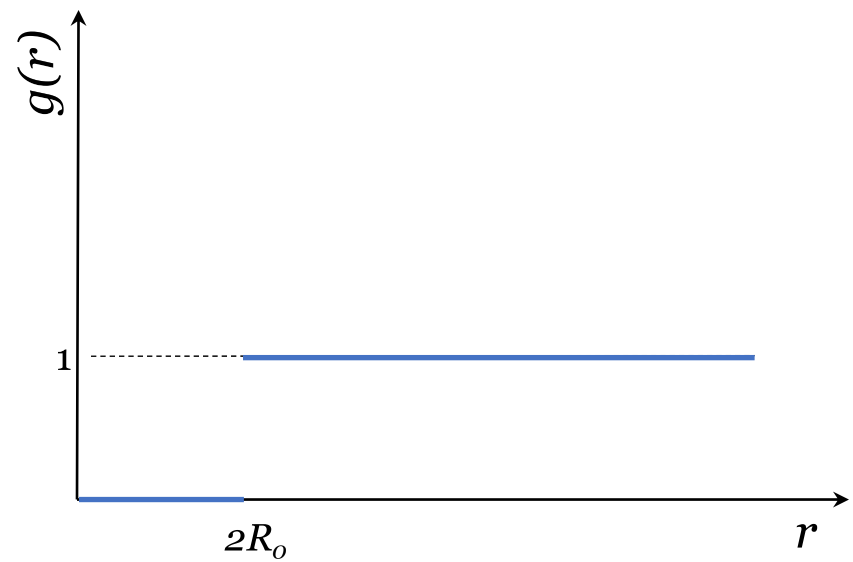


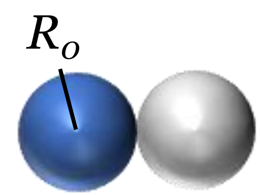


Pair distribution function for a gas

- atoms (or molecules) are uncorrelated, no short-range order
- Below the hard-sphere diameter $2R_o$ the probability finding another atom is zero (as for all materials)
- Beyond the hard sphere diameter, the probability of finding another atom is equal to the average gas density, $g(r) = 1$



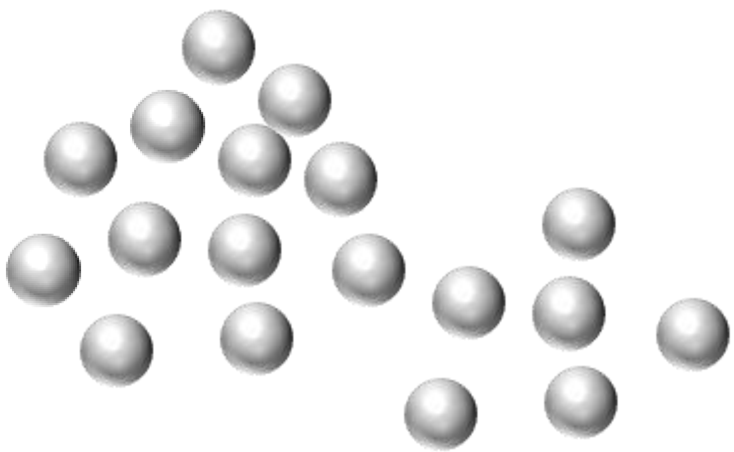


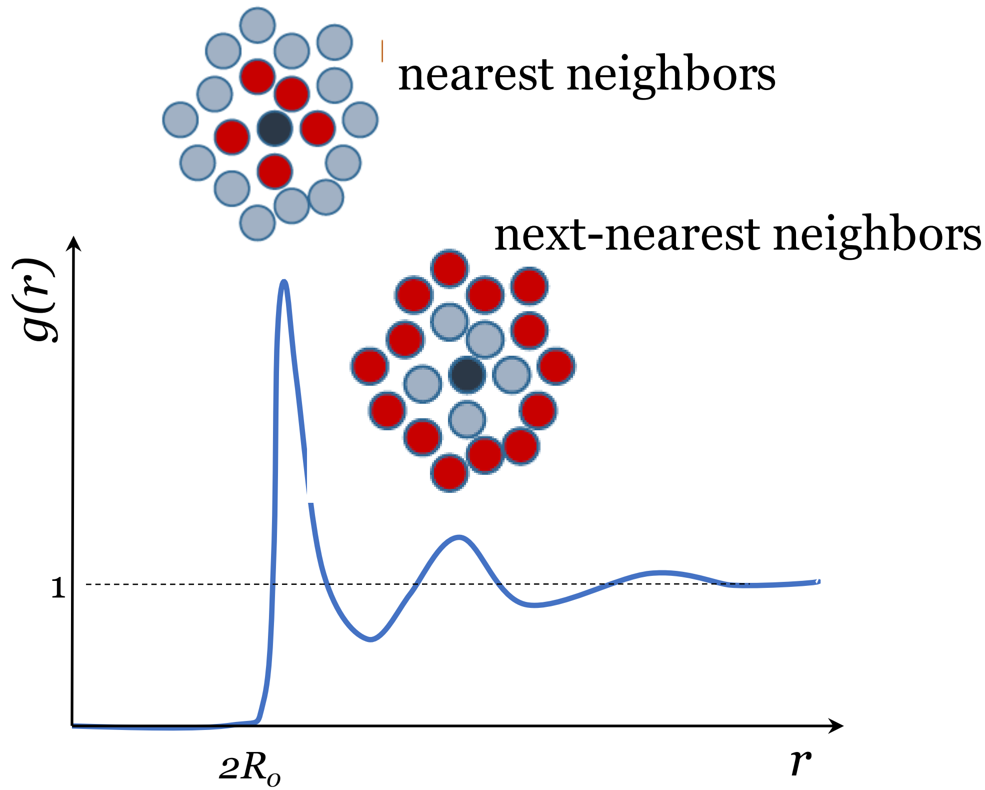


$g(r < 2R_o) = 0$

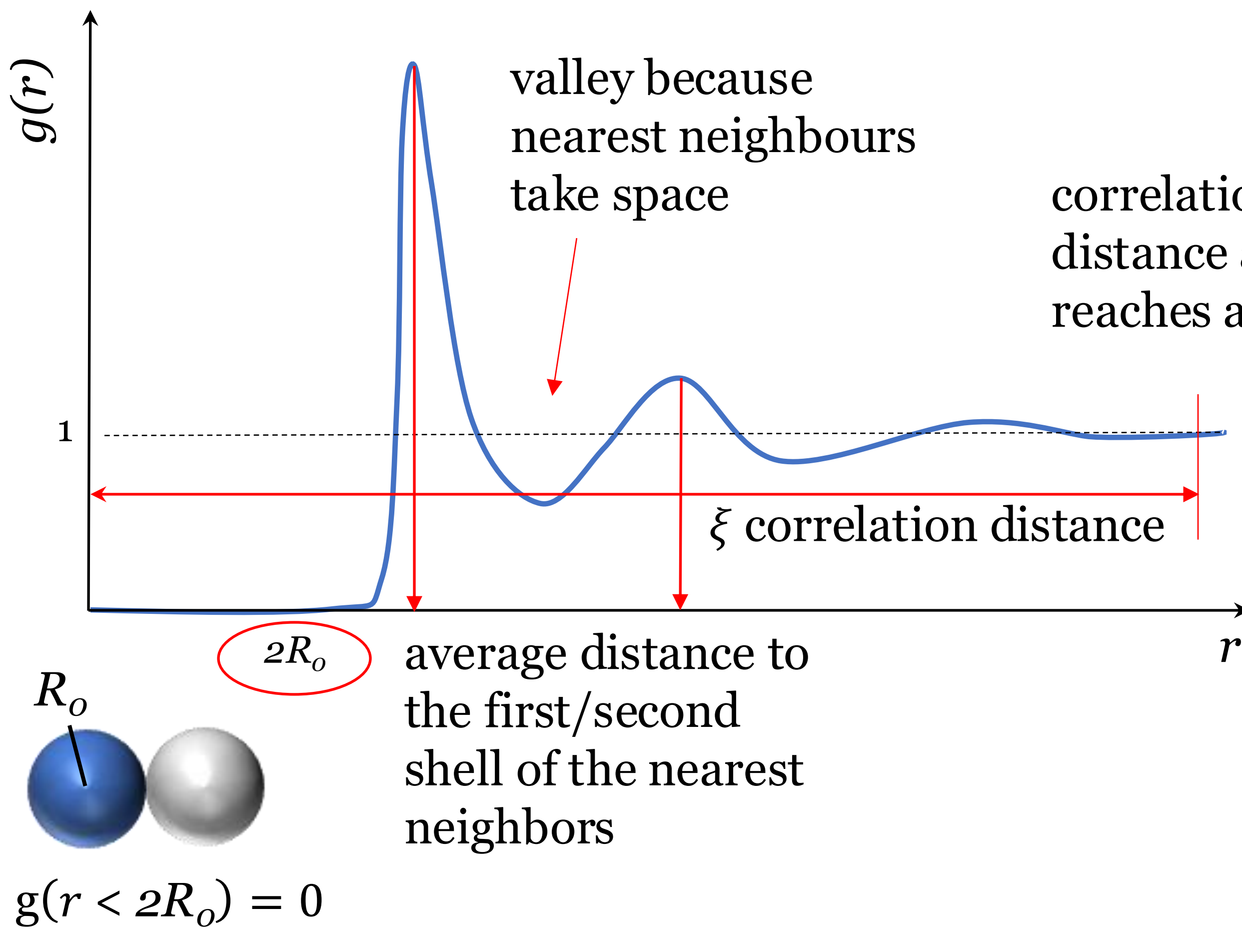
Pair distribution function for liquid/glass

- short-range order
- *g(r)* several broad peaks and valleys until reaching a constant value at large distance r

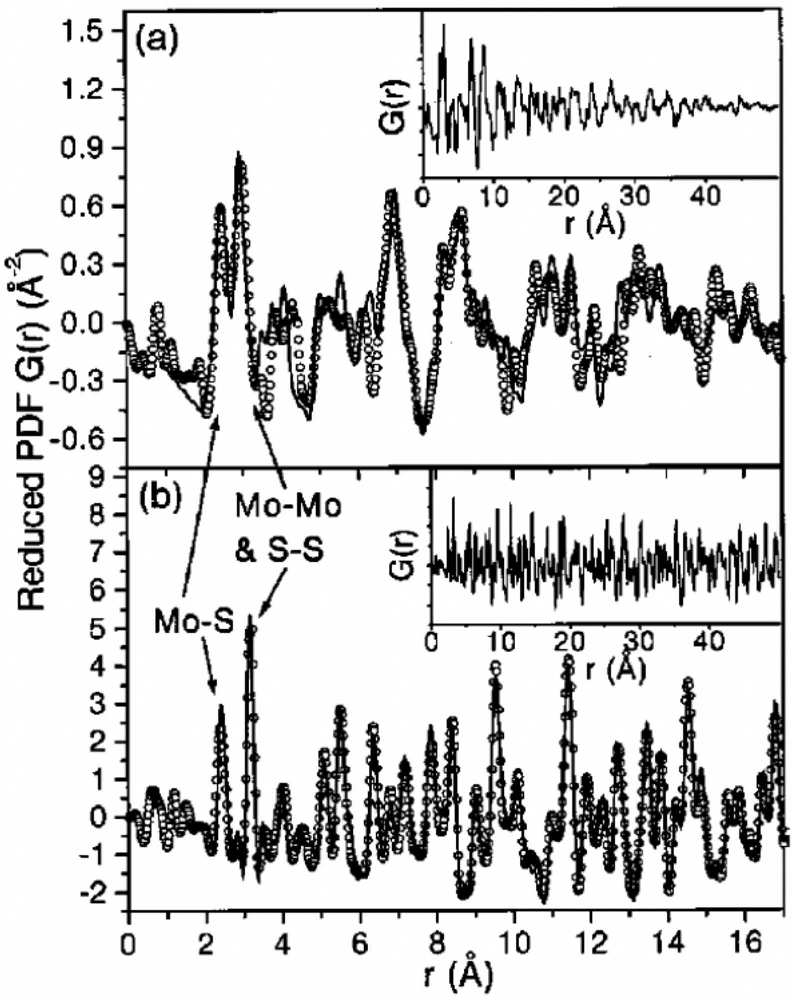




Pair distribution function for liquid/glass



PDF of crystalline materials



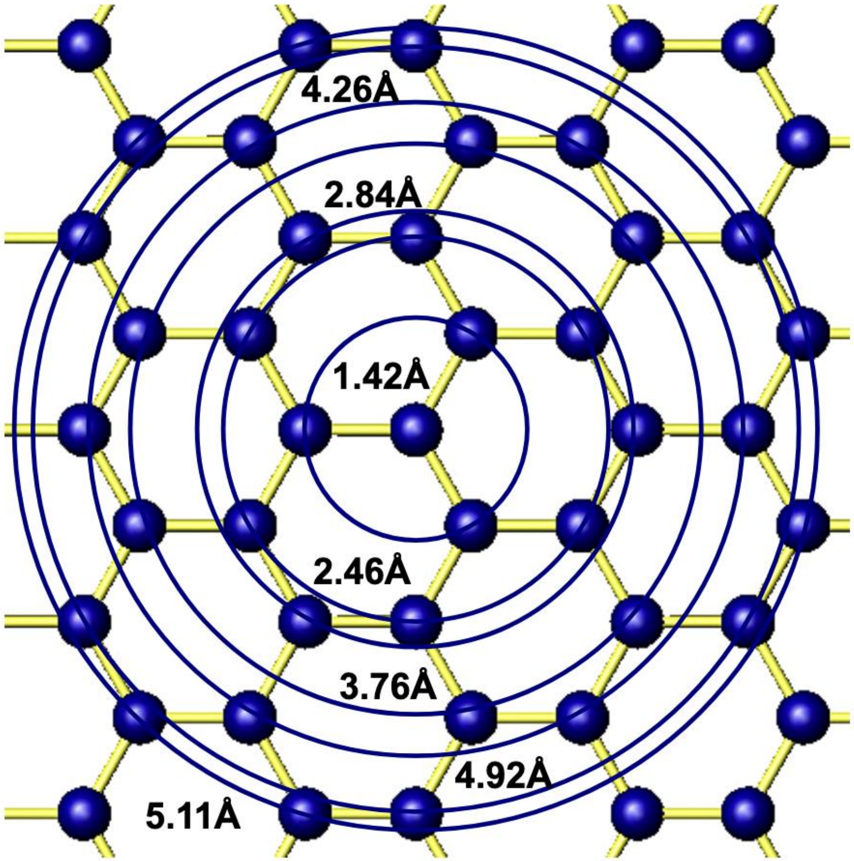
$LiMoS_2$

MoS_2

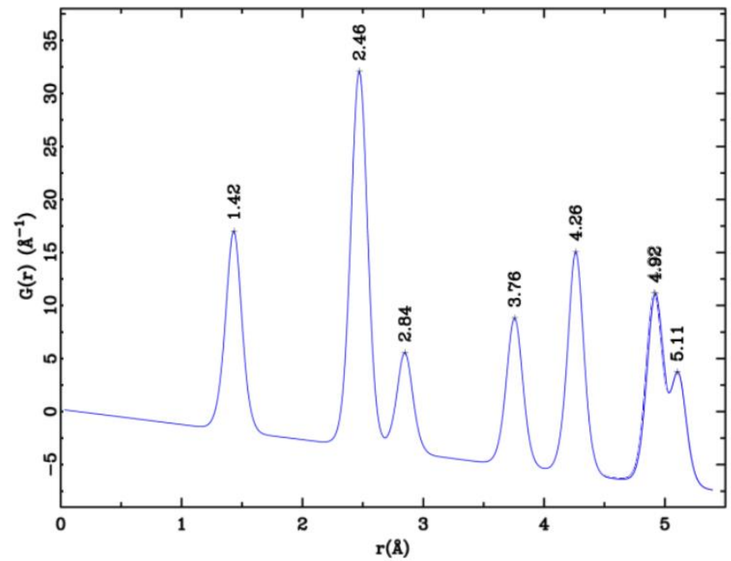
Fig. 6 PDFs from (a) $LiMoS_2$ and (b) MoS_2 from the data in Fig. 5 (dots). The experimental data are shown on an extended scale in the insets. Solid lines in the main panel are PDFs calculated from structural models.

Billinge and Kanatzidis. *Chem . Commun*., 2004, 749 – 760
Beyond crystallography: the study of disorder, nanocrystallinity and crystallographically challenged materials with pair distribution functions

Coordination number



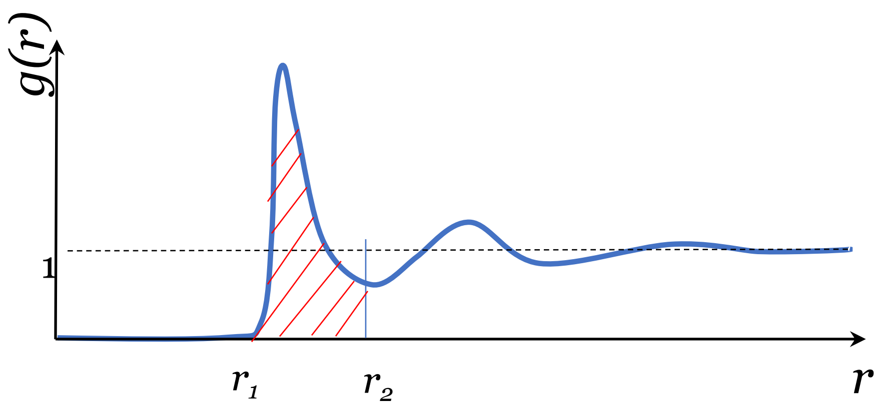
Peak area: proportional with the number of the neighbours in each shell



Coordination number

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

N_c: Coordination number (average number of neighbors around a central atom)
ρ = Atomic number density
r1,r2 = limits of the first coordination shell



Measure PDF experimentally → scattering

- the pair distribution function g(r) is related to the measured X-ray or neutron powder diffraction pattern through a Fourier transform

$$g(r) = (2/\pi) \int_{Q=o}^{Q_{max}} Q[S(Q)-1]\sin(Qr)dQ$$

- where S(Q) is the "liquid (or glass) structure factor"

measured and corrected Intensity from powder diffraction

$$S(Q) = \frac{I^{coh}(Q) - \sum c_i |f_i(Q)|^2}{\left|\sum c_i f_i(Q)\right|^2} + 1$$

the atomic form factor

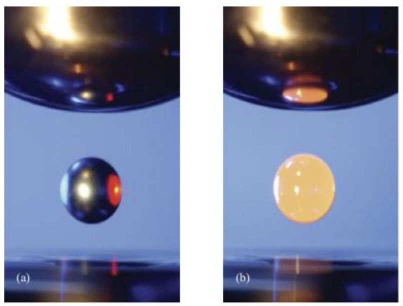
→ the interaction term of the scattering
i.e. structure factor, see analogy with diffraction of crystal unit cell and later SAXS!)

Measure PDF experimentally → scattering

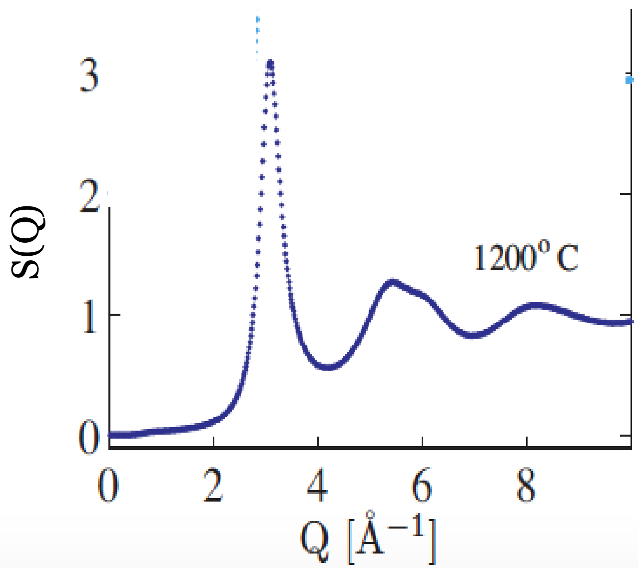
example of PDF of liquid metal

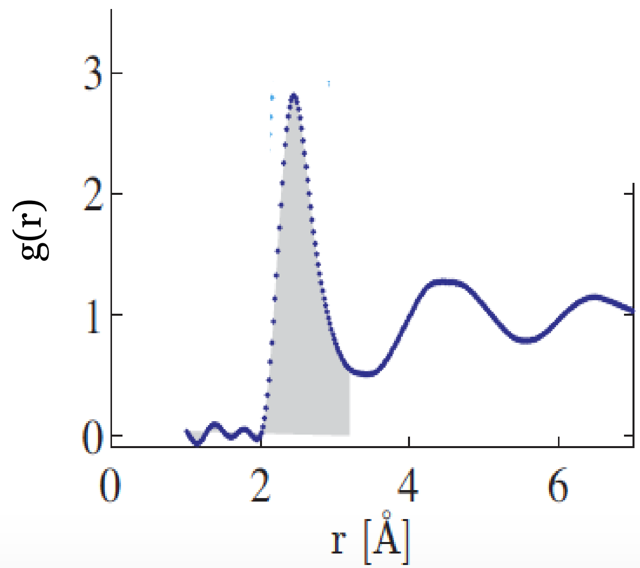
structure factor:
in reciprocal space

PDF
in real space

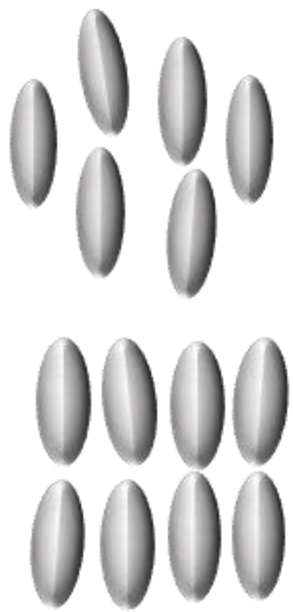


leviating liquid metal droplet
heated with a laser





PDF of liquid-crystals



long-range order
orientational symmetry (nematic)
orient. & transl. sym. (smectic)
liquid (2D or 3D)
densly packed
liquid-crystalline

orientational symmetry is important:
PDF in 2D in order to capture orientation order

PDF of liquid-crystals

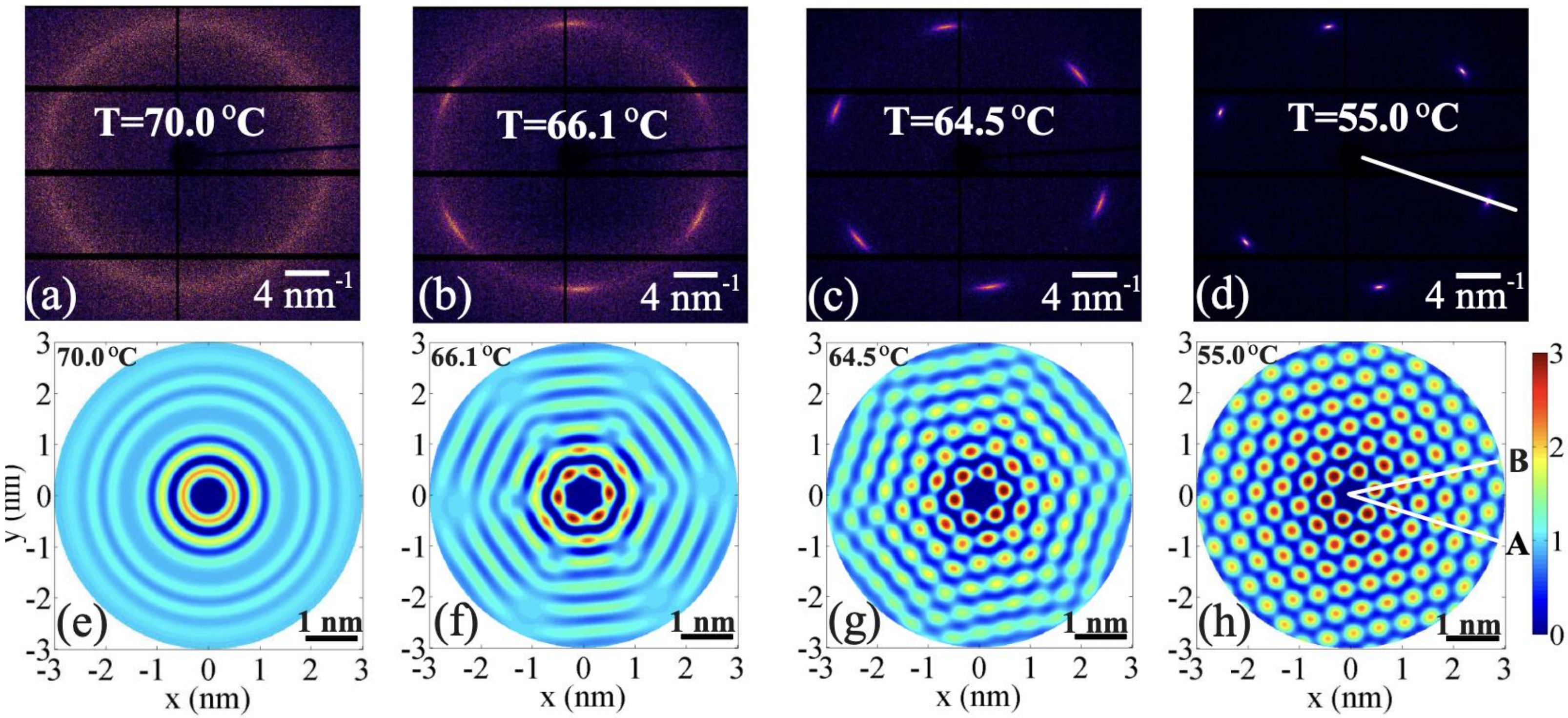


FIG. 1. (a)–(d) Diffraction patterns measured at different temperatures from the LC film undergoing the smectic-*A*-hexatic-*B* phase ansition. (e)–(h) The PDFs $g(\mathbf{r})$ determined from the diffraction patterns (a)–(d).

PDF of liquid-crystals

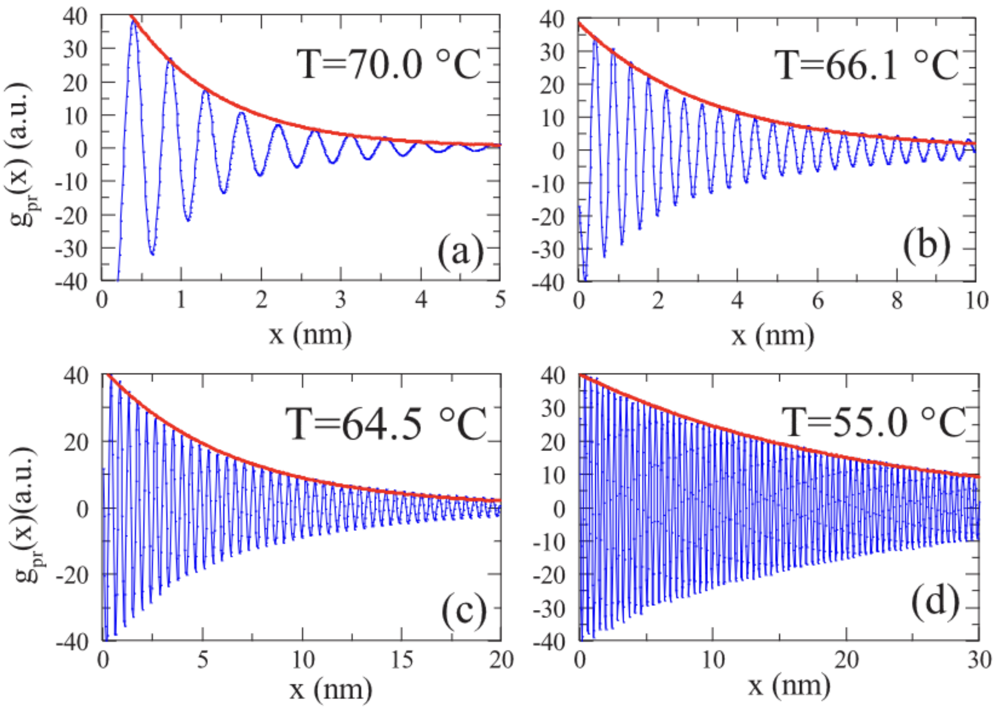
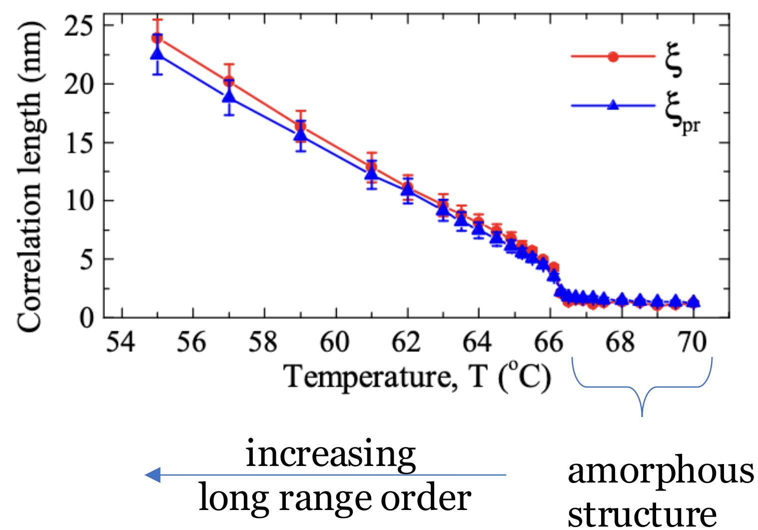


FIG. 3. Projection of the PDF $g_{pr}(x)$ on the direction of the diffraction peak A [see Fig. 1(h)] at different temperatures. The projection $g_{pr}(x)$ is shown with the blue line and the envelope function in the form of an exponent $A \exp(-\gamma x)$ is shown with the red line.

note that in this paper a different definition of gr was used, so negativ values and no correlation at 0 not at 1

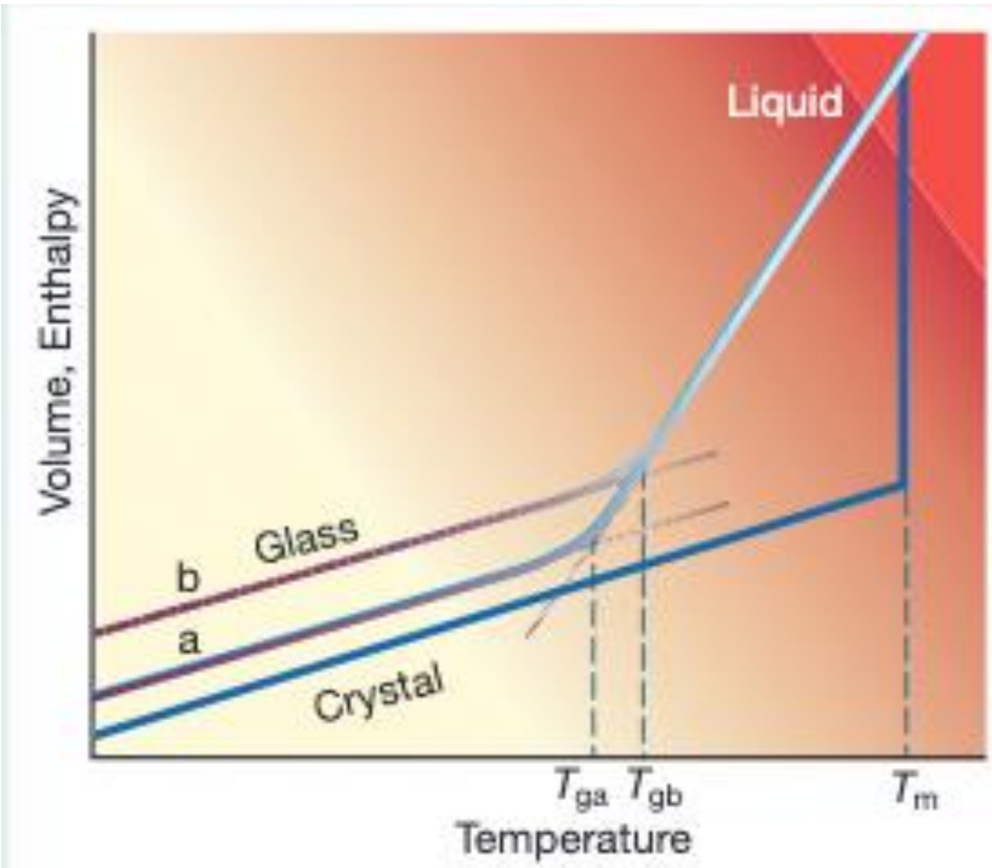


Amorphous solids: glasses

- metals usually form crystalline solids, but can form glasses → metal glasses
- ceramic materials can be either crystalline or amorphous → mineral glasses
- polymers can be semi-crystalline or completely amorphous → organic glasses

- the amorphous solid state is not thermodynamically stable, crystal structure is preferred
- but depending on the cooling rate most liquids can form amorphous solids, for metal glasses extremly high cooling rates needed, realistic for alloys, not pure metals
- some material can only solidify in glass form, for example branched polymers, too much disorder to crystallize

Glass transition temperature



Crystallization happens at a well defined melting temperature T_m with an abrupt change in the specific volume

Glass transition: The temperature where the glass transition happens depends on the cooling rate
→ glass a) with a slower cooling rate than glass b)

thermal expansion coefficient changes (different slope) but no abrupt change in specific volume

Debenedetti, P. G., & Stillinger, F. H. (2001). Review article Supercooled liquids and the glass transition. *Nature*, *410*(March), 259.

Glass formation

Glass formation is a matter of bypassing crystallization → cooling “quick enough” from above the melting point (T_m) to below the glass transition temperature (T_g) for silicate that can be very slow, for metals it must be very fast.

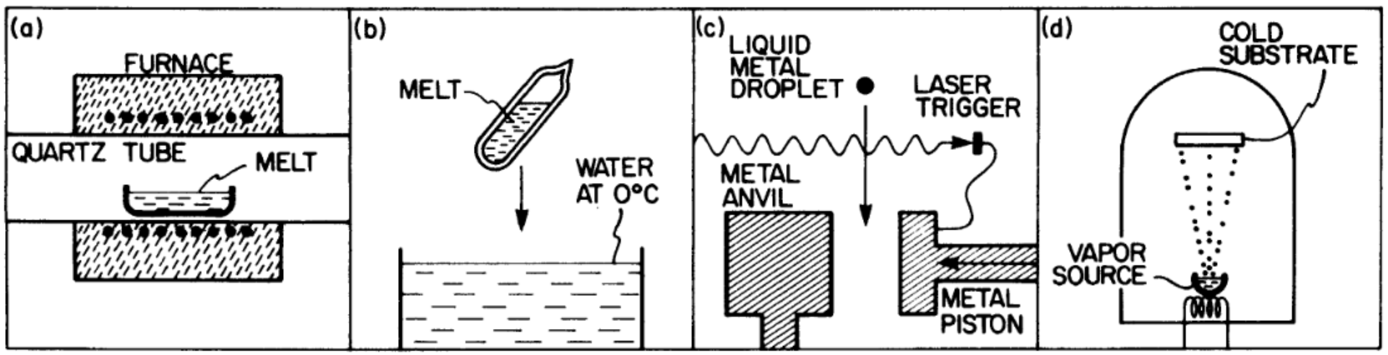


Figure 1.4 Four methods of forming amorphous solids: (*a*) slow cooling, (*b*) moderate quenching, (*c*) rapid “splat-quenching”, and (*d*) condensation from the gas phase.

slow → fast

$10^{-4} – 10^{-1}$ K/s $10^{1} – 10^{2}$ K/s $10^{5} – 10^{8}$ K/s

bypass liquid phase
atom-by-atom
(thin films)

Glass formation

glass-forming tendency is greater for mixtures than for elemental one

example binary mixture of Silicon and Gold

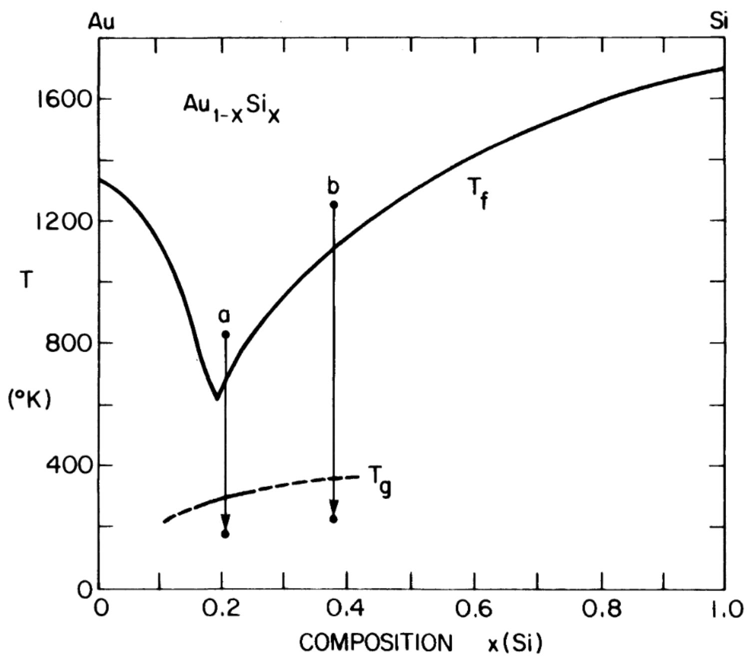


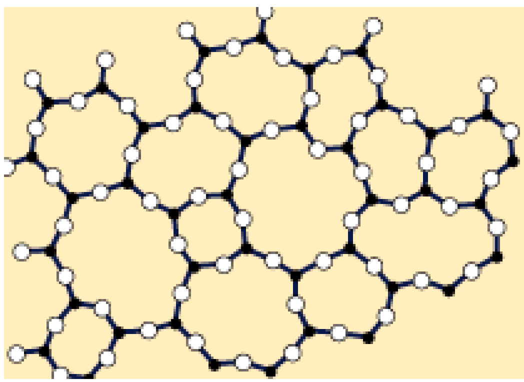
Figure 1.5 Glass formation in the gold–silicon system. Two quenches from the liquid state, at two compositions, are indicated. Glasses can be prepared much more readily in quench *a* than in quench *b*, since the latter must cross a greater temperature range between T_f and T_g in which it is "at risk" vis-à-vis crystallization. (The T_f curve is from the work of Predel and Bankstahl, 1975; the T_g curve is from the work of Chen and Turnbull, 1968.)

eutectic composition has the highest glass-forming tendency

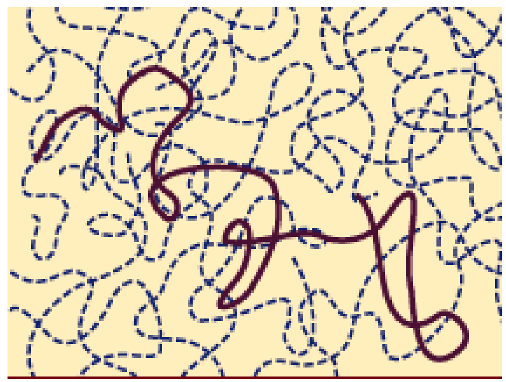
Richard Zallen, "The physics of amorphous solids" Wiley 1998

Atomic scale structure: models

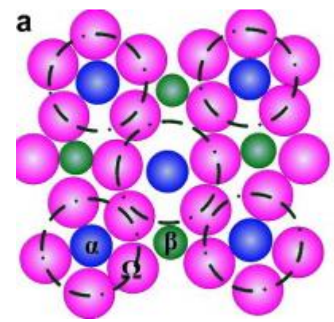
random-network model → covalently bonded glasses (amorphous silicon, oxide glasses)
random-coil model → polymer-chain organic glasses
random close-packing model → metallic glasses



continous random-network model for network glasses



random-coil model for polymeric glasses

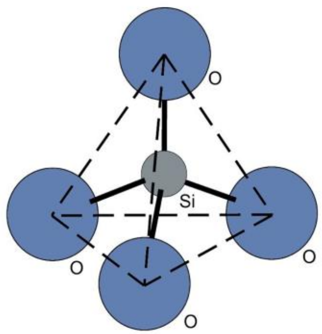


random close-packing model "efficient cluster packing" for metallic glasses

Enyclopaedia Britannica

see polymer lecture week 11 polymers

Silica glass

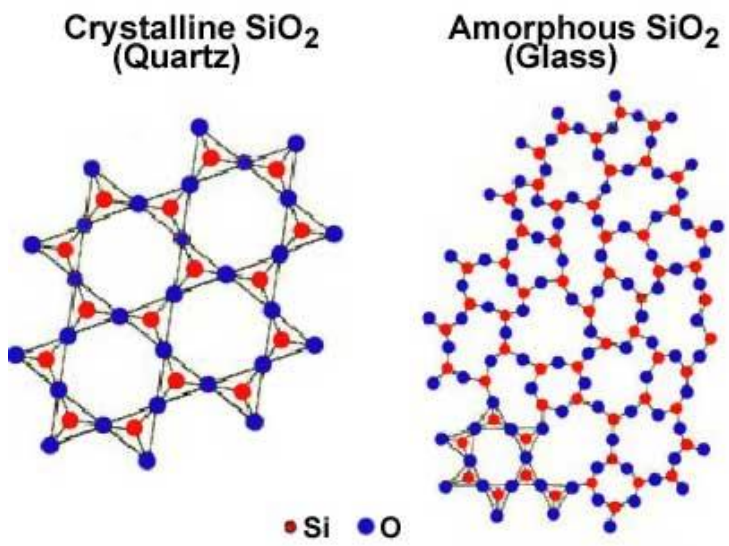


Silica: SiO_2

Si_{14}: $1s^2\ 2s^2\ sp^6\ 3s^2\ 3p_x^1\ 3p_y^1$
O_8: $1s^2\ 2s^2\ 2p_z^2\ 2p_x^1\ 2p_y^1$

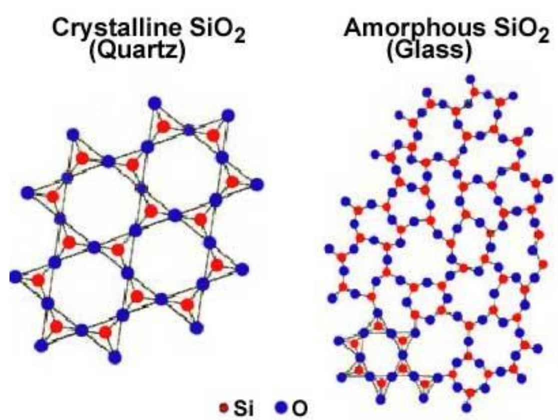
sp^3 bonds

Tetrahedra can order in crystalline order or amorphous

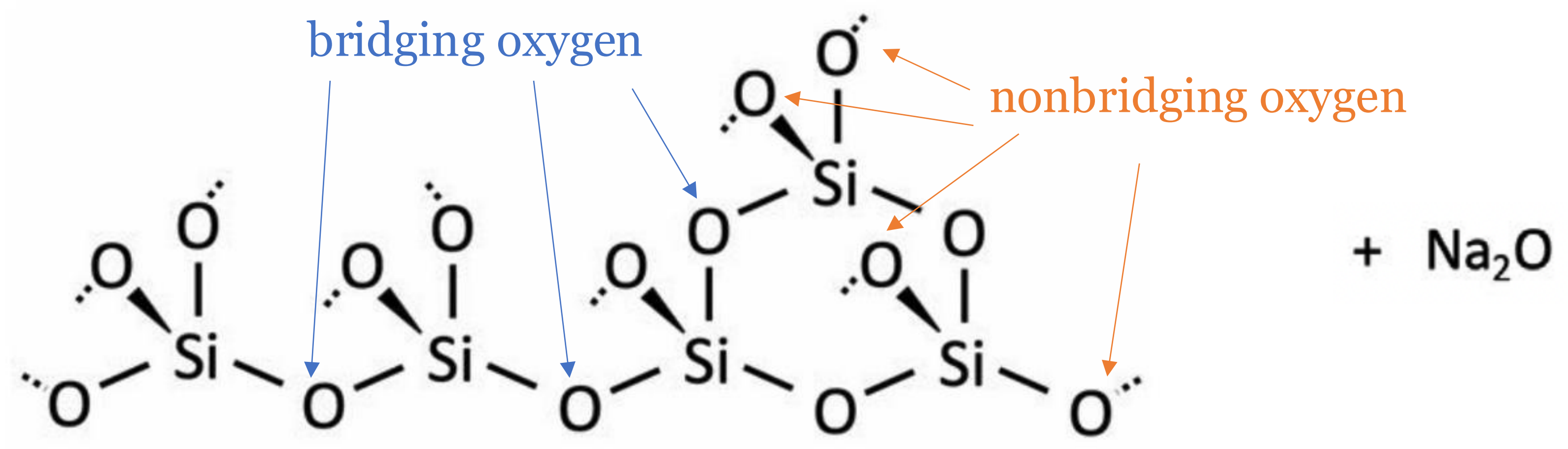


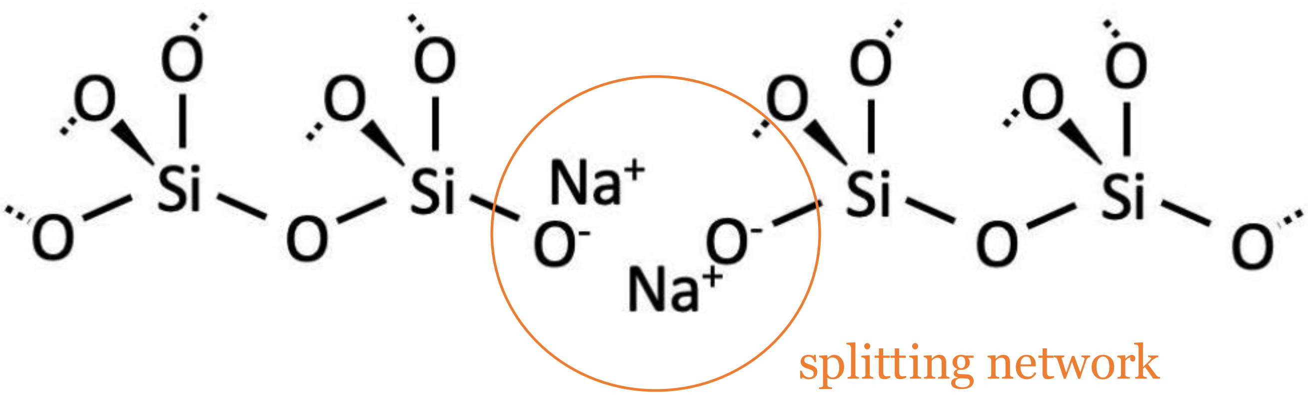
Continous random network model

- Based on the observation that oxid glasses have similar mechanical properties (elastic modulus etc) as crystals: properties are driven by the local bonding
- → continous random network model: three-dimensional network of bonded units that lack translational symmetry, but respects bond functionality and can be extended indefinitely (W.H. Zachariasen 1932)
- chemical species which enter into the structure of the network forming strong chemical bonds with oxygen are called network formers. Chemical species such as Na or Ca, which do not bond directly with the network but sit (in ionic form) within its interstitial holes are called network modifiers → they modify interaction



Network modifiers for Silica

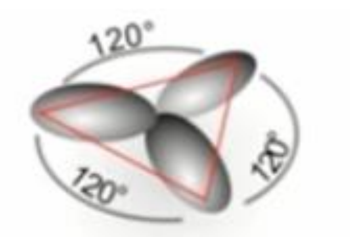




decreases connectivity
number of bridging oxygen is reduced
→ change mid-range order
→ change properties and T_g

SiO2 has a very high viscosity, does need very high temperature to get into working range to be formable: network modifiers added to reduce the temperature needed

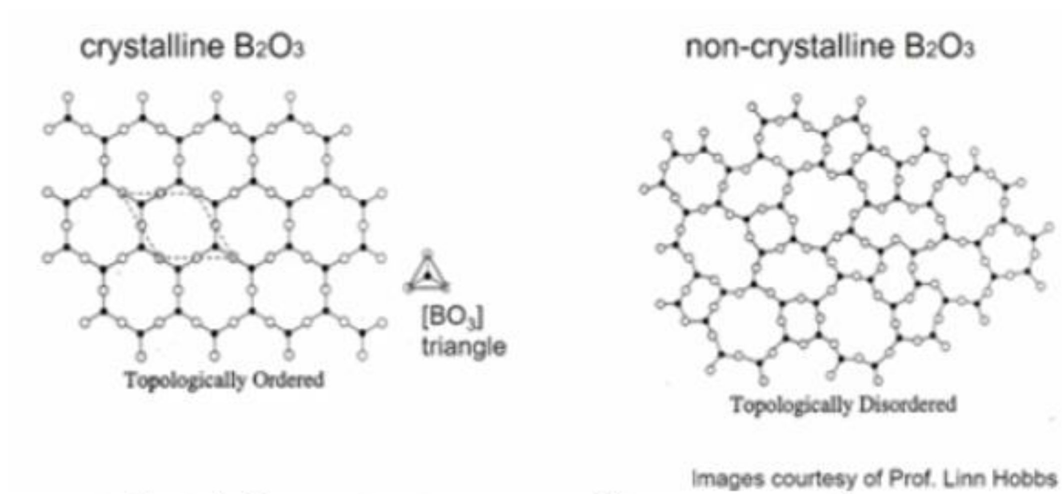
Borate glass



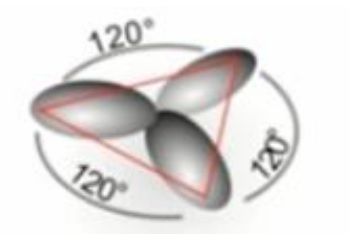
Borate: B_2O_3

B_5: $1s^2\ 2s^2\ 2p_x^1$
O_8: $1s^2\ 2s^2\ 2p_z^2\ 2p_x^1\ 2p_y^1$ } sp² bonds

<u>planar</u> can order in crystalline order or amorphous



Borate glass and network modifier



Borate: B_2O_3

B_5: $1s^2\ 2s^2\ 2p_x^1$
O_8: $1s^2\ 2s^2\ 2p_z^2\ 2p_x^1\ 2p_y^1$

} sp^2 bonds

<u>connected in plane</u>

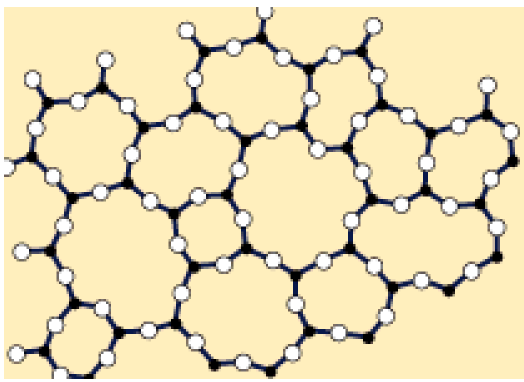
$+Na_2O$

sp^2 bonds → sp^3 bonds

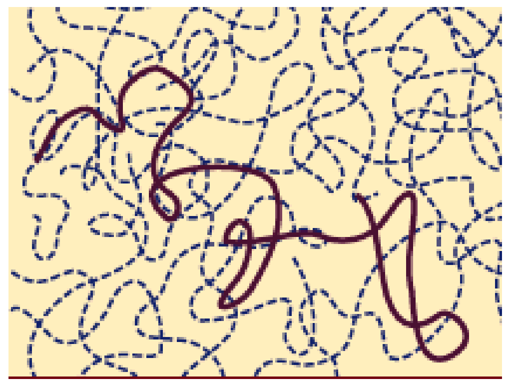
connection will increase as additional connections in three dimensions are possible
stiffer material due to stronger bonding
→ the Boron anomaly

Atomic scale structure: models

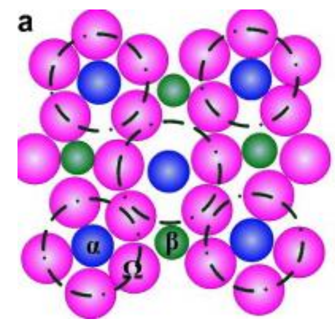
random-network model → covalently bonded glasses (amorphous silicon, oxide glasses)
random-coil model → polymer-chain organic glasses
random close-packing model → metallic glasses



continous random-network model for network glasses



random-coil model for polymeric glasses



random close-packing model “efficient cluster packing” for metallic glasses

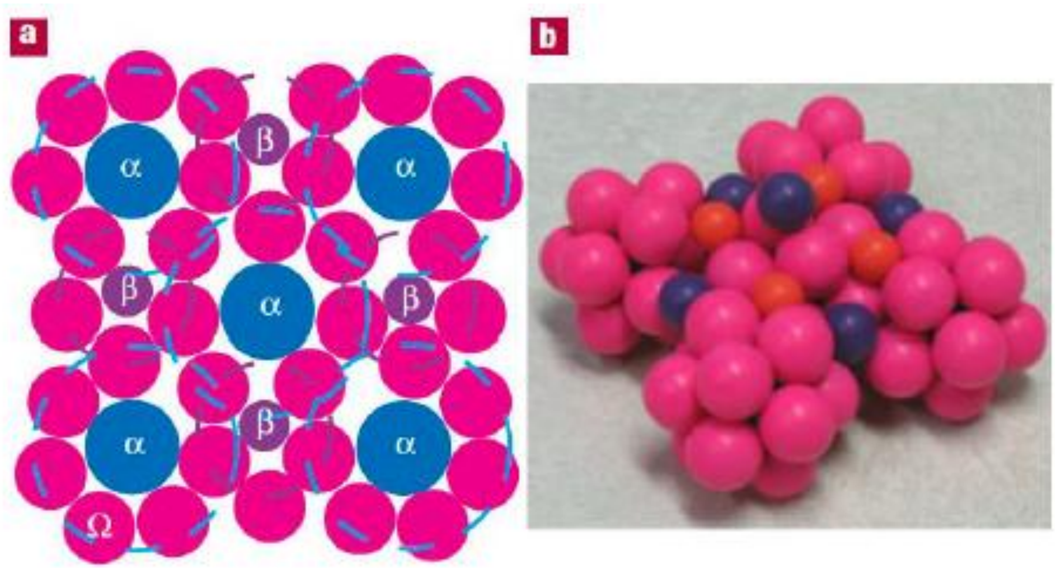
Enyclopaedia Britannica

see polymer lecture week 11 polymers

Metallic glasses

- Packing density:
- Face-centered cubic: 74%
- dense random packing of hard spheres: 64% → too low for metallic glasses
- How to pack atoms efficiently without introducing long-range translational order? → certain degree of short- and medium-range order (beyond next neighbour) is required!

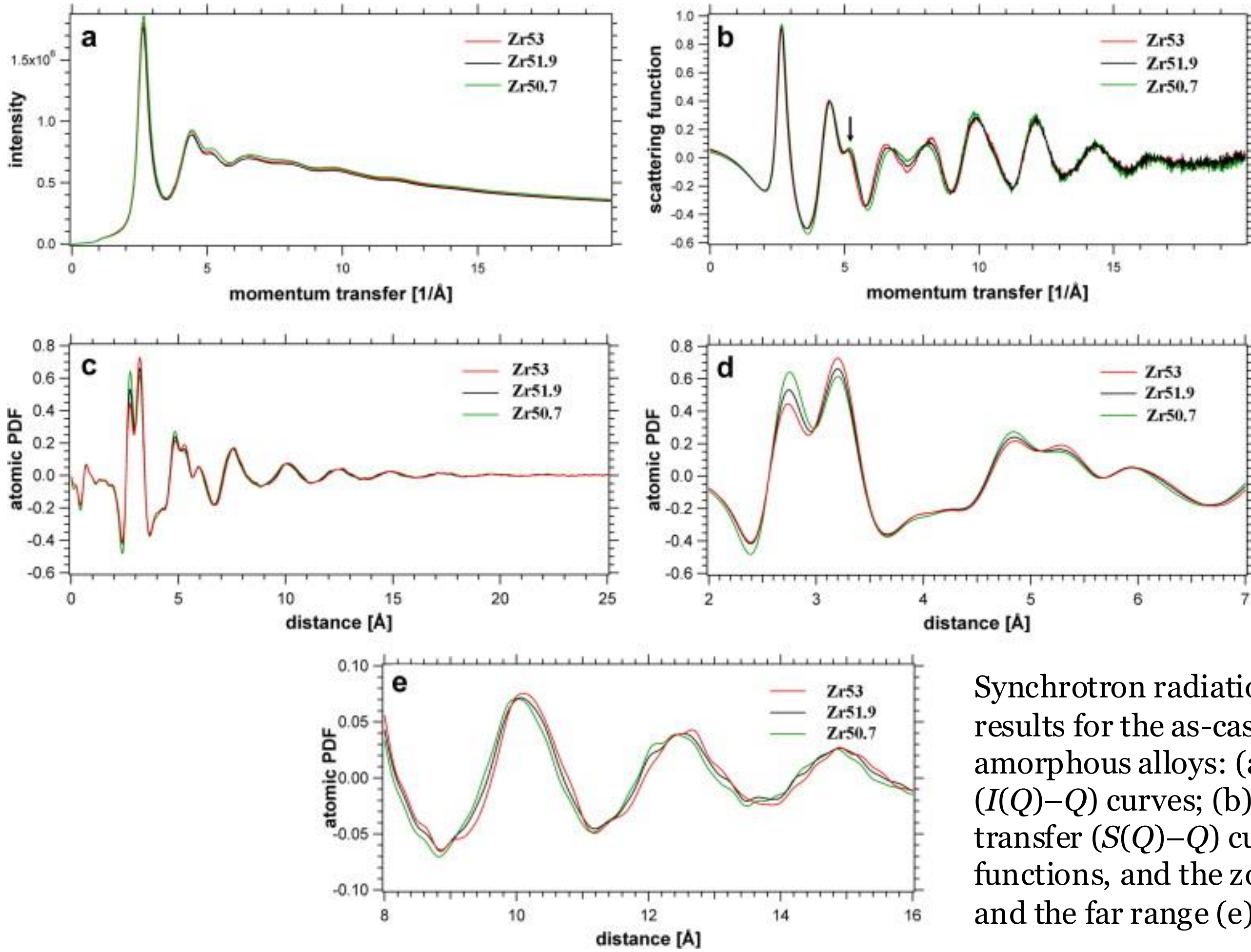
Efficient cluster packing



solute-centered clusters in a way similar to face-centered cubic (fcc) or hexagonal close packing
cluster overlap in first coordination shell
no orientational order amongst the cluster (atoms occupy random positions)

D.B. Miracle, *Nature Materials* 3 (2004) 697-702

Metallic glass: PDF analysis



→ mid-range order extending further than the nearest neighbor

Synchrotron radiation high-energy X-ray diffraction results for the as-cast Zr53, Zr51.9 and Zr50.7 bulk amorphous alloys: (a) intensity-quantum transfer ($I(Q)$–Q) curves; (b) scattering function-quantum transfer ($S(Q)$–Q) curves; (c) atomic pair distribution functions, and the zoomed view of the near range (d) and the far range (e) of (c).

Y.J. Sun, *et al*. Zr–Cu–Ni–Al bulk metallic glasses with superhigh glass-forming ability,
Acta Materialia, 57, 4,2009

Properties crystals vs. glasses

- electrical and thermal conductivity: lower conductivity due to the disorder which impedes the motion of the mobile electrons
- difference in optical spectra
- viscosity: crystal have an aprubt change from liquid to solid with $T_{m,}$ glasses have a continous liquid-to-solid transition

→ tuneable viscosity with temperature (glass-blowing, formable)

→ in polymers above the glass transition temperature: rubber state

Application of glasses

type of amorphous solid	**representative material**	**application**	**special properties**
oxide glass	$(SiO_2)_{0.8}(Na_2O)_{0.2}$ $(SiO_2)_{0.9}(GeO_2)_{0.1}$	window glass fibre-optic	transparency formable purity, ultratransparency, formable
organic polymer	polystyrene, PMMA	structural materials, plastics shatter proof glass	light weight, ease of processing shock resistance
chalcogenide glass	Se, As_2Se_3 Ge-Sb-Te	copiers and laser printers memories	photoconductivity phase change
amorphous semiconductor	$Si_{0.9}H_{0.1}$	solar cells, copiers, flat-panel displays	photovoltaic optical properties, large-area thin films, semiconducting properties
metallic glass	$Fe_{0.8}B_{0.2}$ $Mg_{60}Zn_{35}Ca_5$ $Zr_{58}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$	transformer cores Bone implants Sports, anti-wear	ferromagnetism, low power loss dissolves in body elasticity, resistance, corrosion
ionic glasses (salts)	Esomeprazole	Pharmaceuticals	Bioavailability (soluble)

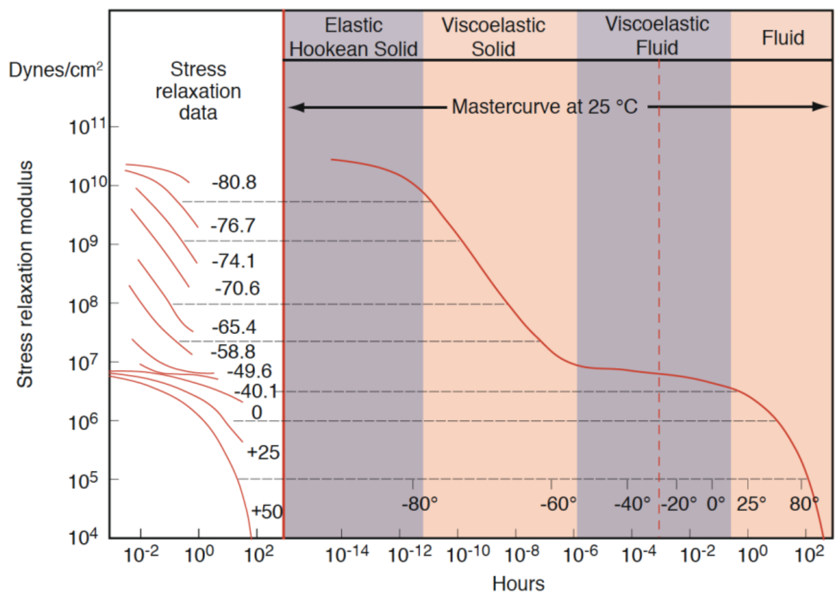
from Britannica Academic

Glasses in pharameceutics: Bioavailability

- drug in glass state have in general a better solubility and therewith a better biological availability than their crystal state
- in mixtures glasses are formed much easier, since crystallization is hindered
  → drug formulations with polymer mixture to stabilize the amorphous form

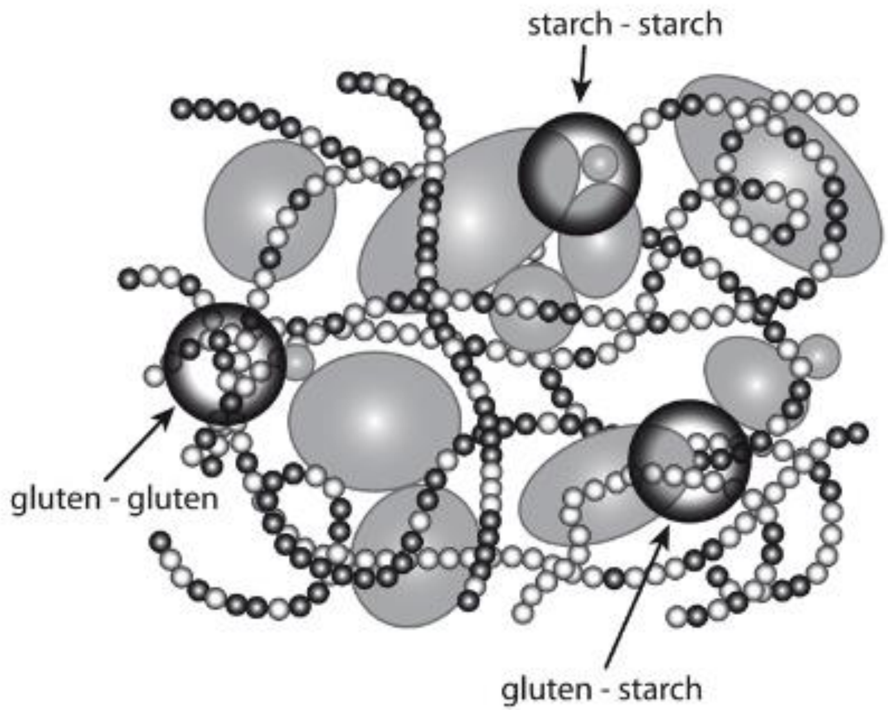
Glasses in Food: Texture

- amorphous structure such as rubber and glass have very different texture compared to crystalline structures
- Bread becoming hard/stale: recrystallization of previously amorphous starch
- Polyisobutylene: chewing gum, glass transition at around -70°C, but influenced by water content



Glasses in Food: Pasta

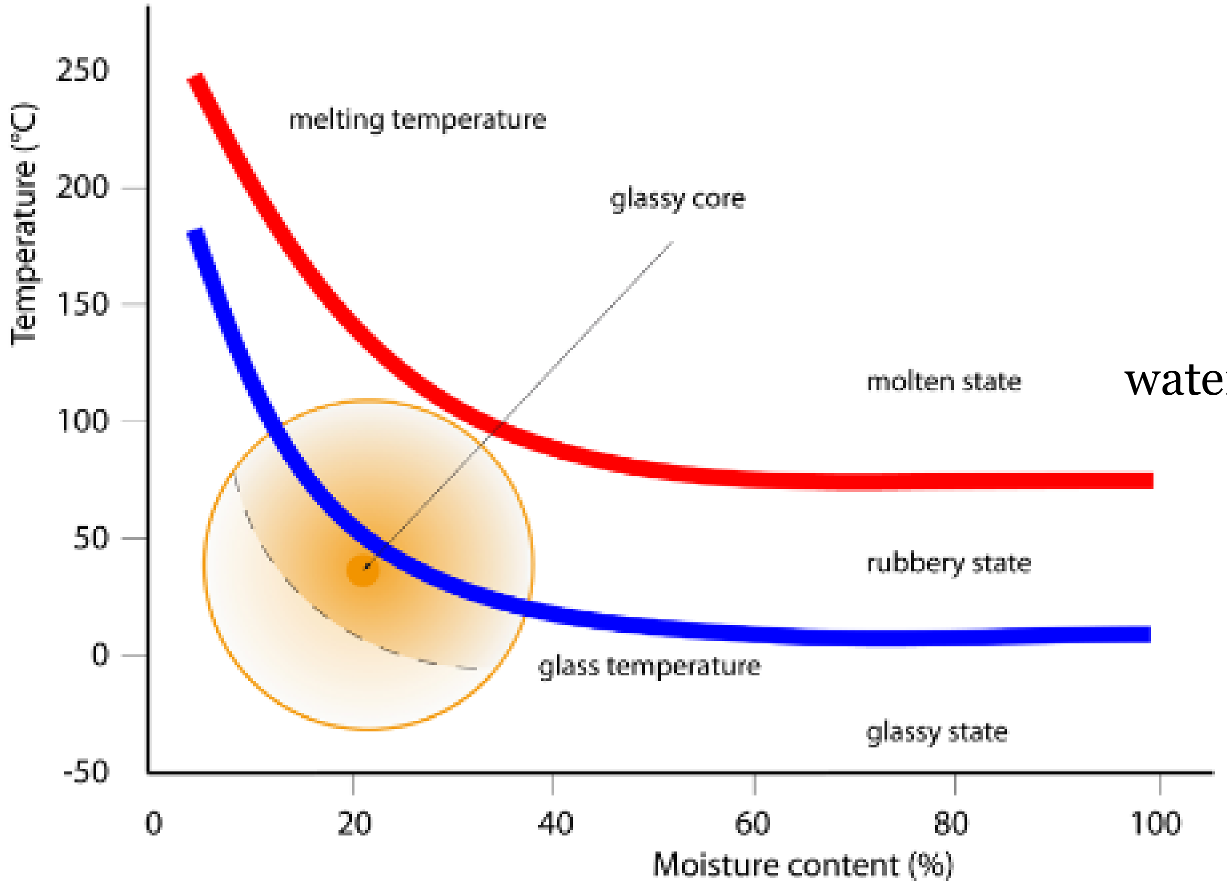
- dough: starch, gluten and water (and air bubbles)



starch in native state is crystalline, in mixture higher glass forming tendency

“Soft matter food physics – the physics of food and cooking”
T.A. Vilgis, Rep. Prog. Phys. 78, 124602, (2015)

Pasta – al dente

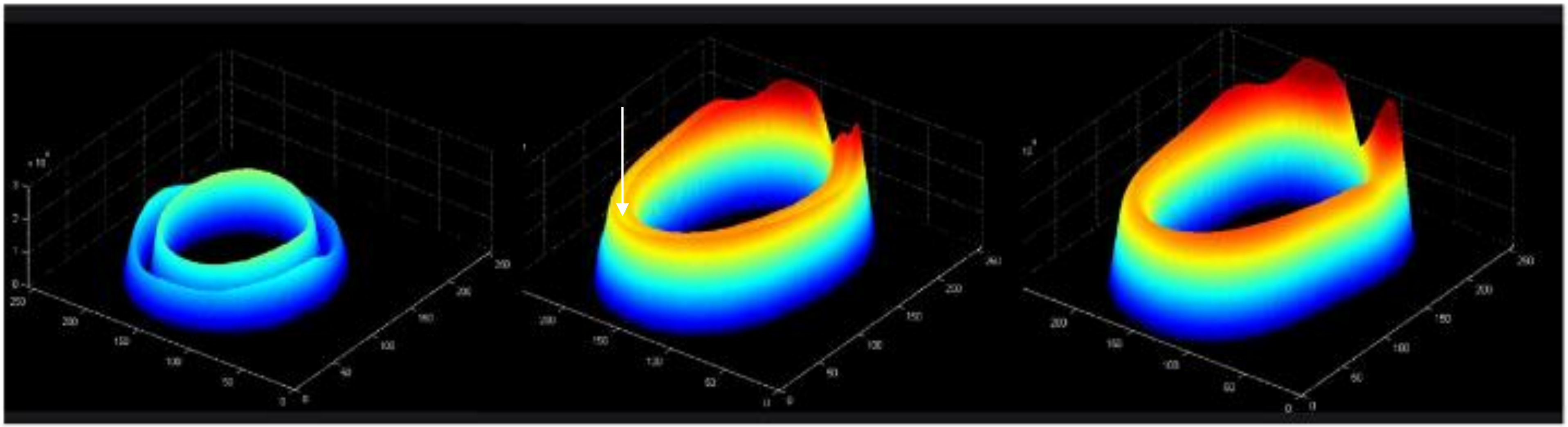


water acts as plasticizer!

T.A. Vilgis, Rep. Prog. Phys. 78, 124602, (2015)

Pasta – al dente

NMR imaging: qualitative visulization of water uptake in penne



after short cooking time   right cooking time   overcooking

T.A. Vilgis, Rep. Prog. Phys. 78, 124602, (2015)

Glasses in Food: Texture

- amorphous structure such as rubber and glass have very different texture compared to crystalline structures
- Polyisobutylene: chewing gum, glass transition at around -70°C, but influenced by water content
- al dente pasta: core is still in glassy state
- Bread becoming hard/stale: recrystallization of previously amorphous starch
- Potato chips: glassy state: if left open and humidity is taken up → transition to rubber state

Summary

- structure characterization of amorphous structure → average parameters, statistical description instead of one fixed parameter (for coordination number, bond length, bond angle distribution etc.), density, free volume
- long-range, mid-range and short-range order
- pair-distribution function: local density in the structure of a reference atom/molecule: typical curves for crystalline, gas, liquid/glass
- liquid crystals: orientational long-range order
- types of glasses: metal, mineral and organic glasses
- glass formation and glass transition temperature: bypass crystallization
- atomic scale structure models
  - continous random-network model (silica and borate glass), network modifieres
  - random coil model (polymeric glasses) → next week
  - efficient cluster packing (metallic glasses)
- examples of application and properties of glasses