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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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MODELLING OF LIQUIDS AND AMORPHOUS SOLIDS

(Lectures II - V)

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LECTURE 2 SHORT-RANGE ORDER IN SPHERICAL + NETWORK GLASSES.

1. SHORT RANGE ORDER (SRO) IN THE DENSE RANDOM CLOSE PACKED MODEL.

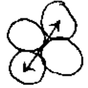
The random close-packed sphere model serves as an ideal model of a zero temperature glass of hard spheres. It's detailed local structure – as described by the radial distribution function (RDF) – reflects the packing constraints of hard spheres.

It is possible to identify the local geometries corresponding to prominent features in the RDF, approximately as follows:

Certain distances are more probable than others – a consequence of packing constraints.

(1) First peak at 1.0 diameters corresponds to first neighbour contacts : ○○. The area under this peak relates to the first neighbour coordination number.

(2) The first component of the split second peak occurs at about 1.73 diameters, or $\sqrt{3}$ diameters. This is the same distance as that found across two edge-sharing equilateral triangles :



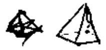
(3) The second component is at 2.0 diameters, and corresponds to second neighbours along a line : $\overset{\longleftrightarrow}{○○○}$. Such "collineations" occur frequently in the random packed model.

Note that these characteristic distances occur in close-packed crystals, but (a) with different frequency, and
(b) characteristic crystal distances are missing.
Of particular interest is the absence of the $\sqrt{2}$ diameter peak found in f.c.c. crystals – in the random packing model, in fact, there is a minimum at this distance.

Thus, although both crystal + glass models show some of the same characteristic distances, this does not mean the structures are in any real sense "similar". Rather, BOTH crystal + glass show local configurations which are to be expected when spheres are packed together. The relative occurrences of these configurations describe the SHORT RANGE ORDER of the model.

We can see the same in 3 dimensions, where the dominant polyhedra found are (1) the tetrahedron

(2) the octahedron (or half octahedron)



which occur also in close-packed crystals – which is not surprising as both these polyhedra are natural ways of arranging spheres in close contact. There are two major differences however between the ideal crystal + ideal glass structures:

(1) Both relative frequency + relative arrangements of the tetrahedra + octahedra are different – in the crystal they are arranged in a regular manner (a lattice), in the glass they are not. The same building blocks are used, but their topology, or connectivity, is different.

Note Boerdijk spirals + pentagonal arrangements in glass – absent in crystal.

(2) The glass model contains small fractions of other more complex polyhedra where the packing constraints prevent even distorted tetrahedra or octahedra from fitting together.

[It is interesting that for soft sphere models – lecture 3 – these more complex polyhedra tend to become squeezed out, + both crystal + glass models can be considered as made up largely of tetrahedra + octahedra only: again, the topology and relative frequencies of these two building blocks are different. See Finney + Wallace reference below.]

References: Bernal, Proc. Roy. Soc. A280, 299 (1964)
Finney + Wallace, J. Non-Cryst. Solids 43, 165 (1981). * Copies available.

For the hard sphere glass model, we built a model to
- have the correct density
- be consistent with the potential function
- be not a lattice structure.

In this case the potential was particularly simple, in particular it was spherically symmetrical.

y to answer [illegible] the chemistry [illegible] system

We can now do the same for silicate glasses: the problem is to build in the structural consequences of the potential function. For this, we look at the wide range of silicate structures, & note they can all be rationalised in terms of the linking of SiO_4 tetrahedra. In fact, crystal chemical arguments suggest this tetrahedral unit: the problem now is to decide how to link together the tetrahedra through the corner-linked oxygens in a way which is consistent with the known RDF.

Consider the peaks in the RDF in conjunction with what we know of the chemical ordering – the local short range order which is in the silicate case determined by the chemistry rather than the packing constraints of the hard sphere model.

From the RDF, we find:
- each Si surrounded by 4 Os, as expected.
- 1st neighbour O-O peak shows us the SiO_4 tetrahedra are reasonably perfect
- 1st neighbour Si-Si peak tells us the distribution of Si-O-Si angle allowed: this is particularly important when trying to build the model.
- higher order correlations can be examined to obtain other information useful for building a plausible model.

Then we build the model, trying to retain the prescribed Si-O-Si bond angle distribution.

The results for a completely 4-connected RANDOM NETWORK MODEL show excellent agreement with experiment.
- note partial RDFs agree well with those postulated from experimen
- bond angle distribution Si-O-Si of model may be somewhat distorted from the desired distribution
- gives information on vibrational spectroscopy

This RANDOM NETWORK 4-COORDINATED MODEL serves in a similar way to the hard sphere model as an ideal reference structure where the intermolecular interactions are strongly directional.

Application to related systems.

1. Other systems have similar tetrahedral bonding and can be modelled in a similar way, eg. amorphous Si, Ge.
2. In extending the idealised model to non-ideality (eg. ~~imperfect bonds~~ incomplete tetrahedral coordination) things become more difficult.
   eg. amorphous semiconductors
   water.

Nevertheless, the ideal reference structure still may serve as a starting point.

References. Zachariasen, J. Am. Chem. Soc. 54, 3841 (1932)
Mozzi + Warren, J. Appl. Cryst. 2, 164 (1969), 3, 251 (1970)
Evans + King, Nature 212, 1353 (1966). Also p. 1354 (Bell + Dean)
P. Dean + R. J. Bell New Scientist 45, 104 (1970)
Bell, Bird, + Dean J. Phys (C) 1, 299 (1968).

3. SUMMARY: IDEAL GLASS MODELS.

The RANDOM CLOSE PACKED HARD SPHERE MODEL
and the RANDOM 4-COORDINATED NETWORK MODEL
can be considered as ideal structures for two extreme systems:

- (1) the ideal hard sphere glass at 0°K: spherically symmetrical potential;
- (2) the ideal 4-coordinated network glass: tetrahedral directional bonding (some variation in bond angle possible – eg Si-O-Si angle)

In (1), the SHORT RANGE ORDER is determined solely by packing constraints, not by chemistry.

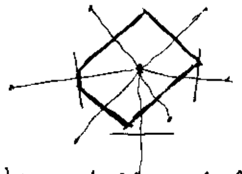
In (2), there is strong "CHEMICAL ORDERING" leading to a tetrahedral building block. The linking of these units through the Si-O-Si bond angle determines the short range order in the intermediate range.

These two extremes should be kept in mind as reference structures as we begin to discuss more complex "real" systems, which may be considered as variations of either the packed structure, or the network structure or a mixture of both.

NOTES ON THE VORONOI POLYHEDRON.

The RDF gives average information, projected from 3 dimensions onto 1 dimension. Although this is all we require for the thermodynamics, it is useful to be able to compare local structure in non-crystalline packed models.

The concept of the VORONOI POLYHEDRON has often been used. This allows us to partition the space occupied by a model into polyhedral regions, one associated with each "atom." The construction, which is totally non-arbitrary, draws perpendicular bisectors through lines joining atom centres; the smallest closed polyhedron so formed about each atom contains all space closer to that atom than to any other.



Various metric and topological characteristics of the polyhedral assembly can be used in comparing different packed structures, eg

- polyhedron volumes & distributions
- number of faces per polyhedron: average & distribution
- number of edges per face: average & distribution
- polyhedron type $(n_3 n_4 n_5 n_6 \cdots)$, where n_i is the number of faces to the polyhedron with i edges.

– Although undoubtedly useful, the procedure must be interpreted with care.
– Certain polyhedron types relate to fcc, hcp, bcc, or icosahedral local structures, so can be used as a diagnostic for crystallisation.

References:
Rahman, J. Chem. Phys. 45, 2585 (1966)
Finney, Proc. Roy. Soc. A 319, 279, 495 (1970) * copies available
Hsu & Rahman J. Chem. Phys. 70, 5234 (1979)
Cape et al J. Chem. Phys. 75, 2366 (1981)

A generalisation ("Radical Plane Polyhedron") has been developed for multicomponent systems.

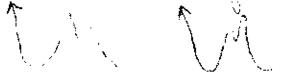
LECTURE 4 : COMPUTER MODELLING OF SPHERICAL/SIMPLE ONE COMPONENT GLASSES.

1. INTRODUCTION.

The ideal hard sphere dense "random" packing model reproduces qualitatively the correct experimental density (hence is consistent with packing constraints)
RDF.

There are, however, major problems in using the ideal hard sphere as a true model of real systems. When compared with the RDF of amorphous (slightly impure) Ni [illegible] to,

- the relative position of the second split peak components are incorrect by [illegible] %. This is outside experimental error.
- the relative intensities of the two components are reversed



In addition, most amorphous metallic systems are alloys, & thus contain a second component. Although in the early x-ray experiments, the contribution of the second component to the scattering is small – in $Ni_{76}P_{24}$ about 8% – it is not at all negligible

Clearly our hard sphere model is adequate only as an ideal/reference system, and requires refining (a) with respect to potential functions (eg L-J)
(b) with respect to the presence of a second component.

To make progress, we must develop less ad hoc methods of "model building" which can handle these subtleties. Attempts have been made therefore to build (initially hard sphere) models on the computer. These attempts have forced us to try to rationalise the decision making processes adopted partly subconsciously in laboratory model-building procedures, and in addition focussed upon the importance of adequate control of density (packing constraints) and boundary conditions, in addition to the potential function.

We consider model "refinement" in two parts:

(1) Hard sphere model-building by computer;
(2) Refinement using different (soft) potentials;
(3) Use of Monte Carlo & molecular dynamics simulation techniques for liquids & (possibly) glasses.

2. HARD SPHERE CONSTRUCTION METHODS.

2.1. BENNETT & DERIVATIVES.

Using a pre-existing seed (usually 3 spheres in contact, or possibly a planar surface), add the (n+1)th sphere to a tetrahedral pocket. The process (a "sequential addition") is continued until the model is of desired size.

Ref. Bennett: J. Appl. Phys. 43, 2727 (1972).

Choice of Pocket. At any stage in the building process, many "tetrahedral pockets" are available, and a choice must be made. The following criteria have been used.

(a). Bennett "global": choose that ~~pocke~~ pocket closest to the centre of mass of the existing model. Approximately equivalent to adding at the lowest energy site for a gravitational or long range potential.

(b). Bennett "local": choose the deepest available pocket – perhaps related to the lowest energy site in a short-range potential.

(c). Ichikawa (Phys. Stat. Sol. A29, 293 (1975)). Choose a pocket on the basis of a pre-specified degree of "tetrahedral perfection" k, where

$$K_{123} \equiv \max.(r_{ij})/(R_i+R_j) \qquad i,j=1,2,3,\ i>j,\ i\neq j$$

Note that k=1 corresponds to perfect tetrahedra, k=2 to the Bennett criterion. A "perfection window" (eg. $K \leq 12$) is usually defined, + only pockets within these limits are used.

· Properties of Bennett-type models

(1). Density decreases as model size increases. This reflects the incomplete exertion of packing ~~criteria~~ constraints, and suggests clusters of spheres - with a free boundary - can attain higher densities than "infinite" packings, where the packing constraints are fully effective. This is the EMBEDDING PROBLEM which is a severe limitation of "cluster" models.

Projected density of an infinite model built by this technique is ~0.61, significantly lower than the laboratory model. This is a basic problem of sequential addition methods to achieve higher densities, we need to program into the building procedure "collective rearrangements" which are done in the laboratory by shaking, vibrating, or "kneading".

(2). The RDFs have incomplete second peak splitting: thus it appears that higher densities (+ hence stronger operation of packing constraints) are necessary for this characteristic feature to be obtained.

Note that - in comparison with the dense (0.637) laboratory model, Bennett models are even less in agreement with the experimental relative intensities of the second peak components.

(3). The RDF's are different, depending upon direction! ie. the models are strongly anisotropic, a consequence of the fact that, during building, only the packing constraints to one side (towards the centre) are controlling the packing.

(4). As we limit the "tetrahedral perfection" according to Ichikawa's procedure, the model density falls even further and the RDF

splitting becomes even less prominent. We suspect that as the "perfection" is increased, the resultant models become of very low density + probably mechanically unstable.

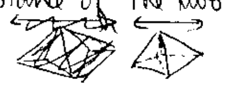
Thus, basic defects of sequential addition models are:

- inadequate density ⇒ inadequate 2nd peak splitting
- not consistent with an "infinite, embedded" packing.
- anisotropic.

To cure these problems, some way of programming in collective rearrangements is required.

2.2. SADOC POLYTETRAHEDRAL PROCEDURE. (J.Non-Cryst.Solids 12, 46(1973))

Sadoc noted that the first component of the second peak occurred in experimental systems at about 1.65 ($Ni_{76}P_{24}$) to 1.69 (Co) diameters, + that this was close to the ~~value~~ separation distance of the two furthest spheres in a pair of face-sharing tetrahedra (1.633). He thus tried to build in these units preferentially (see original paper for details).



A model so built could in fact qualitatively reproduce the position of this 1st component, which was also more intense than the 2nd component, as found experimentally,

BUT . . . .

(a) the model is inadequately dense ($\rho \sim 0.52$)
(b) it does not fill space. Voronoi analysis in fact shows it is composed of distorted icosahedra which partly interpenetrate (J. Phys. (Paris) 36, Colloque C2, p1-11 (1975)) *copy available

Although icosahedra are very dense local structures, when packed together, the interfaces are very imperfect. It seems from other work that to obtain higher densities, the icosahedral units are necessarily largely destroyed by the operation of full packing constraints (Finney: in "Diffraction Studies on Non-Crystalline Substances", eds. I. Hargittai & W. J. Orville-Thomas, Akademiai Kiado, Budapest, 1981). ***copy available**

Summary: Sadoc Polytetrahedral Model.

- A sequential addition model, no collective rearrangements, & therefore of inadequate density
- RDF features of experimental amorphous alloys appear reasonably reproduced, BUT ρ far too low.

An adequate model must BOTH (1) be of adequate density}
AND (2) fit the RDF }.

Either can be done separately, but to do both simultaneously is difficult, & probably impossible for hard sphere sequential construction models.

2.3. BMF "GAS COMPRESSION" MODEL (Finney, ~~[illegible]~~ Mater. Sci. Eng. 23, 199 (1976)) ***copy available**

This method (1) programs in collective rearrangements
(2) can be used with periodic boundary conditions & hence can help overcome the embedding problem relevant to cluster models.

It is not a sequential addition method – but is computationally expensive.

Method. (1) Place N points at random in a (periodic if necessary) box.
(2) Expand the points to a given radius r_1.
(3) Check no spheres overlap. If any two overlap, move them apart along their line of centres, irrespective of whether further overlaps are created thereby.
(4) Repeat (3) until all overlaps are removed.
(5) Increase $r_1 \rightarrow r_2 = r_1 + \delta r$.
(6) Repeat (3) & (4)
(7) Repeat (5), until required density achieved.

Resultant models.

(1) Dense. Clusters with $\rho \sim 0.67$ have been produced. Note however that such high densities (>0.637) are possible only where free boundaries effectively reduce the strength of the packing constraints.
(2). Models with $\rho \sim 0.637$ resemble in RDF the laboratory hard sphere model.
(3). Models with $\rho > 0.64$ show reversal of split peak intensities $\Rightarrow$ experimental, but positions still incorrect.
(4) Small peak occurs at 1.4 diameters at both low (0.57) & high (0.66) densities.

BUT because these models are clusters only we cannot reasonably argue they are valid models for real systems.

Summary: Hard Sphere Computer Construction Methods.

- Sequential construction methods fail to achieve adequate density $\Rightarrow$ inadequate second peak splitting.
  ** LOW DENSITY STRUCTURES TAKE INADEQUATE ACCOUNT OF PACKING CONSTRAINTS.**
- Sequential construction methods $\rightarrow$ clusters with free boundaries, & hence suffer from the "embedding problem!"
- BMF (VERY expensive) "gas compression" is NOT a sequential method, but programs in "collective rearrangements" necessary to achieve a high density. Can also be used with periodic boundary conditions (or perhaps other boundary conditions) to mimic a semi-infinite structure.

3. RELAXATIONS UNDER SOFT POTENTIALS.

Using various starting configurations (e.g. hard sphere model, sequential computer-built models), we can assume the atoms interact through various potentials, and examine the changes in RDFs obtained.

NOTE (1) that ~~although~~ periodic boundary conditions can (& probably should) be used to reduce the embedding problem, most work has been done on isolated clusters of ~ 1000 atoms;

(2) the ~~[illegible]~~ energy minimisation procedures used (steepest descents, conjugate gradients (better)) are available on many computers as standard packages. For N ~ 1000, computations are not rapid!

This kind of work is discussed in, e.g.
Barker et al, Nature 257, 120 (1975)
von Heimendahl, J. Phys. (F) 5, L141 (1975)
Finney, Nature ~~27~~ 266, 309 (1977); also ref. ~~at~~ top of p. 4/5.

Overall, we can conclude:
(1). Relaxation significantly changes RDF;
* (2) Resultant RDF can depend sensitively on the potential used *
(3). Free boundaries can lead to strange effects for long-range potentials (e.g. Morse).
(4). Relative intensities of split 2nd peak components reverse of hard spheres + agree more closely with experiment.
(5) Lennard-Jones 6:12 brings in position of outer component of split peak, but not the first ~~[illegible]~~ to a significant degree.
(6) Very soft potentials are required to bring in the first component close to experiment.
(7). Result of relaxation can depend upon the starting point chosen. Thus sequentially-constructed models must be treated with care even as starting points for relaxations.

4. COMPUTER SIMULATION TECHNIQUES.

These techniques are very well developed to model liquids. In principle, assuming ~~at~~ a potential function $\phi(\underline{r},\theta)$, then we can set up in the computer assemblies of model particles at a given state point (e.g. volume + temperature) which are consistent with a Gibbs ensemble.

There are two main methods:

(a) Monte Carlo (MC) techniques: essentially a method of estimating ensemble averages (multidimensional integrals) using random numbers. ~~[illegible]~~ The standard method ("Metropolis sampling") is usually used (J. Chem. Phys. 21, 1087 (1953)). See J.P. Valleau et al, chapters 4 and 5 of "Modern Theoretical Chemistry", vol. 5, ~~[illegible]~~ (Statistical Mechanics part A: Equilibrium Techniques), ed. B.J. Berne, Plenum, New York, 1977.

Application to simple liquids is well explored. For more complex liquids (e.g. water) there are not insignificant ergodic problems. These are even more severe when the technique is applied to glasses, and probably are a severe limitation.

(b) Molecular dynamics (MD): the time evolution of a box of particles (interacting through a prescribed potential) is followed by repeated solution of Newton's laws of motion.
In addition to equilibrium thermodynamics & structural information, MD provides time-dependent information.
Ergodic problems also may occur.

For early liquid application see Rahman, J. Chem. Phys. 45, 2585 (1966).

Both techniques have been applied to glasses, but it is unclear how far the results can be taken as referring to a "glass" – which except in the hard-sphere & possibly soft sphere L-J system will be expected to relax its structure on cooling – or to a "configurationally-arrested liquid," which is of far less interest.

Take, for example, a MD simulation of a Lennard-Jones "glass". Starting from the liquid configuration, we progressively reduce the temperature, following all the time the molecular motions of the system.

Ideally, we would like to reduce the temperature at a rate consistent with that used in preparing the glass in the laboratory. Typically, cooling rates of up to 10^6 K s^{-1} are used experimentally. Such SLOW RATES ARE COMPUTATIONALLY INACCESSIBLE, & much faster rates must be used in simulations. Our simulated configuration may therefore bear little resemblance to the glass we are trying to model.

Work to date on simple systems (hard spheres, Lennard-Jones glasses) give results ~~so~~ effectively the same as ~~at~~ modelling & relaxation procedures discussed earlier, implying computer + "laboratory" quench rates for these simple systems are almost commensurate. There is evidence for quench-rate dependent properties in the Lennard-Jones glass, but these have not been fully explored.

Summary: Simulation Techniques.

(1) Use definitely for liquids. Beware ergodic problems, & remember the result depends strongly on assumed potential.

(2) For glasses, there are problems, except perhaps for the simplest atoms. Laboratory quench rates cannot be achieved on the computer. Judicious quench rate variation + energy minimisation procedures might profitably be explored.

LECTURE 5: MODELLING REAL BINARY AMORPHOUS METAL ALLOYS.

It is unlikely that this can be treated in adequate detail in the time available. Much of the discussion material is in the preprint ("Modelling the Atomic Structure") of which ~~has been~~ copies have been made available by the centre.

Major problems.

(1) Inadequate experimental information: we need partial correlation functions ($g_{AA}(r)$, $g_{AB}(r)$, $g_{BB}(r)$), & few of these are available. Without the chemical ordering information this data can give us, there are so many possible model structures that little useful progress can be expected.

With partials available, or other information on chemical ordering, we can begin to tackle the problem.

(2) (a) The alloys are dense: ∴ packing constraints operate.
(b) Chemical ordering may be present.

The problem is to produce a model consistent with (a) & (b).

(3) Methods tried.

(a) Start from spherical end, using Bennett method modified for 2 components, emphasise packing constraints first, & try to relax to retain chemical ordering.
(Boudreaux et al. J. Appl. Phys. 48, 152, 5057 (1977)).

(b) Start from chemical ordering end & build a "network model" based upon known chemical ordering. Subsequently relax to bring in packing constraints. (Gaskell, J. Non-Cryst. Solids 32, 207 (1979))

It is not clear which – if either – of these approaches is better. Note the generalisation of the Voronoi technique for 2 component systems (B.J. Gellatly & J.L. Finney, J. Non-Cryst. Solids, in press).

Other methods should be tried – see preprint available.