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"Modelling of liquids and amorphous solids"

J.L. FINNEY

Liquids & Disordered Systems Lab.
Department of Crystallography
Birkbeck College
Malet Street
London, WC1E 7HX
UK

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"MODELLING THE ATOMIC STRUCTURE"

J. L. Finney, Department of Crystallography,
Birkbeck College, Malet Street, London WC1E 7HX

INTRODUCTION

Amorphous alloys were prepared first by the rapid cooling of the melt[1], bypassing crystal nucleation. An obvious parallel exists with the preparation of silicate glasses, in which the essential structure of the liquid is retained, although some structural relaxation will probably occur during cooling. When polycrystalline, distorted lattice, dislocation and other models of amorphous alloys failed to account for the experimental structural data[2] (the radial distribution function or the pair correlation function - see chapter 5), it therefore seemed sensible to look towards the parent liquid structure to assist our understanding of these new materials, although non-liquid related preparation techniques (chapter 3) leave open the possibility of the existence of structural variants ("amorphous polymorphism"[3]).

Unfortunately although we know in great quantitative detail the structures of crystalline materials, our ability to handle the structures of non-crystalline condensed liquid phases is limited. Assuming we know how the N constituent particles interact (the potential function) we require to construct the configurational integral :

$$Q = \frac{1}{V^N N!} \int \ldots \int e^{-\phi/kT}\, dv_1 \ldots dv_N \qquad (1)$$

where ϕ is the potential energy of the assembly with atom 1 in volume element dv_1 etc. Once Q is known, we can calculate the thermodynamics of the assembly by purely formal manipulations.

Although the high coordination and density of the crystal means we must take into account a relatively large number of interactions in calculating ϕ, the crystal lattice allows us to make a drastic simplification : eg for a primitive ideal crystal (one asymmetric unit per unit cell), Q can be written as the product of N identical partition functions, which can be calculated knowing the atomic positions. For a real crystal, we can use the ideal crystal as a reference state for a perturbation-type analysis. At the other end of the spectrum - a perfect gas - there are no interactions between atoms except on collision, hence $\phi \equiv 0$, making the evaluation of Q trivial. For a dilute real gas, as contributions to ϕ arise from the small number of close interatomic approaches, Q can be evaluated in terms of pairs of atoms. As the density increases, we must consider larger clusters of atoms (three, four, ...). This "cluster expansion" procedure[4], however, becomes mathematically intractable for reasonably dense gases, and fails to converge before we reach liquid densities.

Calculating Q for a dense assembly is made difficult by the need to consider a relatively large number of intermolecular interactions. For a crystal, the approximate identity of local environments allows us to drastically simplify the problem by making use of lattice symmetry - hence the popularity until relatively recently of lattice models of liquids (and glasses). Where there is no underlying lattice structure, this approximation cannot be made, and we are unable to calculate the configurational integral unless the number of interactions is very small, as in a dilute gas. Thus, other methods have to be developed, and this leads us into liquid state theory[5,7]. Even here, unphysical approximations must be made to make calculations tractable; there is still no adequate theory of the liquid state[8].

In the absence of an adequate theory, we are driven to an alternative structural approach which constructs approximate models either in the laboratory or on the computer which are arguably representative of the structural arrangement in the liquid or glass. In the liquid case, our model - a set of positional coordinates of atom centres - represents an instantaneous snapshot of atomic positions in the real liquid. For an amorphous solid, translational motions will have been frozen out, and our stationary model will relate directly to possible atom positions in the real assembly. Once such a model has been constructed, its structural properties - in particular its radial distribution function (RDF) and density - can be calculated and compared with experiment.

Such liquid models are now constructed routinely in the computer, using computer simulation techniques which, within the limitations of the assumed potential function, result in sample molecular assemblies which are consistent with the required equilibrium Gibbs ensemble. For non-crystalline solids - which are non-equilibrium assemblies - the use of such techniques is problematical (see below). Initially, we prefer to consider simpler approaches which illustrate more clearly the structural principles of non-crystalline dense structures. Earlier detailed reviews of such model-building techniques can be found in the literature[3,19,29,46,61,62].

THE IDEAL HARD-SPHERE GLASS : THE BERNAL MODEL

Bernal argued[9] that the structure of a simple liquid - one of spherical molecules with an angle-independent potential function - is determined by volume exclusion. As the liquid density is about the same as (though generally a few per cent lower than) the crystal density, the constituent atoms must have high coordination numbers, with surrounding atoms generally in contact, an argument consistent with experimental coordination numbers of around 8-12[5,6,7]. Hence, he proposed a zeroth order model in which the atoms were considered as hard-spheres, and their local structure determined by the restrictions on space-filling consequent upon the inability of two atoms to approach closer than one diameter. The structure of crystals of spherical molecules such as the inert gases and simple metals had long been rationalised in this way, the familiar f.c.c. and h.c.p. structures being the consequence of high density and the presence of a crystal lattice. What Bernal did was to extend this approach to liquids, for which theoretical[10] and experimental evidence argued against lattice organisation. The ideal liquid might therefore have a structure similar to that realised when equal hard-spheres are

packed together at high density without allowing any "crystallisation" to occur.

Such models were physically constructed in the laboratory, and their structural properties examined, independently by Bernal and coworkers[9,11,12] and Scott[12]. Bernal's models were built[11,14] by pouring several thousand steel balls into a suitable flexible container (originally a football bladder) placed within a previously-prepared irregular surface to prevent surface crystallisation. The assembly was tightly bound by several metres of rubber strip to exert a compressive force, and then "kneaded" to facilitate sphere rearrangements to maximise the density. The mass was "fixed" by pouring through it a molten mineral wax (earlier experiments[11] used paint), and after setting, the exterior skins were peeled off. The coordinates of each sphere were measured using a converted toolmakers bench[13]. Scott's procedure[12] involved filling a beaker or spherical flask with spheres, densification being achieved by mechanical vibration.

Both procedures appear somewhat ad hoc - yet the results from the two different laboratories were in excellent agreement. In particular, both concluded that the maximum density of a hard-sphere non-crystalline packing was 0.6366, to within 0.1%. Moreover, recent attempts to reproduce this structure on the computer[15] yield an essentially indistinguishable radial distribution function.

This model "random close-packed structure" is shown in fig.1, and its lack of crystallinity is immediately apparent. Calculations on the sphere coordinates demonstrated the model possessed many of the structural features of simple liquids, and gave appealing qualititative explanations of supercooling, nucleation, melting, fluidity and diffusion[9,17]. Although very simple, this structure contains within it the essential physics of simple liquids[8], and provides an illuminating structural framework within which to consider the structure of other simple non-crystalline systems.

Because the model is static, and of maximum density (although lower density - "random loose" - packings can be constructed[12]), it is particularly appealing as a model of a zero temperature ideal glass of spherical molecules. Its specific application to amorphous metallic alloys was proposed in the early 1960s by Cohen and Turnbull[18], although it was nearly ten years later before both model and experimental data were adequate to justify Cargill's making a quantitative comparison using data from Bernal's laboratory. He concluded that the experimental RDF of an amorphous $Ni_{76}P_{24}$ bore a strong resemblance to that of a dense random packing[2]. The two RDFs are shown in fig.2a: the random packing was the only model that could reproduce the experimental splitting of the second peak.

There are however, two major problems with this identification between experimental structure and the simple model. The first is quantitative, in that the positions and relative intensities of the two components of the split second peak are in significant disagreement. This problem can be largely removed by refinement of the model using soft potentials[19,37]. The second is more serious: we have identified a two-component real alloy with a single component model. Although in the X-ray measurements on $Ni_{76}P_{24}$ the nickel will dominate the scattering, the phosphorus contribution of about 8% of the X-ray scattering power is not negligible. Moreover, the presence of a second component - especially a "glass former" such as phosphorous - could be a significant determinant of the structure. Rather than identifying the random close-packed hard-sphere model with the structure of a specific amorphous alloy, it seems more useful to consider it as an ideal single component glass. It contains the essential consequences of volume exclusion in a non-crystalline structure, and hence should be thought of as a reference structure - perhaps a hard-sphere glass at OK - useful in the discussion of real structures.

COMPUTER CONSTRUCTION OF HARD-SPHERE MODELS

In order to progress to real alloys, we require less ad hoc modelling procedures which allow us to probe the structural consequences of more realistic potentials and finite temperature. As the early structural work on amorphous alloys coincided with a rapid increase in available computing power, most subsequent modelling studies have used computer construction techniques. The need to program a construction procedure focussed attention on factors which might affect the resultant structure of a model. This in turn highlighted problems with deterministic building procedures, and showed that distinctly different "non-crystalline" organisations of the same hard-sphere unit could exist. Although most current work has moved away from hard-spheres to soft potentials and two (and more) component assemblies, it is instructive to consider the basic methods used in computer construction for hard-spheres, and how the resultant structures may vary with the building procedure used.

1. Sequential Addition

Most computer construction methods add spheres sequentially to a starting seed. At any stage in the building process, there are several stable positions in which a further sphere can be added: these "tetrahedral pockets" are defined by three spheres, upon which a fourth can be placed in contact with the pre-existing triplet. Within this general procedure, variations are possible in (a) the criterion used to choose between the available tetrahedral pockets and (b) the initial seed.

The simplest addition criterion is that of Bennett[20], whose "global" criterion chooses that pocket closest to the centre of the original seed cluster, corresponding roughly to the site with the lowest energy in a gravitational or other long-range potential. A second "local" procedure in which the "deepest" pocket is chosen favours sites that would be most strongly bound by a short-range potential. The global criterion was used independently by Adams and Matheson[21], and Norman et al[22]. A further variant due to

Ichikawa[24] restricts the utilised pockets to a pre-specified subset defined in terms of the "tetrahedral perfection" of the pocket where :

$$k \equiv \max\ (r_{ij})/(R_i+R_j)\,[i,j=1,2,3;\ i>j;\ i\neq j] \qquad (2)$$

Here, r_{ij} is the distance between spheres i and j, and R_i is the radius of sphere i. Thus, k = 1 corresponds to a pocket formed by three touching spheres while k = 2 describes the "lowest" perfection possible for spheres of equal size, and corresponds to the Bennett global criterion.

Two further modifications of the sequential pocket filling method attempt to build models with a more intense first component of the split second peak than obtained either in the laboratory models or the sequential methods so far listed. Fig.1a shows that the first component is relatively more intense in $Ni_{76}P_{24}$ than in the hard-sphere model, suggesting we might try to devise an addition criterion to enhance the first component. Mrafko and Duhaj[25] discriminated against those pockets which would contribute more to the *second* component of the split peak than to the first; where no clear choice could be made this way, the pocket closest to the centre was chosen. Sadoc *et al*[26] noted that the first component of the split peak in amorphous $N_{84}P_{16}$ occurred at about 1.65 "diameters", a value consistent with the presence of a large fraction of icosahedral units. Their algorithm therefore tries to bias the resulting model towards such units in the folloing way. A *central* sphere A is chosen, together with a neighbouring *secondary* sphere B. A third sphere C is brought into contact with both A and B, and, retaining contact, is rotated round the AB axis until it contacts a fourth sphere. Next, another *secondary* sphere is chosen (the central sphere remaining unchanged) and the process repeated. Only when no further additions can be made is a new central sphere chosen. This retention of the central sphere ensures the construction around the central sphere of face-sharing tetrahedra (a characteristic distance of which is 1.633 diameters - of the 1.65 observed experimentally). The resulting units around each central sphere will resemble an icosahedron, distorted such that the "surface" atoms are "condensed" towards one side of the central sphere.

Although most models have been constructed spherically outwards from a regular tetrahedron, Bennett-type models have been grown from planes[23,27,28].

These sequential addition procedures raise several important points. The first is that they are sequential: once a sphere has been added, it cannot be moved. They produce packings which - from the similarities between pocket filling procedures - might be expected to relate more to the laboratory *loose* packings, rather than to the close packings which require further densification. This conjecture is borne out by their relatively low extrapolated densities ($\lesssim$ 0.60), compared with the 0.637 of the random *dense* packings. *Associated with this lower density is a failure to resolve adequately the split second peak of the RDF* (fig.2b). Without the achievement of a high density, therefore, a model does not show the full required structural properties: therefore *sequential construction methods used alone must always be suspect*.

As might be expected, the Bennett global procedure produces the highest densities ($\sim$ 0.60); as tetrahedral perfection is increased using the Ichikawa variant, the density falls - models constructed with k = 1.2 show significant porosity and could be mechanically unstable. The Sadoc model has also a relatively low density $\rho(0.52)$[19]: yet we know that the distorted icosahedral sub-units which the algorithm produces are themselves dense structures ($\rho \sim 0.67$[30]). The low density of the total assembly is explained by the existence of voids which occur at the "interfaces" between the locally dense sub-structures, and illustrates the difficulty of packing together dense structures efficiently. Because of its prescribed bias towards distorted icosahedra, the positions and relative intensities of the two components of the RDF split second peak are in reasonable agreement with experiment. The unrealistically low density however, shows that this was achieved *at the* *expense of bypassing the packing constraints which must exist in the high density real material* and therefore the model is inadequate. *It is relatively simple to produce a model with either the experimental density or a reasonable RDF*. *To do both simultaneously is necessary, but difficult*. As we describe later, it is probably impossible for an infinite hard-sphere packing.

2. Collective Rearrangements

Sequential addition procedures can produce different "random" structures depending on the pocket criterion. All, however, are "loose-packed" structures which fail to show the structural details found in real amorphous alloys: to reproduce those, collective rearrangements are required to increase the density.

These movements are easily made on laboratory models by *ad hoc* shaking and kneading. It is difficult - and *very* expensive - to program the computer to make them. Two approaches have been followed for hard-sphere structures. The first[31,32,33] simulates the compression of a hard-sphere gas. N positions are chosen at random in a box (usually spherical) and a small sphere assigned to each point. Checks are made that no two spheres overlap; when an overlap occurs, the two spheres are moved apart along their line of centres until they just touch (ignoring overlaps created thereby). When all overlaps have been cleared, the sphere radius is increased and the overlap-clearance procedure repeated. This method had been attempted by Bernal[9] in the late 1950s, but his computer was not up to the task, and the method was first used successfully by Mason[31]. Several such 500-sphere models of density between 0.57 and 0.67 have been built, and their RDFs and local structures examined[32] Strong similarities were found between the laboratory-built dense packings and computer-built assemblies of similar density (figs.2a and 2c). This suggests - but not conclusively - that the "statistical structure" of a *hard-sphere* random packing above the loose packing density (~ 0.60) may be unique

for that density. Below $\rho \sim 0.60$, this is not so. The main point of interest, however, concerns our apparent ability to build a model with a density some 4% higher than the apparent laboratory limit of 0.637. Moreover, in the RDF of such a high density packing the relative intensities of the split peak components have reversed (fig.2d).

Both these effects can be put down to a further failure to take full account of packing constraints - this time at the boundary. Ideally, our finite model should be a valid sample from an effectively infinite statistically-equivalent assembly. The laboratory model attempted - apparently successfully - to do this by using irregular surfaces as model boundaries, while both the sequential computer building and the hard-sphere gas compression methods do away with the boundary altogether. This is particularly serious for the hard-sphere gas compression method, in that the absence of a boundary, by removing a strong packing constraint, allows the spheres to rearrange unrestricted by the requirement that the model should be capable of being embedded in an equivalent assembly. Thus, although this method can give apparently good agreement with both the experimental RDF and density, it can do so only at the expense of a relaxation of the required packing constraints. The local structures of these high density clusters also show significant differences from the laboratory dense packing[32].

We could largely solve this "embedding problem" by performing the collective rearrangements on an assembly using periodic boundary conditions, in which the (in this case cubic) box containing our hard-sphere gas is surrounded by identical "image" boxes. This has been done successfully in two[34], but apparently not in three dimensions for hard-spheres. Woodcock has, however, performed a lengthy molecular dynamics calculation in which the density of an assembly of 500 spheres with periodic boundary conditions was slowly increased from a low density fluid state to almost close-packing. The projected maximum density limit was at 0.637 ± 0.002 indistinguishable from that of the laboratory model (0.6366 ± 0.0004). Moreover, the RDF at the highest density achieved (at 0.628 still significantly below the apparent maximum) was identical to that of the hard-sphere model within computational and experimental uncertainties. Despite the apparent ad hoc nature of the laboratory-built model, its density and structure appear to be indistinguishable from that of this "configuratonally-arrested" hard-sphere fluid, supporting our tentative assignment of the hard-sphere dense packing as a zero temperature ideal glass. The collective rearrangements produced by either molecular dynamics, or laboratory kneading and shaking, appear very similar.

3. Summary

Computer construction methods raise a basic problem of constructing a model consistent with the packing constraints imposed by the high density of the real systems we are trying to model. Sequential addition procedures necessarily result in lower density models which do not show the characteristic RDF features found in real systems: collective rearrangements are apparently necessary to increase the density adequately to show a clear second peak splitting. The addition of a sphere on to a partly-built model is constrained only by the packing constraints exerted by the already-existing model on one side only of the new sphere. Similarly, collective rearrangements with free boundaries take inadequate cognisance of the packing constraints that would be effective were the cluster consistent with being embedded in a statistically-equivalent ensemble. The additional freedom allowed by a free boundary facilitates very high density packings with apparently improved (with respect to experimental) RDFs. Just as low density models with good RDFs must be considered inadequate, so must high density models if they are incapable of being extended in size indefinitely without the consequent exertion of packing constraints changing the density and RDF. The icosahedral model of Sadoc is an example of the embedding problem on a finer scale: the density and RDFs of the subunit clusters are reasonable, but

they cannot be packed together without drastically reducing the density.

Although these remarks refer to hard-sphere packings they apply also to more "realistic" "soft" sphere models. Experimental comparison must be made with both density and RDF at least: we can fit either with many models, but to fit both by one fully embedded model is difficult, but necessary. Otherwise, we would have failed to consider sufficiently the packing constraints which, in dense systems, are strong determinants of the structure.

"REAL" AMORPHOUS ALLOYS

No real alloy consists either of hard-spheres, or of only one type of atom. We need therefore to examine the effects of softer (ideally realistic) potentials on the ideal hard-sphere structure, and to see how this structure changes when two (or more) components and their chemistry are considered.

1. Potential Functions

Two main routes are followed to probe the effects of soft potentials. First, a previously-constructed hard-sphere assembly is rescaled to a soft potential, and energy minimisation calculations performed. Most work on single component systems has used simple potentials such as those of the Lennard-Jones or Morse variety, and conjugate gradient minimisation methods have allowed relatively large structures (of a thousand or more atoms) to be handled[36]. Secondly, the use of computer simulation - molecular dynamics (MD) and Monte Carlo (MC) - techniques has been explored.

In the molecular dynamics procedure, an assembly of atoms is set up in a (usually cubic) box, with periodic boundary conditions to minimise boundary problems. The atoms are each assigned a velocity at random, ensuring the average kinetic energy corresponds to the required temperature. The forces acting on each atom are calculated, and the atoms allowed to move according to Newton's laws. The temporal development of the system is followed until the assembly has apparently equilibrated, when its structural and dynamic properties can be extracted. The Monte Carlo procedure works rather differently but produces sample configurations which are in the limit consistent with the molecular dynamics assemblies. Again starting from an initial configuration of the required density, a randomly chosen atom is moved in a random direction by a (modulated) random amount and the potential energy change ΔU calculated. If ΔU is negative, the move is accepted and the process repeated; otherwise, the move is accepted with a Boltzmann weighting. It can be shown that both MC and MD methods converge towards configurations that are consistent with a Gibbs ensemble of the model molecules chosen.

These computer simulation techniques have been applied very successfully to liquids, and in fact were used early on to demonstrate the similarity between inert gas liquids and Bernal's model[17]. Provided the calculation is pursued for long enough (though how long this is is arguable especially for non-simple molecules) the validity of the resultant structure (MC and MD) and dynamics (MD only) depends on the adequacy of the potential functions used. The method is often used to test proposed potential functions.

When applied to amorphous solids, the reservation with respect to potential functions remains, and we have an additional problem: we are trying to simulate a non-equilibrium assembly. Using molecular dynamics, we start with a liquid assembly and then reduce the temperature progressively. However, computational restrictions force us to reduce the temperature at a rate which is unrealistically high (perhaps $\sim 10^{11}$ Ks^{-1}) compared to laboratory quench rates ($\lesssim 10^{6}$ Ks^{-1}). The resultant structure is really a "configurationally-arrested" liquid, rather than an amorphous solid which has been allowed to adjust its structure during the quench. Monte Carlo suffers similar problems in that temperature must be reduced (or pressure increased) unrealistically rapidly.

Relaxation calculations[3,36-38], molecular dynamics[15,35,39,40] and Monte Carlo[41-44] simulations have been reported on single component systems using

largely Lennard-Jones or Morse potentials. Many of these calculations were performed under different conditions; as a result, it is possible to draw tentative conclusions concerning the variability of the resulting amorphous structure with respect to the different conditions used. We give here a brief summary relevant to the binary alloy work discussed below, fuller details having been published elsewhere[3,38].

(a) Potential function and model boundaries. Both RDF and internal structure can vary with potential function[3]. For a very soft potential such as a Morse 3, structural differences are also induced by the different truncation procedures used in energy calculations[3]. These latter differences are particularly evident when free boundaries are used, and might be attributed to a long-range compression effect which would be much reduced for an embedded model.

The same starting configuration relaxed under free and confined boundary conditions showed structural differences. However, the boundary problem may be less critical for soft potential assemblies than for hard-spheres. In the hard-sphere case, the "free volume" available for internal rearrangement depends strongly on the presence of an unconstrained boundary; for soft spheres, internal adjustments are facilitated in addition by the softness of the repulsive core. Nevertheless, as such calculations require only a minor increase in computer time, it would seem sensible to use periodic boundary conditions to reduce the free boundary problem.

(b) Starting configuration for energy minimisation. If we could show that the relatively low density sequentially constructed assemblies led to relaxed structures indistinguishable from those obtained from dense, collectively-rearranged hard-sphere starting configurations, then the objections raised earlier to sequential construction methods could be ignored. The limited evidence on this point suggests[3] that, although resultant RDFs of relaxed models using starting configurations of densities 0.637 (close-packed) and 0.60 (loose-packed) are statistically indistinguishable, there are measurable differences in internal structure. Which starting point is more realistic is unclear, as is the effect on resultant structure of using even lower density starting configurations. Although one might argue that the detected local structural differences are physically unimportant, the remaining uncertainty advises prudent use of several different starting configurations.

(c) Computer simulation. Just as the hard-sphere MD calculation of Woodcock[35] tended towards a structure whose RDF is apparently identical to that of the hard-sphere dense random packing[16,35] so MD calculations on rapidly quenched Lennard-Jones atoms yield RDFs very similar to those obtained from free boundary relaxations[39,40]. Thus, despite the reservations raised earlier about the identity of structures produced at realistic laboratory quench rates and at accessible computer quench rates, indistinguishable RDFs can be obtained. We should stress several points, however. First an amorphous Lennard-Jones system has never been experimentally prepared, and it may well be that the unrealistically high quench rates used in the simulations may be theoretically necessary to produce one. In this case, the apparent structural similarity between MD and relaxation calculations would be expected although we could not justifiably generalise this similarity to alloys which are produced at quench rates low enough to allow internal structural rearrangements on the time scale of the quench. Secondly, the RDF is a relatively crude measure of structure, and similar RDFs can hide subtle structural differences. Thirdly, some MD work suggests there may be a significant structural dependence on quench rates[40], and structural data exists to allow a detailed investigation of this point[45].

2. Binary Amorphous Alloys

Each of the model-building techniques discussed above has its disadvantages. When we consider trying to model real amorphous alloys, the two procedures that look most attractive are (i) computer simulations and (ii) relaxation calculations, preferably using periodic boundaries. Monte Carlo or molecular dynamics quenching of a previously set-up liquid configuration will produce a "configurationally-arrested liquid" which will necessarily ignore those rearrangements that will occur on the time-scale of the laboratory quench. The relative importance of such processes to the final structure is unclear, and detailed examination of particular cases is required. The possibility of identifying these processes - or perhaps relaxations from sequentially constructed computer models - with structural relaxation of as-quenched glasses could be pursued (see chapter 10).

A major problem with relaxation calculations is the choice of starting configuration. For single component models, we have evidence for a dependence of structure on starting configuration. For a multicomponent system, this dependency will be much greater. In addition to the packing constraints that dominate the single-component structure, we must consider the "dispersion" of the two components in the alloy. This is generally termed "chemical ordering", and refers to the relative arrangement of A atoms around B, B around A, etc. Relaxing a sequentially-constructed dense starting configuration will not significantly perturb the topology of the local chemical ordering: if it is incorrect at the start, it will remain incorrect - the structure will be locked into an incorrect local energy minimum. "Correct" topology of the starting configuration is therefore essential; subsequent relaxation is merely a refinement, though one which - on the evidence of single component hard → soft sphere relaxations - will significantly change the model RDF.

Thus, either method must be used with care, and the possible consequences of variations in procedure explored fully. For sequential model-building followed by relaxation, alternative starting configurations should be used, while for simulation calculations, quench-rate dependencies must be examined.

A hybrid of the two approaches seems attractive, though has yet to be attempted. On the reasonable assumption that - provided the potential functions are "adequate" - a computer-simulated liquid alloy has the correct liquid "chemical ordering", then that retained on rapid quenching would be a reasonable starting configuration for a relaxation calculation[46]. Within the constraints of available computer time, quench rate dependencies of the starting structure could be examined, and the detailed local structures of the final "relaxed" models compared.

At this point, it is perhaps useful to restate the three major problems facing the would-be serious modeller of binary or more complex amorphous alloys. First, the potential functions. We know single component amorphous structures depend upon the potential, and this dependency is probably stronger for the binary metal alloy. For any resemblance of reality, therefore, we must abandon the oversimplified Lennard-Jones and Morse forms. This raises additional problems. In metals, we cannot ignore many-body effects from the delocalised electrons, and hence density-dependent potentials must be used. When we consider the second component B, we need a description of the AB interaction which is consistent with the resulting "chemical ordering" found in the liquid. For "simple" metals, some progress is possible using established techniques in metal physics, as in the fundamental work of Hafner[47]. Where metalloids are involved, we have even bigger problems: directionality of the metal-metalloid interaction - which would have consequences for "chemical ordering" - must somehow be considered.

In the light of these rather basic problems of potentials, it could be argued that more ad hoc model potentials could be used, provided the model potential is designed to reproduce successfully - or at least be consistent with - the observed local chemical ordering. This raises our second problem, that of knowing what the chemical ordering is. For single component models, one RDF is the maximum structural information that can immediately be

obtained from a diffraction experiment. For two components, we require three partial RDFs - one for each of the three possible pairs AA, AB, BB (see chapter 5). Merely obtaining this data for a given alloy is a tall order: three independent scattering experiments are required in which the scattering power of the atoms is different. In principle this can be done for a limited number of suitable alloys using isotope substitution in neutron work, and anomalous dispersion for X-rays. Only very limited partial RDF data is currently available, though work in progress should lead to much better local ordering characterisation in a few alloys. Other techniques such as EXAFS, Mössbauer and NMR have also been used to try to obtain similar local information, although the interpretations of especially the last two are strongly model dependent[46].

Thirdly, even knowing the "chemical ordering", it is not a trivial task to construct an amorphous alloy model with the two components suitably dispersed to reproduce it. For the single-component models, packing constraints are strong structure determinants, yet they are poorly understood. For the binary, within this poorly-understood framework, we must build in the additional constraint of a prescribed "chemical ordering".

In this final section, we can do little more than indicate the approaches that have been tried to tackle these problems. This discussion could be framed in terms of how simultaneous satisfaction of these two (competing?) packing and "chemical ordering" constraints is attempted. All methods have used subsequent relaxation of the initial configuration, using potentials (generally Lennard-Jones variants) which are sometimes designed to bias the assembly towards the desired local structure.

(a) "Dense random packing" models. Under this heading we consider model-building approaches which satisfy packing constraints preferentially to "chemical ordering". Although earlier laboratory models were built by Scott and Kovacs[48] and Cherry and Finney[49], no attempt was made to bias the model towards a particular local ordering. Boudreaux and Gregor[50-52] applied Bennett's sequential addition procedure to (initially) hard-spheres of size and composition ratio designed to mimic $Fe_{80}P_{20}$ or $Pd_{80}Si_{20}$. Technical modifications were made to the building procedure to ensure compositional homogenity[52], and an attempt made to input some chemical order constraints by forbidding near neighbour P-P contacts. The initial hard-sphere models (of several compositions to allow investigation of structural variations with composition) brought out a general defect of the sequential addition procedure: the structure was highly anisotropic. The addition procedure - probably partly because a site closest to the centre would tend to be planar - showed a characteristic RDF (see fig.2c) only in the radial direction. Collective rearrangements would be expected to take full account of the packing constraints in all directions and thus remove this anisotropy. This was successfully done by relaxing the assemblies under Lennard-Jones potentials. As no attempt was made to design potentials which might bias the relaxation towards either retaining or enhancing ordering, the "chemical ordering" was fed in soley through the exclusion of near-neighbour small (metalloid) atoms. Relaxation increased Fe-Fe and P-Fe coordination numbers by 30% and 41% respectively, to values in reasonable agreement with experiment[52]. Related structures have been built to model $Fe_{85}B_{15}$[60] and $Fe_{\sim 80}P_{\sim 20}$[55] and the results compared only partially successfully with limited partial RDF data.

The main problem with sequential addition procedures for modelling binaries with "chemical order" is feeding in local ordering constraints which are consistent with the packing constraints *at each stage during construction*. The free boundary forming half the neighbourhood of each atom means *only half the constraints are defined at each addition stage*; therefore decisions must necessarily be made on limited information. Forbidding close contacts of particular types of atoms is straightforward, but the more complex constraints that will probably be required to fully reproduce required chemical ordering seem far more difficult to feed in to the sequential addition process.

(b) *Built-in chemical ordering*. An alternative is to *first* build in the desired chemical ordering - perhaps to excess - and to allow the relaxation process to bring in the dense packing constraints, perhaps using model potential functions designed to favour the original locally-ordered structures. This approach is strongly-related to established model-building techniques for network glasses such as vitreous silica and amorphous silicon and germanium, although here the absence of significant packing constraints means the prescribed chemical ordering remains. Gaskell first explored the possibilities of the method in his work on $Pd_{80}Si_{20}$ and related transition metal-metalloid alloys[53] for which experimental coordination numbers measured by EXAFS and neutron scattering gave results which were similar to those found in corresponding crystalline modifications which showed a trigonal prismatic coordination (fig.3a). Considering the widespread occurrence of this kind of coordination polyhedron over a wide composition range, it seems reasonable to expect it to occur frequently in the amorphous alloy.

A model was therefore built - initially in the laboratory, later transferred to the computer - by joining trigonal prismatic units in the manner of fig.3b. This emphasises the strong trigonal prismatic chemical ordering at the expense of packing constraints (the model in fact contains large cavities). The packing constraints are then brought more into play by computer relaxing the assembly. Again Lennard-Jones potentials were used, though for one model the second neighbour Pd atom is treated differently to try to emphasise the trigonal prismatic ordering in the relaxed structure. The resultant structure shows encouraging agreement with experimental total RDFs: no partial RDF data are available for comparison.

The interplay between the initial trigonal prismatic coordination and the increasingly strong effect of the packing constraints as the relaxation proceeds is a particularly interesting problem which requires attention. At experimental densities, widespread perfect trigonal prismatic order appears not to be possible in a non-crystalline assembly, but how small the distortions need be to accommodate such local ordering is unclear. Using recently developed techniques[54] we can begin to probe the degree of "trigonal prismaticity" remaining in these structures. Initial results show that many such units do indeed remain, although generally distorted, and there is evidence that significant movements are forced on some atoms, in particular several Si atoms become close to being first neighbours. We could speculate on the possibility of constructing a more perfectly trigonal prismatic - yet densely packed - non-crystalline assembly from a totally different starting point, with such an assembly inaccessible by relaxation from a configuration conforming to the starting hypothesis of fig.3b.

There is also the interesting question of how far the Boudreaux and Gaskell approaches might tend towards similar relaxed structures. Fujiwara and Ishii[55] constructed Boudreaux-type models of $Fe_{100-x}P_x$ alloys, and attempted to characterise the local ordering. Although it is not clear how capable their analysis techniques were of unambiguously describing the phosphorous coordination geometry, they argued for a strong tendency to trigonal prismatic organisation. Further work using more sensitive analysis techniques is under way to examine this point in more detail[54].

(c) Other methods. In addition to computer simulated quenching suggested above - relying on realistic potential functions to reproduce the desired chemical ordering in the liquid structure starting configuration - one further approach seems worth pursuing. Boudreaux's approach puts primary emphasis on the packing, (rather weak) constraints being added to try to mimic some of the features of expected chemical ordering (although the sequential nature of the building procedure means that the packing constraints cannot be fully considered every time a sphere is added). Gaskell's method which

emphasises local ordering primarily, leaving relaxation to sort out packing constraints secondarily, seems a more flexible approach. An interesting third possibility currently being tried[57] starts from an already-constructed densely-packed single component model, and feeds into it chemical ordering information. The philosophy behind this approach argues that a pre-existing single component model contains the essential packing constraints in a dense non-crystalline structure. The (variable) topology is precisely defined, and therefore complete data is available for investigating the possibilities of labelling the atoms A or B consistent with the desired local ordering. Allowing a degree of statistical variation in the topological and metrical perfection of the local orderings we are trying to insert, many different possible combinations of A and B labellings can be explored and screened; relaxation calculations can then be performed in the usual way using periodic boundary conditions. The simplest case of such an approach was used by von Heimendahl and Hafner[58] for $Mg_{70}Zn_{30}$, using hopefully realistic potentials developed from pseudo-potential theory[47]. As zero chemical ordering was assumed, A or B (Mg or Zn) labels were assigned randomly (subject to composition). The related procedure of Maeda and Takeuchi[59] includes much weaker packing constraints, their starting configuration being set up by a random parking algorithm.

Extending this "seeding" approach to the non-random chemical ordering case is far from trivial. It attempts to partly decouple the topological disorder (packing constraints) from chemical ordering so as to allow their (partially) separate consideration, by using a completely defined non-crystalline structure within which to probe the combinational possibilities. As such a single-component "random lattice" (!) is a better approximation to the packing constraints operating in a binary where the two components are nearly equal in size, it seems sensible to start by modelling a weakly-ordered alloy of approximately equal size components.

SUMMARY

The major problem with modelling real amorphous alloys is to construct a non-crystalline assembly that is consistent with both local chemical ordering and the overall packing constraints of high density structures. Network glasses such as vitreous silica present much less of a problem as the chemistry (linked SiO_4 tetrahedra) dominates the structure, which exhibits very strong chemical ordering with only minor considerations of packing. Single component "ideal" glasses - be they of hard or soft spheres - provide the opposite extreme, where packing constraints dominate and the chemistry of molecules with spherical symmetry is not a significant consideration. The real problems lie in between where the interplay between "packing" and "chemistry" is crucial in determining the structure.

We are handicapped in tackling this problem in two major ways. First, we lack good, *model-independent* data on chemical ordering, though current work will remove this problem for selected alloys. Secondly, our understanding of the operation of packing constraints in dense non-crystalline assemblies is poor. Even for single-component "ideal" model systems, we have no adequate theory, and we are forced to model-building studies to gain some-albeit restricted-insight. Even here, there are complications in that different construction procedures can lead to structurally different model assemblies ("amorphous polymorphism")[3] - although there is evidence to suggest that at the higher densities of interest for real systems, a single ideal hard-sphere - and perhaps soft-sphere - structure can be (statistically) defined.

Although we have much experience of single-component models - which have been useful in helping to at least see (if not to understand) how variable model construction parameters can affect final structure - only a limited amount of work has been done to model binary amorphous alloys. Two main approaches put different stresses on chemical ordering and on packing constraints in the starting structure, and have raised interesting questions concerning the interplay between these two constraints which are crucial in determining the model structure. Despite the severe problems in effectively modelling the structures of real binary - and eventually ternary - amorphous alloys, progress is expected also via new "topological seeding" techniques. Although we might make use of computer simulation to set up liquid configurations with chemical ordering determined by the assumed potential functions neither MC or MD methods will solve all problems, being restricted to unrealistically high quench rates. Simpler, cruder methods are still appropriate, and may do more in the long term to improve our understanding of these fascinating structures.

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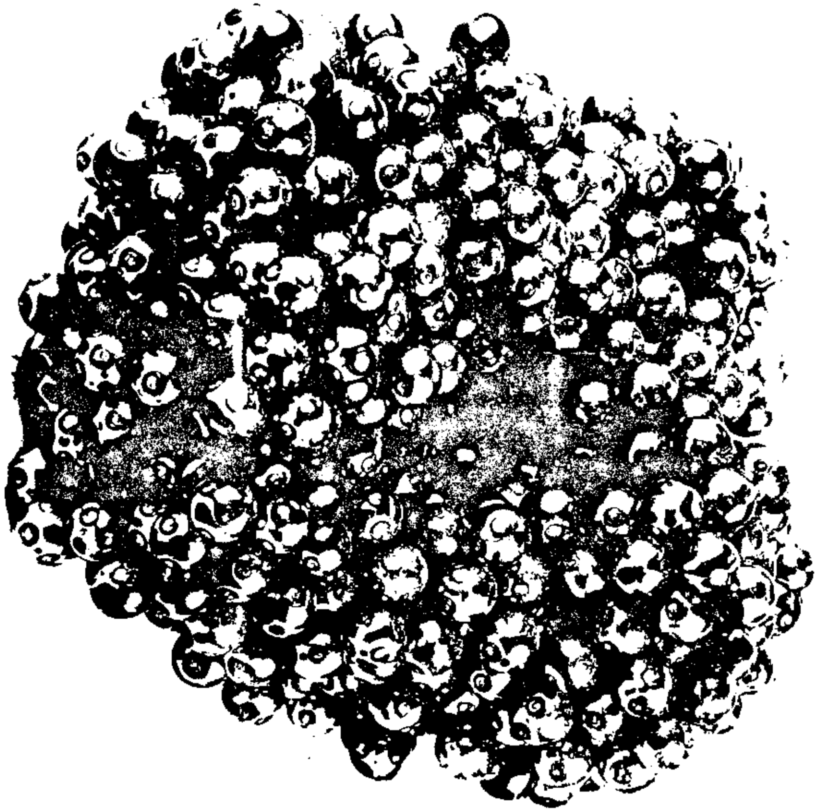
FIGURE CAPTIONS

Figure 1 : A laboratory-constructed random close-packing of hard-spheres, showing the absence of lattice ordering.

Figure 2 : Pair distribution functions out to about two diameters of several single component hard-sphere models. (a) Hard-sphere dense packing[17] ($\rho = 0.6366$) compared with experimental $Ni_{76}P_{24}$ data[2] (continuous line); (b) computer-constructed model using Bennett's "global" criterion[20]; (c) and (d) "gas-compression" models of densities (c) 0.639 and (d) 0.664.

Figure 3 : (a) Trigonal prismatic units used in building Gaskell's starting configuration by adding together units as in (b). ● Si; ○ first neighbour Pd; ⊘ second neighbour Pd.



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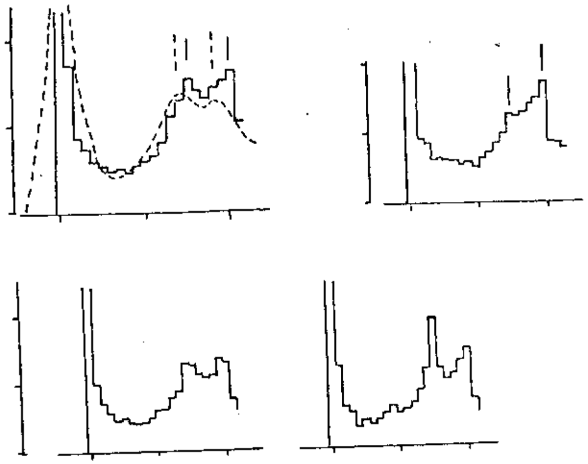

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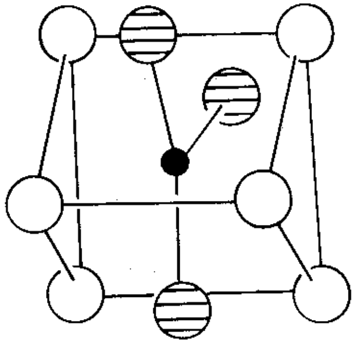

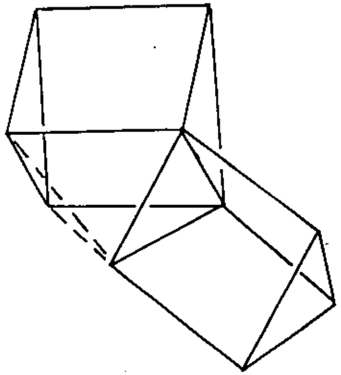

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34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392-I

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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

MODELLING OF LIQUIDS AND AMORPHOUS SOLIDS

(Lecture I)

J.L. FINNEY

Liquids & Disordered Systems Lab.
Department of Crystallography
Birkbeck College
Malet Street
London, WC1E 7HX
UK

GENERAL SCOPE OF COURSE.

The development & use of techniques to model the structures of non-crystalline dense assemblies in the laboratory & on the computer. Stress will be given to amorphous solids & glasses where the technical problems are greatest, & examples drawn from current work on binary amorphous alloys and - if time permits - liquid water.

LECTURE 1. INTRODUCTION; IDEAL SINGLE COMPONENT ASSEMBLIES LABORATORY MODELS.

1. CRYSTALS, GASES, & LIQUIDS: THE NATURE OF MODELS.

The nature of ideal crystal & ideal gas models; time scales & the meaning of structure.

Imperfect (real) crystals & gases as perturbations from ideality

Thermodynamics & the equation of state: to derive from a theory or a model requires evaluation of the partition function

$$Z = \sum_{\substack{\text{all}\\ \text{configurations}}} e^{-\mathcal{H}/kT}$$

where $\mathcal{H}$ the Hamiltonian. The kinetic energy terms in the Hamiltonian are independent & may be integrated out giving

$$Z = Z_K . Q$$

where Q, the configurational integral contains structural input through the potential energy $U(q_1 \rightarrow q_N)$

$$Q = \frac{1}{V^N N!} \int \cdots \int e^{-U(q_1 \rightarrow q_N)/kT} dq_1 \rightarrow dq_N$$

In general, a model is required to evaluate $U(q_1 \rightarrow q_N)$, be it a theoretical statement/approximation, or a set of sample coordinates which could be termed a structural model. The problems of liquids & non-crystalline solids means we normally appeal to models such as these.

2. MODELS OF GASES & CRYSTALS. APPLICABILITY TO LIQUIDS?

Ideal gas: instantaneous positions determined solely by statistics (no intermolecular potential & no molecular size). — Q ≡ 0 i.e. there is no structure [illegible] RDF $g(r)$ no features

→ Imperfect gas: few, weak interactions, which can be considered in terms of pairs (→ triplets & higher as density increases).

"Cluster expansion" (standard statistical mechanics & liquid texts) fails to converge as density increases. Hence not easily applicable to liquids.

Ideal crystal: unlike gas (small no weak interactions) we have large no. of strong interactions, ...

BUT we effectively know the location of every atom: described on a lattice. Hence from structure can write down $U(q_1 \rightarrow q_N)$.

→ Real (imperfect) crystal: perturbation from ideal: we know the mean position of each atom, & the problem is now of characterising the lattice vibrations.

Liquids: the problem is intermediate: large number of strong interactions

|| Gas approximation: fails to converge for large no. of interactions (cf more sophisticated liquid state theories)

|| Crystal approximation: we cannot make because we have no crystal lattice.

SO WE LOOK TO OTHER POSSIBLE APPROACHES.

3. MODELS OF IDEAL SINGLE COMPONENT LIQUIDS

By analogy with the ideal crystal, we try to construct a model – initially in the laboratory – of an ideal liquid. Real liquids may then be referred to the ideal in a similar way that real crystals relate to ~~real~~ ~~liqu~~ ideal crystals.

An acceptable model must be consistent with
- density } both available experimentally.
- RDF }

Early attempts.

JCP 1 (1933) (1) Bernal & Fowler : water 1933. Relate to variable topology in silicates & ices. Too difficult at the time → simple liquids.

JCP 12, 1-18 (1944) (2) O.K. Rice 1944 : suspended gelatin spheres → light scattering measurements & comparisons with liquid x-ray scattering.

(3) Bernal late 1950's work from RDF to see what looks like.

* (4) Look more at geometrical consequences of interatomic interactions.

Crystal : a structure consistent with density, potential function, & lattice
Liquid : ——— " ——— density, potential function, & no lattice.

Ideal crystal based on hard spheres no overlap consequences of volume exclusion. Accepted models of close packed crystals

TRY : Ideal liquid : based on hard spheres no overlap, consequences of volume exclusion. → model of ideal liquid

JDB : PRS A280, 299 (1964)

MODEL CONSTRUCTION.
(1) Pack together hard spheres.
(2) Prevent crystallisation
(3) Knead / vibrate to maximum density
(4) Fix
(5) Strip
(6) Measure coordinates. (7) Reconstruct ball & stick.

MAJOR RESULTS.

(1). Density $\rho \sim 0.637$. cf $\rho_{\text{crystal close packing}} = 0.7405$.

NOTE $0.637 < \rho < 0.7405$ a prohibited region for a homogeneous assembly (except b.c.c. ~ 0.68)

cf $\Delta V_{\text{melting}} \sim 0.15$

Ⓣ (2). RDF : cf liquid looks ~ OK (but note first peak ?).

Thus, this "homogeneous, coherent, & essentially irregular assemblage of molecules containing no crystalline regions" is taken as our ideal liquid model. This essentially simple idea is seen by Ziman (Models of Disorder, § 2.11) as "the key to any qualitative or quantitative understanding of the physics of liquids," & "supersedes various other theoretical approaches based on phenomenological constructs such as 'holes in lattice', 'paracrystals', 'significant structures', 'dislocations', ... etc"

It is a model that is "homologous to that of the crystalline solid, as well as radically different in kind, and [has] a general quality of homogeneity" (Bernal). Qualitatively, it accounts for the essential fluidity and high entropy of the liquid, & explains qualitatively the discontinuity of state at the melting point, together with the contrasted continuity with the vapour phase & the existence of a critical point.

It can be demonstrated (see later) that the simple model & a simulated liquid can be referred to each other in a simple way, effectively validating the ideal model (cf real & ideal crystals).

4. APPLICATIONS TO AMORPHOUS SOLIDS.

More accurate model characterisation (ie. better measurements) reveal additional structure in RDF second peak — this will be important later. Compare what is known ~~of~~ when freeze out atomic motions from simple liquid → "glass" : perhaps consider ideal RCP (random close-packed model) as an ideal zero temperature glass rather than a liquid. Note continuity of state between liquid & glass is consistent with this (though remember possible relaxations may occur → differences in detailed local structures between "glass" & "instantaneous liquid").

Experimental data on amorphous metals (?) & metal alloys : shows general agreement, but note differences in detail

SUMMARY :

CRYSTAL STRUCTURE : Consistent with density, potential function, lattice
LIQUID/AMORPHOUS STRUCTURE : ——— " ——— density, potential function, no lattice

All modelling studies concerned with realising structures consistent with these constraints, either on the computer or in the laboratory.
Note the constraints may be different quantitatively (eg. silicates where hard spheres are just not a correct approximation), but the general philosophy is still the same.