



# Properties and Applications of Amorphous Materials

Edited by

M. F. Thorpe and L. Tichý

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# Properties and Applications of Amorphous Materials

edited by

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## Preface

The aim of this NATO ASI has been to present an up-to-date overview of current areas of interest in amorphous materials, with particular emphasis on electronic properties and device applications. In order to limit the material to a manageable amount, the meeting was concerned almost exclusively with semiconducting materials. This volume should be regarded as a follow-on to the NATO ASI held in Sozopol, Bulgaria in 1996 and published as "Amorphous Insulators and Semiconductors" edited by M.F. Thorpe and M.I. Mitkova (Kluwer Academic Publishers, NATO ASI series, 3 High Technology - Vol. 23). The lectures and seminars fill the gap between graduate courses and research seminars. The lecturers and seminar speakers were chosen as experts in their respective areas, and the lectures and seminars that were given are presented in this volume. During the first week of the meeting, an emphasis was placed on introductory lectures while the second week focused more on research seminars. There were two very good poster sessions that generated a lot of discussion, but these are not reproduced in this volume as the editors wanted to have only larger contributions to make the proceedings more coherent.

This volume is organized into five sections, starting with some more unusual aspects of structure than were covered in Sozopol. Section two deals with the very new area of self-organization in glasses and how this relates to the rigidity of the glass. The next section gives an overview of electronic states and transport phenomena. The fourth section deals with an area of photoinduced effects that has recently seen an increase in interest due to possible device applications. Finally in section five, some properties specific to amorphous silicon and amorphous carbon are covered.

This NATO ASI was held in the Iron Mountains in Sec in the Czech Republic. This was the first NATO ASI held in Czech since it joined NATO earlier in 2000, and only the fourth NATO ASI ever held in Czech. The meeting lasted for 10 working days with a day off for a trip to Prague. Each day had either morning and evening sessions [with afternoons free to visit the lake or wander in the hills around Sec] or morning and afternoon sessions. On most of the free evenings, entertainment was provided which included folk dancing and a disco.

Finally, we should like to thank the NATO Science Committee for providing financial support for this meeting. We would like to thank Mykyta Chubynsky for his help to make sure that the format of this book is as uniform as possible throughout. We would especially like to thank Ms. Janet King for her invaluable assistance from the planning through to the report stage of this meeting. Most of the participants corresponded with her and got to know her well via e-mail. The efforts of Ms. Tana Tonarova who helped considerably with the organization of the meeting on the Czech side are also greatly appreciated.

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**September 2000**

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# THE STRUCTURE OF AMORPHOUS MATERIALS

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## 1. Introduction

Amorphous materials are condensed phases which do not possess the long-range translational (or orientational) order – or periodicity – characteristic of a crystal. The terms amorphous and non-crystalline are synonymous under this definition. The term glassy has the same structural meaning, but in addition it also usually implies that the material exhibits a ‘glass transition’ (evidenced by a discontinuous change in, for example, the heat capacity from a liquid-like to crystal-like value at the transition on cooling a melt). Although the presence of *dynamic* disorder in the case of liquids complicates matters, the average atomic structure of liquids can be described in similar ways to that of amorphous solids.

In this article, we will consider only *topological disorder*, viz. aperiodic disorder in the atomic positions. Other types of disorder, associated with an underlying crystalline lattice, are neglected, such as spin disorder (in spin glasses), substitutional disorder (as in metallic alloys), and vibrational disorder with respect to the equilibrium positions of a regular lattice.

The fact that an amorphous solid has no structural periodicity means that the structure cannot be described in terms of a periodically-continued, finite-sized unit cell. The structure of an amorphous solid could be described (somewhat unhelpfully) in terms of an *infinite* unit cell, but in general a statistical description is necessary. The quantity often used to describe the structure of amorphous solids is the atomic-density function,  $\rho(r)$ , or the associated function, the radial distribution function (RDF),  $J(r)$ , given by

$$J(r) = 4\pi r^2 \rho(r). \quad (1)$$

The quantity  $J(r)dr$  is the number of atoms in a spherical shell lying between distances  $r$  and  $r + dr$ . Both  $\rho(r)$  and  $J(r)$  exhibit peaks at distances corresponding to coordination shells from an origin atom, although higher-lying peaks cannot be identified uniquely with a particular shell in the case of amorphous solids, unlike for crystals. At larger distances,  $\rho(r)$  apparently tends to a constant (unity, if normalized to the average density  $\rho_0$ , as in Fig. 1) and  $J(r)$  tends to the average density parabola,  $4\pi r^2 \rho_0$  (see §2.3), indicative of a random structure (more precisely, the lack of density fluctuations) beyond a certain distance. The peaks in  $\rho(r)$  or  $J(r)$  for amorphous solids also become broader with increasing distance  $r$  from an origin atom because of the cumulative effects of static disorder in bond lengths and bond angles. In crystals, with only thermal (vibrational) disorder, the peaks in the RDF are much narrower and do not damp out with increasing distance. As a result, the structure of non-crystalline solids cannot be determined unambiguously, a situation reinforced by the fact that in many cases, at both microscopic and macroscopic levels, the structure of such materials depends on details of the method of preparation and thermal history.

Unlike the case of single crystals, where a single experimental technique, diffraction, can be used to determine the positions of all atoms in the finite unit cell, several complementary techniques need to be employed, besides diffraction, in order to obtain as much structural information as possible. These other techniques can include atom-specific structural probes such as extended X-ray absorption fine-structure spectroscopy (EXAFS), magic-angle spinning nuclear magnetic resonance (MASNMR) and related NMR techniques, and vibrational spectroscopies (e.g. IR absorption and Raman scattering).

The aim of this paper is to lay out a framework for the description of the atomic structure of amorphous materials rather than give an exhaustive survey of experimental results. The description will be illustrated with examples chosen from different classes of amorphous solids, e.g. covalent, ionic and metallic systems.

## 2. Structural order

In order to provide a description of the structure of amorphous solids, and hence to provide an interpretation of the results of experimental techniques used to probe the structure, it is convenient to consider the various types of structural order that can exist in such materials at various length scales. Such a categorization is convenient in two regards: the classification is hierarchical, so that a particular type of order at one length scale can be dictated by order at a smaller scale (but not necessarily the converse); the



division is also pragmatic in that different structural probes are generally sensitive to structural correlations at various length scales (Elliott 1991).

## 2.1 SHORT-RANGE ORDER

Short-range order (SRO), as its name implies, concerns structural order involving the nearest-neighbour coordination shell. This is easiest to discuss in the case of covalently-bonded amorphous solids since the presence of their directed stereochemical bonds simplifies the description considerably. For such materials, SRO is defined in terms of well-defined local (cation-centred) coordination polyhedra, e.g. planar triangles (e.g.  $\text{BO}_3$  triangles in  $\text{B}_2\text{O}_3$ ), pyramidal units (e.g.  $\text{AsS}_3$  units in  $\text{As}_2\text{S}_3$ ) and tetrahedra (e.g.  $\text{SiO}_4$  tetrahedra in  $\text{SiO}_2$ , or  $\text{SiSi}_4$  tetrahedra in Si).

The parameters which are sufficient to describe topological SRO in stereochemical systems are the (coordination) number,  $N_{ij}$ , of nearest neighbours of type  $j$  around an origin atom of type  $i$ , the nearest-neighbour bond length,  $R_{ij}$ , the bond angle subtended at atom  $i$ ,  $\theta_{ijk}$  (when the atom of type  $k$  is different from  $j$ ), and the corresponding quantities when atom  $j$  is regarded as the origin, viz.  $N_{ji}$  and  $\theta_{jik}$ . The bond angle is found from the first (nearest) neighbour distance  $r_1=R_{ij}$  and the second (next-nearest) neighbour distance  $r_2=R_{jk}$  (or  $R_{ji}$ ) by the relation:

$$\theta_{jik} = 2 \sin^{-1}(r_2/2r_1) \quad (2)$$

Note that in this definition of SRO, nothing is stated explicitly about the detailed *connectivity* of the local coordination polyhedra (e.g. corner-, edge- or face-sharing), except for the implicit information about the connectivity contained in the coordination number  $N_{ji}$  of the linking anions at the apices of the cation-centred coordination polyhedron. The connectivity of polyhedra dictates the type and extent of medium-range order, as will be seen in §2.2.

Note also that the structural disorder characteristic of amorphous solids can manifest itself in variations in these quantities, e.g. bond-length and bond-angle fluctuations in the case of iono-covalent systems. This disorder can be both thermal (vibrational), as in the case of crystals, and also static, particularly in the case of bond angles, where variations of 10% are not uncommon:

$$\sigma_{am}^2 = \sigma_{th}^2 + \sigma_{dis}^2, \quad (3)$$

where  $\sigma^2$  is the mean-square fluctuation in atom-atom distances. Thus, a statistical description is unavoidable, even at this spatial level of structural order. The strong stereochemical bonding characteristic of such materials ensures that the overall coordination number is maintained at all sites (except for occasional coordination defects, e.g. 'dangling' bonds).

An additional parameter is required if the degree of *chemical* SRO needs also to be described, e.g. in the case when *different* types of atoms constitute the coordination polyhedron around a given origin atom (e.g. cation). Thus, in nonstoichiometric compositions, for example, excess atoms can be accommodated by the introduction of "wrong" (i.e. homopolar) bonds, and the chemical order which might otherwise occur at the stoichiometric composition (e.g. every As atom surrounded by three Se atoms, and every Se by two As atoms in  $\text{As}_2\text{Se}_3$ ) is thereby broken; the relevant parameter in this case would be the proportion of wrong bonds. (Such considerations can also apply even for stoichiometric compositions, since chemical ordering may not exist even in that case when elements of comparable electronegativities are involved.)

A related type of chemical order is when the different types of atomic species in the coordination shell around a given origin atom are in fact the *same* element but can have different charge states, bonding connectivity etc.. An example of this is the case of nonbridging anions (e.g. oxygen atoms) introduced (in say silicate glasses) by the introduction of network-modifier cations (e.g. alkali ions). Cation-centred polyhedra then can contain different numbers of nonbridging and fully bridging anions. In the case of silicate glasses, five possibilities exist, denoted as  $Q_n$  (quaternary) species, with  $n=0-4$  being the number of *bridging* oxygen sites in a given  $\text{SiO}_4$  tetrahedron. Nonstoichiometry in the oxygen composition is then accommodated by changing the proportion of nonbridging oxygens (NBOs).  $Q_n$  speciation in silicate glasses can be determined experimentally by  $^{29}\text{Si}$  MASNMR.

The question of chemical ordering and its effect on SRO is most simply addressed for the case of binary compositions of covalent systems, e.g.  $\text{A}_x\text{B}_{1-x}$ , where if elements A and B are in columns  $a$  and  $b$  of the Periodic Table, coordinations of  $8-a$  and  $8-b$ , respectively, will generally occur, thereby satisfying their normal valence and the so-called "8- $N$ " rule (strictly valid only for groups IV-VII). Neglecting the effect of coordination defects (e.g. dangling bonds), in general A-A, A-B and B-B bonds can coexist in a compound of arbitrary composition; two models can describe the distribution of such bond types (Lucovsky et al 1977).

In the *random covalent network* (RCN) model, the distribution of bond types is treated as being purely statistical, determined only by the local coordinations  $N_a=8-a$  and  $N_b=8-b$  and the concentration variable  $x$ . Any effects leading to preferential ordering (e.g. arising from differences in bond energies) are neglected. The RCN model admits *all* types of bonds, A-A, A-B and B-B, at all compositions (except at  $x=0,1$ ). In contrast, the chemically ordered network (CON) model assumes that heteropolar (A-B) bonds are favoured. A chemically ordered phase thus occurs at the stoichiometric composition  $x_c = N_a/(N_a + N_b)$ . Only A-A and A-B bonds are allowed for A-rich compositions ( $1 > x > x_c$ ), and, conversely, only B-B and A-B bonds for

$0 < \alpha < \alpha_c$ . The RCN and CON models are obviously most appropriate for covalent systems where coordination numbers are well defined as a result of the pronounced stereochemical bonding.

The above description of SRO in terms of well-defined coordination polyhedra is obviously inappropriate for those systems in which the bonding is nondirectional, e.g. metallic, van der Waals-bonded and ionic systems, in which the structure can be regarded simply as a random packing of spheres. In such cases, well-defined single types of coordination polyhedra do not exist and large site-to-site variations in the nearest-neighbour coordination number can occur. SRO in such systems can therefore only be characterized by statistical means in terms of suitable average quantities, e.g. the order parameter defined as (Sadoc and Wagner 1983):

$$\alpha = 1 - \frac{N_{12}}{x_2(x_2 N_1 + x_1 N_2)} \quad (4)$$

where  $N_i = \sum_{j=1}^2 N_{ij}$ . Negative values of  $\alpha$  indicate chemical ordering, i.e. the occurrence of unlike nearest neighbours. The average nearest-neighbour coordination of systems with centro-symmetric bonding is also much higher ( $N_{ij} \sim 12-13$ ) than that characteristic of covalent systems ( $N_{ij} \sim 2-4$ ). The nearest-neighbour coordination number of a particular atom in such densely packed amorphous solids can be found by construction of the Voronoi polyhedron (or Wigner-Seitz cell), which is the smallest convex polyhedron formed by planes which bisect perpendicularly the vectors from the origin atom to its nearest-neighbours: the number of faces of the Voronoi polyhedron gives the coordination number.

## 2.2 MEDIUM-RANGE ORDER

Medium-range order (MRO) is less easy to define (and to measure unambiguously) than SRO. Perhaps the clearest description is in terms of an hierarchical definition. MRO can be regarded as constituting the next higher level of structural organization beyond that of SRO, existing on a length scale of, say, 5-10 Å. Since SRO is defined by 2-body ( $r_i, N_{ij}$ ) and 3-body ( $\theta$ ) correlation functions, MRO can be associated with yet higher-order correlation functions (for the case of ionic-covalent network materials, where covalent bonds can be defined). It is convenient further to divide the types of MRO into three categories, corresponding to progressively increasing length scales.

### 2.2.1 Short-range MRO

If SRO can be defined in terms of well-defined local coordination polyhedra, short-range MRO is concerned with the type of connection of such polyhedra, as well as their relative orientation. Thus, corner-, edge- and

face-sharing of polyhedra lead to very different ordering schemes at a local scale, as well as to pronounced differences at larger distances in terms of network dimensionality (§2.2.3).

In an hierarchical sense, short-range MRO can be quantified in terms of a 4-body correlation function, involving the positions of atoms A, B, C, D, namely the dihedral angle,  $\phi$ , which is the angle of twist about a common bond (AB) between two coordination polyhedra, necessary to bring into coincidence the projections onto the plane normal to AB of two outlying bond vectors (e.g. AC, BD). In fact, it is disorder in the dihedral angle that destroys the translational periodicity characteristic of crystals. The distribution of dihedral angles,  $P(\phi)$ , for crystals consists of a single delta function (or a discrete set): e.g.  $\phi=60^\circ$  for all bonds in the diamond-cubic, tetrahedrally-coordinated structure (e.g. c-Si, Ge). It is this regularity in the relative positions of four connected atoms that generates the periodicity. A disordered structure in which there is a *random* distribution of dihedral angles connecting coordination polyhedra,  $P(\phi)=\text{constant}$ , the most disordered network structure envisageable, is known as the Zachariasen continuous random network (CRN). However, it is not clear whether such a true CRN would be dense at all length scales, as a result of ring formation, or whether it would form a Cayley tree (or Bethe lattice), a continuously branching structure, whose density decreases with distance from the core. In practice, actual structural models of covalent amorphous solids that agree well with experimental diffraction data, say, and hence presumably real amorphous materials, invariably have broad, but not flat, dihedral-angle distributions.

*Departures* from a uniform (i.e. random) distribution  $P(\phi)$  are correspondingly a hallmark of short-range MRO. Favoured values  $\phi$  are associated with features of MRO such as (small) rings.

### 2.2.2. *Intermediate-range MRO*

In an hierarchical description, intermediate-range MRO is determined by 5-body (and perhaps higher) atomic correlation functions, that is, correlations between values of dihedral angles defined for *adjacent* bonds. A common example of such a correlation is if the magnitude of the dihedral angle is constant, or has the same average value, for every bond, but the *sign* of  $\phi$  (i.e. the sense of angular rotation) is correlated between adjacent bonds. If the sign is everywhere the same, e.g. ++++..., then ring formation is favoured. If, on the other hand, the sign alternates, +-+..., chain formation is favoured instead. Thus, very different types of structural organization can result from different types of 5-body atomic correlation function. An example is Se. Crystalline polymorphs contain either rings or chains with  $\phi\sim 102^\circ$ ; a-Se can contain rings and chains (with alternate or random signs of  $\phi$  down the chain).

Correlations between successive dihedral angles can also lead to another aspect of intermediate-range MRO, namely superstructural units comprising several basic SRO coordination polyhedra connected together. Such superstructural units, e.g. rings or clusters of atoms of particular shapes or sizes, occur in a considerably higher proportion than would be expected on a purely statistical (random) basis. One example of a superstructural unit is the case of the boroxol ( $B_3O_3$ ) ring in vitreous  $B_2O_3$ , the symmetric breathing vibrational mode of which gives rise to an extremely intense, and narrow, peak in the Raman spectrum. Another example is the case of molecular clusters found in amorphous chalcogenides, e.g. the approximately spherical  $As_4Se_3$  and  $As_4Se_6$  molecules found particularly in thermally-evaporated amorphous thin films of  $As_4Se_3$  and  $AsSe$ , respectively. These again are revealed in Raman spectra as sharp molecular lines, rather than the broader featureless Raman bands characteristic of fully cross-linked network chalcogenide glasses, e.g.  $As_2Se_3$ .

### 2.2.3. Long-range MRO

On a yet larger length scale, say greater than  $10\text{\AA}$ , the structural organization characteristic of long-range MRO can be associated with the local dimensionality of a covalently bonded amorphous network, or perhaps the existence of domains in glassy metallic alloys.

Structural ordering associated with a local dimensionality different from three (spatial isotropy) can arise in a covalent network due to two causes: either the type of connection between coordination polyhedra may impose such a reduced dimensionality, or it may result from network depolymerization due to the introduction of network modifiers. In either case, the local topology of the network structure is traced out by a process of bond percolation along the strong covalent bonds, neglecting the weaker van der Waals or ionic bonds that serve to hold the structure together in the case of low-dimensional systems or network-modified materials, respectively. Thus, 0D (cluster-like), 1D (chain-like) and 2D (layer-like) local dimensionalities can be distinguished. Examples of all three types of long-range structural ordering are afforded by chalcogenide glasses. Thus, for example  $P_4Se_3$  (or  $As_4Se_3$ , etc.) is an example of a superstructural cluster unit forming a 0D structure; complete edge-sharing of  $SiSe_4$  tetrahedra in glassy  $SiSe_2$  generates infinite chains, i.e. a 1D structure; edge- and corner-sharing of  $GeSe_4$  tetrahedra in glassy  $GeSe_2$  leads to a locally 2D structure; in contrast, complete corner-sharing of  $SiO_4$  tetrahedra in glassy  $SiO_2$  yields a structurally-uniform 3D structure, i.e. one devoid of long-range medium-range ordering in the dimensional sense.

Network-modifying cations (e.g. alkalis) introduced non-randomly into a network-forming material (e.g.  $SiO_2$ ) can enter the structure in either a filamentary or a sheet-like fashion, thereby partitioning the unmodified (oxide) network and lowering its local dimensionality. Alternatively, attention can be focussed on the ionically bonded regions incorporating the

network-modifying cations and non-bridging anions, and the local dimensionality of such regions can be ascertained by tracing out the connected spatial profiles of such ionic species.

It has been assumed that structural ordering in amorphous materials at intermediate length scales is a consequence, in an hierarchical sense, of a well-defined SRO. In the case of amorphous materials in which non-directional bonding is predominant, e.g. metallic alloys, the constraints imposed by the stereochemical bonding characteristic of iono-covalent systems on the generation of SRO no longer apply, yet in certain cases (e.g. transition-metal metalloid (TMM) alloy glasses), a well-defined topological and chemical SRO exists (in the form of trigonal prismatic coordination of transition-metal atoms around metalloid atoms). In such cases, it may be that the SRO itself is a consequence of the existence of a certain type of well-defined MRO, i.e. the converse of the situation for covalent systems. An example of this in the crystalline state is the occurrence of tetrahedral and octahedral sites (holes) arising between ordered close-packed arrays of atoms. In the case of crystalline TMM alloys, the trigonal prismatic coordination around metalloid atoms can be regarded as arising from the existence of "chemical twinning" planes, containing metalloid atoms, within close-packed crystalline arrangements of the metal atoms. Dubois et al (1985) have proposed that similar considerations also apply to the structure of glassy TMM alloys, in which the long-range MRO is associated with domains of size 10-20Å, within each of which are more-or-less ordered arrays of chemical twinning planes, within which are located the trigonal prismatic SRO units.

### 2.3 EXTENDED-RANGE ORDER

It has been widely believed that there is no structural order in amorphous materials at a length scale say greater than 10Å from any given atom as origin. In other words, there should be no atomic-density fluctuations in this spatial range, and consequently the atomic-density correlation function,  $\rho(r)$ , or the RDF,  $J(r)$ , should be featureless after this distance. Indeed, RDFs obtained by Fourier transformation of experimentally obtained diffraction data, i.e. the structure factor  $S(Q)$ , generally do appear to be featureless relative to the noise level beyond say 10Å. However, recent improvements in computing power have meant that very large structural models of amorphous solids can now be constructed, containing several tens of thousands of atoms in box sizes of order 100Å on a side, meaning that the RDFs of such model structures can be calculated out to distances of say 50 Å or so. Two large-scale structural models, one of a-Si and one of a monatomic amorphous metal, have been analyzed and both reveal evidence for extended-range order (ERO), i.e. non-random density fluctuations extending to about 15 times the nearest-neighbour separation in both cases.

The pair distribution function for a 13824-atom model of a-Si reveals (Uhlherr and Elliott 1994) that pseudo-periodic density fluctuations persist to a distance of order 35 Å (cf. the nearest-neighbour bond length,  $r_1=2.38$  Å). The approximate period of these fluctuations is  $D\approx 3.4$  Å. This pseudo-period is the same as that between even-even or odd-odd peaks in the neighbour-specific pair-distribution function,  $g_n(r)$ . A projection of atoms in a slice of the model, coloured depending on whether they are odd or even neighbours, respectively, of an origin atom at the centre reveals a concentric circular pattern being a 2D cut through the spherical shell-like pattern of extended-range atomic-density fluctuations, with pseudo-period 3.4 Å, around any atom taken as origin. (The  $g(r)$  curve is a 1D cut through the spherical shells.) The origin of the ERO is believed to arise from the structural frustration encountered in constructing a fully dense amorphous network, with no unsatisfied (dangling) bonds, from highly (tetrahedrally) coordinated structural units. In order to maximise the local density, atomic packing similar to that of the highest density crystalline lattice planes, i.e. the {111} planes of the diamond-cubic structure, will tend to occur. On average, along any line connecting an origin atom and another atom, at a sufficiently large distance, say beyond 10 Å where MRO non-periodic density fluctuations have damped out, {111}-like atomic packing will be seen. The apex-to-basal plane distance in an  $\text{SiSi}_4$  tetrahedron (the {111} interplanar distance) is  $d_{111}=3.3$  Å, to which the pseudo-period  $D$  tends at large distances.

The occurrence of ERO in a-Si can also be understood in terms of propagated SRO. A three-body (conditional) probability function shows this behaviour. Consider an origin atom O and another atom  $i$  located at a fixed distance  $r_i$  ( $\pm dr_i$ ) from it. In this case, one would expect a positive contribution (peak) in the pair distribution function,  $g(r)$ , at  $r=r_i$ . The point at issue is, given two atoms at O and  $r_i$ , what is the probability of finding a third atom,  $j$ , which is a  $\Delta n^{\text{th}}$  neighbour of  $i$ , at a distance  $\delta$  from  $i$  along the vector connecting O and  $i$  on the far side of  $i$  from O? This probability,  $\rho_{\Delta n}(\delta)$ , has been calculated (for  $r_i=14\text{Å}$ ) (Uhlherr and Elliott 1994). The highest, narrowest peak is for  $\Delta n=2$  lying at  $\delta=3.4\text{Å}$ . Thus any peak (or trough) in  $g(r)$  will be propagated with a pseudo-period of  $D\sim 3.4\text{Å}$ . The fact that the dominant contribution to  $\rho_{\Delta n}(\delta)$  is for  $\Delta n=2$  accounts for the fact that the pseudo-period of the density fluctuations observed in  $g(r)$  correspond to the separation of every other peak in the neighbour-specific distribution,  $g_n(r)$ .

Similar ERO behaviour has been found in a very different noncrystalline system, a monatomic random packing of equally-sized spherical atoms interacting via an interatomic potential which favours icosahedral local packing (Dzugutov (1992)). This structural model, containing 16,000 atoms, is contained within a cubic box of 50 reduced units (r.u.) on a side; the average nearest-neighbour distance is 1.15 r.u.. The pair distribution

function,  $g(r)$ , appears to become random at a distance of  $\sim 17$  r.u.. This ERO behaviour has been confirmed by a wavelet analysis (Harrop et al 2000) using a 1D version of the Gabor wavelet,  $\psi(r) = C \sin(\pi r) \exp(-r^2/2)$  as the mother wavelet. Details of the analysis are given elsewhere (Harrop et al 2000), but the results show that the extent of ERO oscillations is indeed  $\sim 17$  r.u., and that the magnitude of the wavelet components (that is the amplitude of the ERO oscillations) decreases exponentially with distance in this spatial range. The same exponential decay is also found for the same system in the *liquid* state, except that the spatial decay rate for it is more rapid and hence the range of ERO oscillations, before the onset of noise, is curtailed.

It is of interest to examine the behaviour of the spatial extent of the magnitude of the wavelet components for two related *crystalline* structures, namely the body-centred cubic (bcc) structure and the  $\sigma$ -phase, a Frank-Kaspar structure, containing a large unit cell (4 r.u. in the largest dimension) which consists of a tetrahedral packing with local icosahedral order. Both crystals, of course, exhibit long-range order in that the magnitude of the wavelet components does not decay at large distances. However, the  $\sigma$ -phase, with an appreciably disordered large unit cell, *does* exhibit a spatial decay of the magnitude for distances up to  $\sim 8$  r.u. (i.e. two unit cells). Furthermore, it is perhaps significant that the spatial decay rate appears to be the same for the  $\sigma$ -phase and the (solid) amorphous phase.

Finally, the period of the ERO oscillations for the glassy model, taken either directly from the  $g(r)$  function or obtained from the wavelet analysis, namely  $D=0.934$  r.u., is the same as the modal average (i.e. peak-maximum position) of the distribution of apex-basal heights of local tetrahedra in the structure, i.e.  $R_{\max}=0.935$  r.u.. This distribution is appreciably broader than, but is centred around the same average apex-basal distance of, the distribution in the case of the  $\sigma$ -phase. Thus, the ERO in this dense-packed amorphous system is also associated with packing constraints, in this case also of tetrahedra.

### 3. Conclusions

Structural order in glasses can be defined, in an hierarchical sense, at increasing length scales in terms of ever-increasing n-body correlation functions. Short-range order is associated with the first coordination shell (i.e. 2- and 3- body correlation functions, viz. bond-length and angle distributions, respectively). Medium-range order at the shortest length scale is associated with 4-body correlation functions (i.e. dihedral-angle distributions), and at the next largest scale with correlations between adjacent dihedral angles. We have also found pseudo-periodic atomic-density fluctuations (extended-range order) in large models of a-Si and a



monatomic metallic system with pronounced local icosahedral ordering. This ERO is due to structural frustrations associated with packing constraints, in this case of tetrahedral units.

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