

Eighty years of random networks

Past & Present

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The 80 years since Zachariasen's famous paper, 20 years before Stephen Elliott was born, on the random network theory of glass structure have seen remarkable progress in our understanding of the structure of glassy materials through the construction of models and comparison with experiment. In the early days, models were hand-built with plastic units and had free boundary

conditions. Today, very much larger computer models have periodic boundary conditions. We recount the progress that has been made in the last 80 years, and discuss the current agreement between models and experiments that remains imperfect. Stephen Elliott's work on medium range order forms an important part of the history of this subject.

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1 Introduction The year 2012 marks the 80th anniversary of the publication of the most famous paper in glass science, viz. *The Atomic Arrangement in Glass* by Zachariasen [1]. Zachariasen's paper is always quoted as the origin of the random network theory of glass structure; an example of which is shown in Fig. 1, although the concept of a disordered array of atoms linked by directional bonding had been introduced 5 years earlier (but not referenced by Zachariasen) in a now long-forgotten paper by Rosenhain [2], and the term *random network hypothesis* was only introduced a year later by Warren [3] – but such are the vicissitudes of history.

The main reason for Zachariasen's lasting fame is his two-dimensional schematic diagram of an A_2O_3 vitreous network, which has been reproduced in countless papers and textbooks throughout the intervening years. His original figure is instantly recognisable, since two oxygen atoms on the right-hand side were chopped off by the publisher, although these have been restored and colour added (blue for the A atoms and red for the O atoms) in the version shown here in Fig. 2. We should note that such a two-dimensional network has never been synthesised and there are good chemical reasons why it may never be, although some clever chemist in the future will perhaps manage it. This however detracts nothing from the importance of Zachariasen's paper that included his rules for glass formation, which are topological in nature and specify the requirements for a

random network to be relatively strain free. Thus the AO_3 structural units in Zachariasen's figure are regular equilateral triangles, and it is amusing to note that, as (poor) copies of his figure have passed down through generations of textbooks, the AO_3 triangles have become more and more distorted and hence further from reality. A particularly bad example is afforded by a well-known solid-state physics textbook that was popular during the authors' student days, but it is left as a challenge to readers to identify it.

Much of the background and history of glass structure and science is covered in the very influential 1984 book by Stephen Elliott *Physics of Amorphous Materials* [5]. The original much-used book remains something often given to new graduate students to introduce them to the field.

Before proceeding, it will be helpful to establish exactly what is meant by a *random network*; i.e., whether there is anything about it that is indeed completely random. For example, the idealised structure of vitreous silica comprises a continuous (no defects in the form of broken bonds) network of corner-sharing SiO_4 tetrahedra, which maintains the local chemical bonding requirements of the atomic elements everywhere, but with small local distortions achieves a non-crystalline network topology. This random network is not periodic, and hence has no long range order and associated Bragg peaks in the diffraction pattern. The distortions mainly involve departures for the oxygen bond angle, β (see figure), from its equilibrium value. In a later

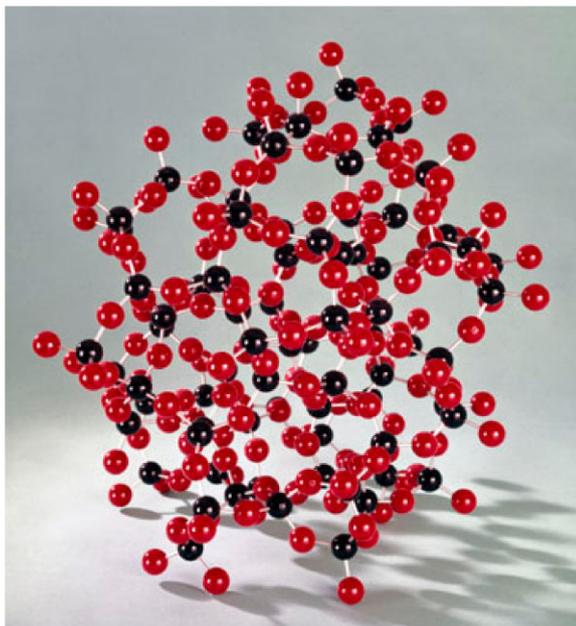


Figure 1 (online colour at: www.pss-b.com) Part of Bell and Dean's 1972 model of vitreous silica [4]. (Courtesy of the Science Museum, London.)

paper, Mozzi and Warren [6] assumed that the distribution of bond torsion angles, α_1 and α_2 , as defined in Fig. 3, is completely random. However, this neglects the requirements imposed by ring closure and steric hindrance and perhaps in hindsight a more neutral term like amorphous network would have been preferable to continuous random network.

The random network theory has been supported in the West by many X-ray and neutron diffraction studies, although for many years Russian scientists preferred the (*modern nano-*) *crystallite theory*, and this argument still breaks out, most recently in 2010 by Gibson, Treacy and

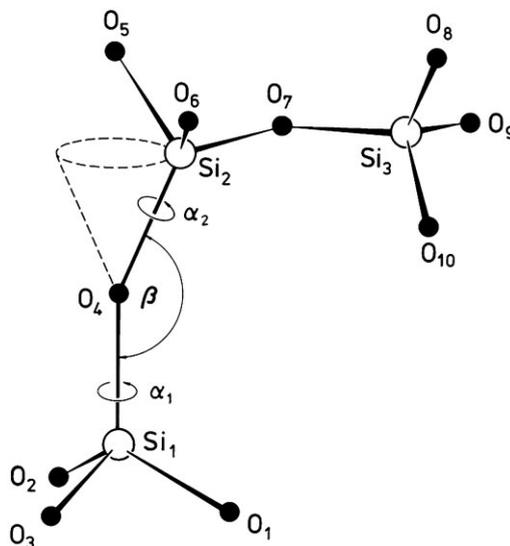


Figure 3 Definition of the oxygen bond angle, β , and the torsion angles, α_1 and α_2 , for corner-linked SiO_4 tetrahedra.

coworkers [7] using fluctuation electron microscopy results – however most scientists today accept the random network model as being the basis for understanding single-component glassy structures – indeed the words glass and random network have almost become synonymous to the glass structure community. It was not until the 1960s that the question began to be asked as to whether it is indeed possible to generate a three-dimensional arrangement of atoms that is simultaneously consistent both with the random network theory *and* diffraction data.

2 Table top models These early ideas led to the advent of structural modelling: the most famous early model being that constructed for vitreous silica by Bell and Dean [4] in 1966, shown in Fig. 1, which was specifically constructed

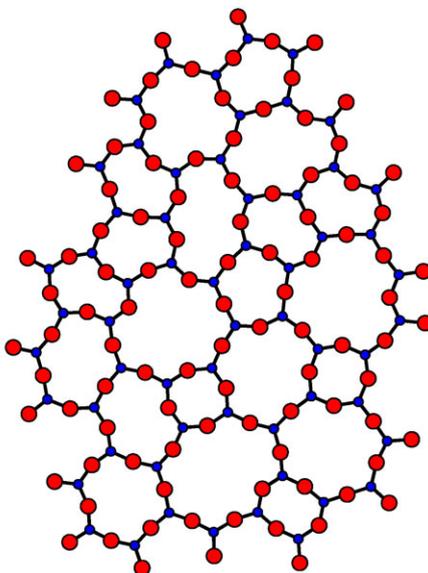


Figure 2 (online colour at: www.pss-b.com) Frederick William Holder Zachariasen (1906–1979) with his two-dimensional schematic diagram with added colour [1].

to validate the random network theory and marked the beginning of the modern era of modelling of glass at the atomic level. Bell and Dean's model has been used by many other authors, mainly because a later paper [4] includes a complete list of their atomic co-ordinates. It is salutary to note that a much larger contemporary model by Evans and King [8] received very little attention because these authors always refused to publish their co-ordinates, which are now lost forever. Indeed as scientists, particularly when supported by public funding, there is responsibility to save model coordinates so they are available to all, although this still often does not happen. Perhaps materials scientists can learn from biophysicists here, where most journals insist that the atomic coordinates of published protein structures are deposited with the protein data bank and so are available to all.

Bell and Dean's original model was constructed by hand, using polystyrene balls for the atoms and wire for the bonds, although a much more elegant version was later constructed by *Crystal Structures* from Bell and Dean's co-ordinates, and it is part of this latter model that is illustrated at the head of this paper. Building an atomistic model by hand gives a 'feel' for the structure that it is difficult to obtain in any other way and may lead to the conclusion that a postulated structure is sterically possible, even if no quantitative information is ever extracted from the finished model. The disadvantage of hand building is that the construction and quantitative measurement of large models is extremely tedious and it is difficult to control the distribution of the various structural parameters during construction in a systematic way. The introduction of computer relaxation techniques (molecular mechanics), however, reduced the accuracy with which it is necessary to measure the atomic co-ordinates and also removed any anisotropy that might result from the effects of gravity on a large model. Computer modelling fixes the topology and subsequent geometrical adjustments find a local minimum in the potential energy. Thus the region of configuration space available to the network of a glass such as vitreous silica is restricted by the energy and steric factors that limit the distortion of the basic structural units and the allowed distribution of bond and bond torsion angles. It is such factors that determine the extent of the intermediate-range order for a random network – the more restricted these degrees of freedom, the greater the distance from any given origin atom before the atomic correlations can be considered truly uncorrelated or random.

The Bell and Dean model clearly demonstrated that it was indeed possible to construct a three-dimensional structure consistent with the tenets of the random network theory, but the question remained as to whether such a structure could also accurately predict the radial distribution function obtained from X-ray diffraction measurements. Initially, the comparison of structural models with diffraction data was at a very superficial level, and did not include the broadening arising from the atomic thermal vibrations and the experimental real-space resolution. This is illustrated in Fig. 4, which shows the interatomic distances from the

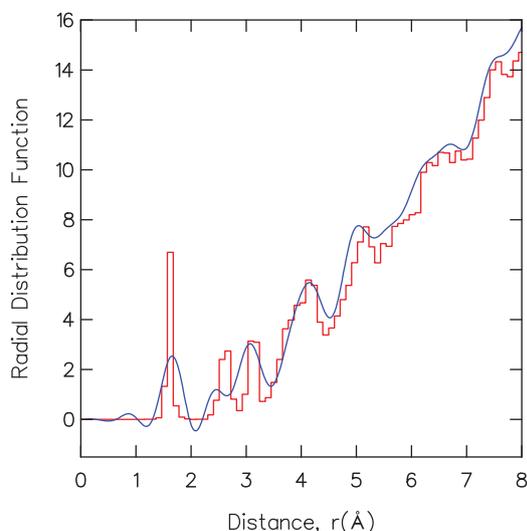


Figure 4 (online colour at: www.pss-b.com) A comparison of the relaxed [9] Bell and Dean [4] model (1980) for vitreous silica (red histogram) with X-ray data (blue curve). The histogram does not include thermal broadening, nor the experimental broadening in real space, whilst the X-ray data of Mozzi and Warren [6] have been Fourier transformed to simulate the earlier (1936) Radial Distribution Function of Warren et al. [10].

model as a histogram and the X-ray radial distribution function obtained from the slightly later X-ray data of Mozzi and Warren [6] published in 1969.

Although the random network theory was developed for glasses quenched from a thermodynamically metastable super-cooled melt, it was later proposed as a model for other amorphous network solids that were developed during the second half of the 20th century, even though their preparation involved processes that are much further from thermodynamic equilibrium. As a result, the structures of such materials involve increased strain, which can lead to significant numbers of broken bonds, and it was less obvious that a random network model was appropriate.

The amorphous network solids that have received most attention are amorphous silicon and germanium, and again the question arose as to whether it was possible to generate a three-dimensional random network structure for these materials. Note that, with the oxygen atoms removed between neighbouring silicon atoms, the link between them is defined by a single torsion angle and so the number of degrees of freedom is very much reduced relative to vitreous silica. Indeed each atom has three translational degrees of freedom, but they are four *shared* bonds for each atom with the associated five independent angular degrees of freedom making seven constraints – far more than the number of degrees of freedom. Something has to give and this turns out to be the weaker angular constraints, where the strain is carried via an angular distribution of $109^\circ \pm 10^\circ$. That such a (random) network structure could be constructed for amorphous silicon, with no broken bonds, was first demonstrated by Polk [11] in 1971, from units such as those

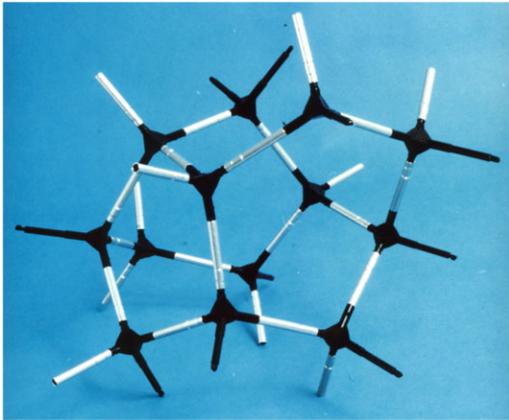


Figure 5 (online colour at: www.pss-b.com) Plastic tetrahedral units and aluminium sleeves used in the construction of the Polk model (1971) of amorphous Si or Ge [11].

shown in Fig. 5. However, Polk's model beautifully illustrates the necessity of using appropriate units that reflect experimental parameters such as bond length and angle distributions – unlike cheaper drinking straws; the rigid aluminium sleeves used for the bonds restricted the flexibility in the silicon bond angle and hence the bond angle distribution for Polk's model was actually much too narrow!

As an amusing anecdote, a random network model was built by Connell [12] in 1974 in his hospital bed as he recovered from a broken leg, and this model has only even membered rings of atoms, to simulate III–V amorphous semiconductors, such as GaAs. This surprising achievement shows the wide diversity of models that come under the general heading of random network models. All hand built models of glasses have a diameter of just under a meter – this of course is so that the builder can move the model through the doorway to impress his or her colleagues down the corridor, etc. Hand-built models of biological macromolecules, which very much parallel random network models in time [1950–1990] also stayed within the rough one meter diameter limit; the most famous of course being the Watson–Crick model of DNA [13].

3 Computer modelling Computer-generated models have now replaced hand-built models, overcoming both the tedium and any unintentional bias associated with hand-built models. The increase in computer power and techniques, such as classical molecular dynamics, have led to much larger models that are better able to predict the various distributions of structural parameters with sufficient statistical accuracy. An early computer model of amorphous silicon and germanium (*'sillium'*) was generated in 1987 by Wooten and Weaire [14], using a bond-switching algorithm together with energy minimisation (relaxation). Crystalline silicon has only 6-membered shortest-path rings of atoms and, by changing the local connectivity to incorporate 5-, 7- and a few higher-fold rings, the network structure can be

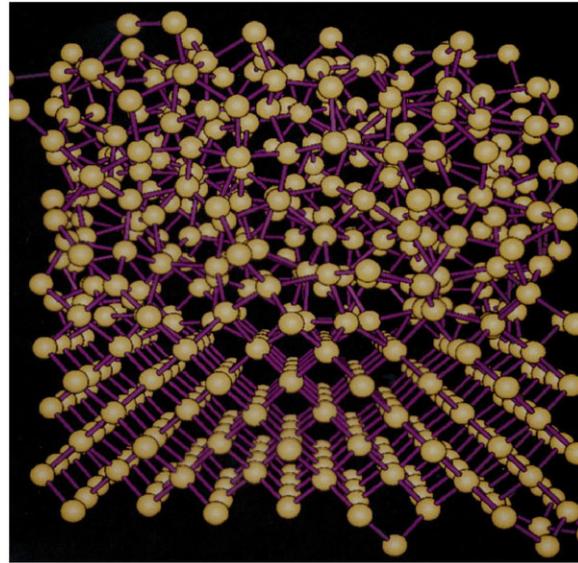


Figure 6 (online colour at: www.pss-b.com) Wooten and Weaire's 1987 model showing an epitaxial amorphous layer (top) attached to crystalline silicon (bottom) [14].

disordered, as shown in Fig. 6, where the upper part of the sample has been *'amorphised'* and remains epitaxially attached to the crystal below.

This kind of computer modelling has been further extended in recent years and very much larger models with a periodic boundary have been constructed by Barkema and Mousseau [15], and also by Vashishta and coworkers [16]. The structure factor for the Barkema and Mousseau [15] model is shown in Fig. 7, together with the X-ray data of Moss and coworkers [17] for as-implanted and annealed amorphous silicon.

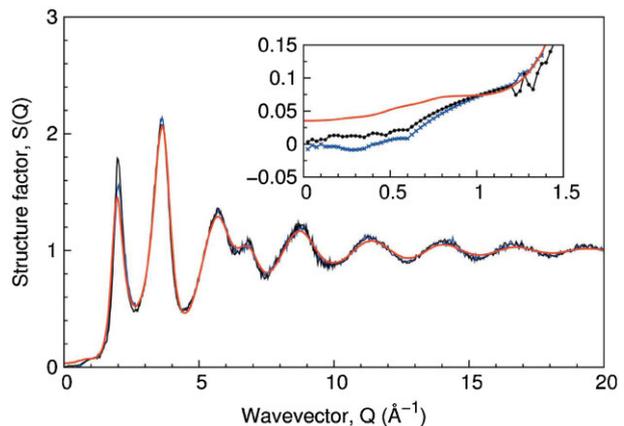


Figure 7 (online colour at: www.pss-b.com) Comparison of the 100 000-atom computer model of Barkema and coworkers [15] from 2001 (red) compared with the X-ray structure factor for amorphous Si, as determined by Simon Moss and coworkers [17] in 1999 [(as implanted (blue) and annealed (black))]. Insert shows blow up of region around the origin [18].

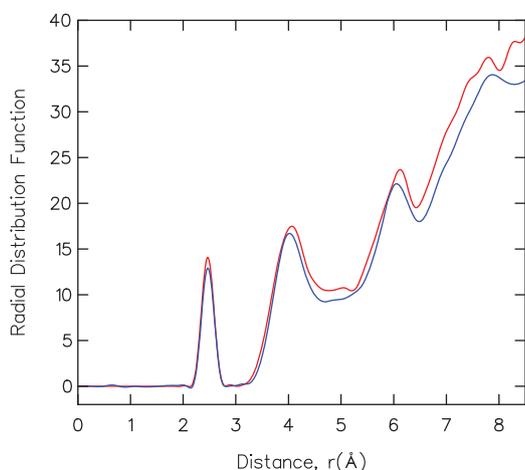


Figure 8 (online colour at: www.pss-b.com) A comparison of the thermally- and resolution-broadened Radial Distribution Function for the Wooten and Weaire 'Sillium' model [14] (red) with neutron diffraction data for amorphous germanium (blue) [19].

The real space correlation function for one of Wooten and Weaire's models is compared with that obtained from neutron diffraction data for evaporated amorphous germanium by George Etherington and collaborators (1982) [19] in Fig. 8. The agreement with experiment is significantly improved over that for the 1971 Polk model, especially in respect of the width of the second peak that reflects the bond angle distribution around the mean tetrahedral angle of 109° . Annealing the sample is thought to relieve strain and minimise the number of broken bonds, and so should be closer to computer models. The medium range order shown as oscillations going out to 8 Å in Fig. 8, actually extends two or three times further out and is known as medium range order; an important distinguishing feature of glasses when compared to liquids, and as stressed by Stephen Elliott [20].

4 The future Whilst the continuous random network model has been widely used and accepted as the basis for the structure of glasses and amorphous materials, it must be used with caution. Just as a crystal with no defects is an idealisation, so is an amorphous network with no broken bonds. However, with carefully prepared samples, this limit can be more and more closely approached for both vitreous silica and amorphous silicon. We say this notwithstanding that the ghosts of the crystallite model of Leningrad from the early twentieth century re-appear occasionally. Indeed there is a wide and rich variety of disordered materials, some of which certainly do consist of nanocrystals of various sizes embedded in an amorphous matrix, but we view these as mixed phase materials. On the other hand, there is no definitive experimental evidence for order in single-component network glasses in excess of that predicted by the random network hypothesis [21]. There is a beauty in the atomic continuous random networks that is irresistible and hard to deny – identical local units strung together to form a disordered whole so that, despite almost perfect local order,

there is no long range order and no Bragg peaks seen in diffraction experiments.

Whilst it is clear that the present computer models of vitreous silica are in very much better agreement with experiment than the original (relaxed) table-top models, the discrepancies between model and experiment are still outside the experimental uncertainty, especially with respect to the spatial extent of the ordering around any given atom. Hence, it is necessary to question whether the algorithms employed to generate these models are capable of yielding such a network, even with an improved inter-atomic potential.

This raises an interesting philosophical question. Supposing an extremely large model (say 1 000 000 atoms) could be generated, which was in perfect agreement with all of the experimental data within their given uncertainties. Even in this case, it would still be only *one* of a potentially *infinite* number of possible atomic arrangements, and there is no way of telling whether it is indeed the '*correct*' structure. A much more important question, however, is how could it be established whether the model actually comprises a random network as defined above? Obviously, it would be possible to check the distributions of bond and torsion angles, but what about the network topology? Thus it may be concluded that, even though an ideal Warren–Zachariasen random network is easy to define theoretically, it is still unclear as to how best such networks can be generated in practice, and similarly it remains unknown as to how closely this first-order model approaches the structure of real network glasses.

After 80 years, experiments and theory do not yet agree as well as one would like. This is probably due to the difficulty of exploring all the possible distributions of rings of bonds and correlations between adjacent rings of bonds, etc. Indeed our inability to get compelling direct experimental information about rings remains a continuing road block. This may be finally solved by going back to a two-dimensional glass like amorphous graphene [22], where the rings can be imaged directly, in a way not possible for three-dimensional networks. This has been recently accomplished in some remarkable experiments for a bilayer of vitreous silica using TEM imaging [23, 24]. When this happens, Zachariasen's famous sketch of a glassy network will finally be fully demonstrated (although without the oxygen atoms) with a full two-dimensional atomic network topology, including medium range order, visible to all.

Acknowledgements As well as acknowledging the contributions of Stephen Elliott on his sixtieth birthday, we should also like to dedicate this article to the late Frank Galeener, who spent much of his scientific life investigating the properties of vitreous silica and other network glasses.

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