

## COMPARISON OF RADIAL DISTRIBUTION FUNCTION FOR SILICA GLASS WITH THOSE FOR VARIOUS BONDING TOPOLOGIES: USE OF CORRELATION FUNCTION

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Radial distribution functions (RDF's) calculated from the bonding topologies of quartz, cristobalite, tridymite and a 1412 atom model of silica glass (35 Å in diameter) have been compared with the experimental RDF for silica glass. The functions,  $4\pi r^3(\rho(r) - \rho_0)$ , computed over the range  $0 < r < 20$  Å from the known structures of quartz, cristobalite, tridymite and the 1412 atom model have been compared with the corresponding function for silica glass by means of correlation functions, giving 0.26, 0.69, 0.82 and 0.91, respectively (0.00 would indicate no correlation, and 1.00, perfect positive correlation). Cristobalite and tridymite are composed entirely of six-membered rings of silicate tetrahedra, whereas the model contains both six- and five-membered rings in a ratio of 2.6:1. The correlation coefficients suggest that the six-membered rings of the type present in tridymite play a dominant role in silica glass, but that other ring sizes are important and result in the higher correlation coefficient for the 1412 atom model. While the correspondence in RDF's is encouraging, the model RDF does not fit the experimental curve to within the accuracy of the experiment. Perhaps the model is not large enough to represent adequately, in a statistical fashion, all the configurations present in a macroscopic sample.

### 1. Introduction

Diffraction data obtained from glasses may be analyzed by the use of the Fourier transform to determine the distribution of interatomic distances in the sample. Because such a radial distribution function (RDF) is composed of the superposition of interatomic distances that arise from the many configurations and orientations contained in a large sample volume, it does not normally provide the basis for a unique determination of the atomic coordinates of an amorphous material. The RDF is, however, an important criterion by which one may judge the validity of any proposed model. A proper model must agree with all of the features of the experimental RDF to within acceptable limits of error. The greater the range over which the RDF is reliable, the more restrictive is the test that it provides for a proposed model.

It has been shown that structurally significant features can be observed in the RDF for silica glass out to about 20 Å [1]. These features become evident when special precautions are taken to reduce the errors introduced into the

analysis by series termination effects, errors in the measurement of the experimental data, and errors that derive from incorrect treatment of the background intensity [1,2]. It could be expected that the additional detail in the RDF out to 20 Å would provide a stringent test for proposed atomic models for silica glass, and that this would result in a more restrictive characterization of the predominant bonding topologies in this glass. It has been shown [3] that the long-range detail in the RDF for silica glass is similar to that associated with assemblages of six-membered rings of silicate tetrahedra such as those present in tridymite and, to a lesser extent, those present in cristobalite.

In this paper RDF's are also calculated from the bonding topologies of quartz and a 1412 atom model and are compared with the silica glass RDF. Comparison between experimental and calculated RDF's are quantified by means of a correlation function. The manner by which RDF's were calculated from the atomic parameters of quartz [4], cristobalite [5], and tridymite [6] will be detailed below.

The 1412 atom model was constructed from the 519 atom model of Duffy et al. for amorphous silicon [7]. To accomplish this, the silicon atom framework was expanded, oxygen atoms were inserted midway between the silicon atoms, and the model was relaxed [8] in order that the shortest Si-O, O-O and Si-Si distances could assume nearly "ideal values". The 1785 Si-O distances in the relaxed model range from 1.596 Å to 1.619 Å with a mean value of 1.608 Å and rms deviation from the mean of 0.003 Å; the 2361 O-O distances range from 2.416 Å to 2.759 Å with a mean of 2.626 Å and rms deviation of 0.030 Å; the 893 Si-Si distances range from 2.981 Å to 3.207 Å with a mean of 3.112 Å and rms deviation of 0.045 Å. The rms deviations for these three classes of distances are nearly the same as the values of 0.003 Å for Si-O, 0.026 Å for O-O and 0.035 Å for Si-Si observed for the crystalline polymorph tridymite [6]. In the 1412 atom model, however, there are nine O-O distances that are greater than  $4\sigma$  from the mean. There are no such Si-O or Si-Si distances. This indicates a shortcoming of the model in these regions. The oxygen atoms involved in these extreme distances are trapped in rather high energy wells. These nine distances constitute only 0.004 of the total number of such distances in the model and their contribution to the RDF is not significant. The techniques available for the construction of models of amorphous solids has been discussed recently in the literature [9].

When the features in an RDF from a crystalline material or a model fragment closely resemble the RDF for an amorphous material, it is quite likely that this function represents something of significance concerning the atomic ordering in the amorphous material. However, even if a model were to succeed in fitting the experimental data to within the experimental uncertainties, it would still remain to be demonstrated that the model is either unique or the correct one among several.

The methods by which the RDF's are calculated will be briefly described and then the computed RDF's will be compared with the experimental RDF for silica glass by means of the correlation function as a measure of the goodness of agreement.

## 2. Computations

The calculations of the RDF's from known bonding topologies were made with a computer program developed in this laboratory [10]. It permits computation of the RDF's with atomic coordinates from either a crystalline material or a nonperiodic atomic model by evaluating the following expression:

$$4\pi r^2 \rho(r) = (2\pi)^{-1/2} \sum_{i=1}^n \sum_{j=1}^m w_i w_j \frac{\bar{f}_i \bar{f}_j}{\sigma_{ij}} \exp\left[-(r - r_{ij})^2 / 2\sigma_{ij}^2\right], \quad (1)$$

where  $4\pi r^2 \rho(r)$  is the probability, weighted by the scattering power of the atomic pair  $ij$ ,  $\bar{f}_i \bar{f}_j$ , of finding atoms  $j$  at a distance  $r_{ij}$  from atoms  $i$ . The crystallographic site occupancy of atom  $i$  is  $w_i$ , and  $\bar{f}_i = Z_i / (\sum_{j=1}^k Z_j^2)^{1/2}$  is the reduced scattering factor for atom  $i$  where  $Z_i$  is the atomic number of atom  $i$  and  $k$  is the number of atoms in the unit of composition. Both the rms thermal displacement along  $r_{ij}$  and positional disorder are included in  $\sigma_{ij}$ . The first sum in eq. (1) is carried out over the  $n$  atoms in the asymmetric unit for a crystalline material. For a finite model, all of the atoms in the particle are included in this sum. The second sum is carried out over the  $m$  atoms in the structure that are separated from an atom in the asymmetric unit by less than the maximum distance selected for the calculation. For crystalline materials, space group symmetry transformations and unit cell translations are utilized to generate the atomic positions used in the second sum of eq. (1).

The average value about which  $\rho(r)$  oscillates is given by

$$\rho_0 = \rho'_0 \sum_{i=1}^n (w_i \bar{f}_i)^2, \quad (2)$$

where  $\rho'_0$  is the number of asymmetric units per  $\text{\AA}^3$  and  $n$  is the number of atoms in the unit of composition. For a model containing a sufficiently large number of atoms, achieved, for example, with crystalline materials by including a sufficient number of unit cells,  $\rho(r)$  will approach the constant value  $\rho_0$  at large  $r$ .

For a finite model,  $\rho(r)$  does not approach a limiting value of  $\rho_0$ , but instead falls to zero at the diameter of the particle.

In the approximation that the model fragment is spherical, a correction for the finite size of the model may be made by dividing  $\rho(r)$  by the RDF for a uniform sphere of diameter  $D$ , where  $D$  is also the diameter of the model fragment. The RDF for a uniform sphere of diameter  $D$  is designated by  $\epsilon(r, D)$  and is defined as [11]

$$\epsilon(r, D) = 1 - \frac{3}{2}(r/D) + \frac{1}{2}(r/D)^3, \quad r \leq D. \quad (3)$$

The RDF for the model fragment that has been "sharpened" by this factor to approximate the RDF for an infinite sample may be expressed as

$$\rho(r, \infty) = \rho(r) / \epsilon(r, D). \quad (4)$$

For simplicity,  $\rho(r, \infty)$  will be used in the following discussion to represent

either the RDF for a crystalline material or a sharpened RDF for a non-crystalline model. In this usage,  $\epsilon(r, D)$  in eq. (4) may be taken as unity for a crystalline material.

It has been observed that a crystalline phase or a non-crystalline atomic model can often be found that possesses features in its corresponding  $\rho(r, \infty)$  that are similar in position and shape to, but greater in magnitude at large  $r$  than the corresponding features in the RDF for an amorphous material of interest. For the case where the comparison is based on a crystalline material, this amplitude disparity occurs because the longer interatomic distances in a crystalline phase are much more highly ordered than they are in an amorphous phase. The amplitudes of the oscillations at large  $r$  for the  $\rho(r, \infty)$  from a model fragment may arise as a consequence of not only greater order in the model than in the amorphous material, but also the somewhat excessive amplification of the few interatomic distances at large  $r$  by the division by  $\epsilon(r, D)$ . An atomic model large enough to adequately represent all of the large interatomic distances in an amorphous material has not been constructed. The 1412 atom model for silica glass discussed in this paper has a diameter of only 35 Å, whereas a more suitable model would have a diameter of several hundred Å and contain  $10^5$  or more atoms.

In the absence of a sufficiently large atomic model, a smaller model or a crystalline bonding topology may be employed in the attempt to find an appropriate model. A simple method that has been found useful for accomplishing this is to modify  $\rho(r, \infty)$  by various  $\epsilon(r, t)$  that represent different sphere sizes or correlation lengths. If  $P(t)$  represents the probability of occurrence of an ordered region with diameter  $t$ , then the pair correlation function,  $G(r)$ , for a distribution of  $t$  may be written

$$G(r) = 4\pi r [\rho(r, \infty) - \rho_0] \int_0^\infty P(t) \epsilon(r, t) dt. \quad (5)$$

$P(t)$  may be expressed conveniently as a sum of  $n$  Gaussian distributions:

$$P(t) = \sum_{i=1}^n \frac{w_i}{(2\pi)^{1/2} \sigma_i} \exp\left[-(t - t_i)^2 / 2\sigma_i^2\right], \quad (6)$$

where  $t_i$  is the mean value of the  $i$ th Gaussian,  $\sigma_i$  is the corresponding width parameter, and  $w_i$  is the weight associated with the  $i$ th distribution.

The multiplication of  $(\rho(r, \infty) - \rho_0)$  by various  $\epsilon(r, t)$  to approximate a  $G(r)$  function for an infinite material assumes that the contribution from the  $[1 - \epsilon(r, t)]$  distances removed from  $\rho(r, \infty)$  introduces into  $G(r)$  a smooth term equal to  $\rho_0[1 - \epsilon(r, t)]$ . Such an approximation may be reasonable at large  $r$ , but is not valid for small  $r$ . The most obvious shortcoming is in the region with  $r$  less than the bonded peak where  $G(r)/4\pi r$  would be  $-\rho_0\epsilon(r, t)$  rather than the correct  $-\rho_0$  value. Since  $\epsilon(r, t)$  are very nearly one at small  $r$  for the  $G(r)$  functions reported in this paper, this shortcoming does not have a noticeable effect. A more rigorous treatment might be based on an equation

analogous to eq. (1) which would contain an elaborate set of disorder parameters more complicated than those characterized by the Gaussian distributions.

### 3. Results and discussion

Eqs. (1, 4, 5, 6) were used to calculate the theoretical  $r^2G(r)$  curves that are illustrated in fig. 1. In these calculations the value of the  $\sigma_{ij}$  for eq. (1) ranged from 0.05 Å at  $r = 1.6$  Å to 0.35 Å at  $r = 20$  Å and was taken to be a function of  $r$  only. For the evaluation of eq. (6), two values of  $t_i$  were employed with  $w_i = 0.7$  for  $t_i = 6.5$  Å and  $w_i = 0.3$  for  $t_i = 12$  Å. The  $\sigma_i$  in eq. (6) were set equal to one. For the nonperiodic model, a diameter of  $D = 35$  Å was found appropriate for computing  $\epsilon(r, D)$  in order to correct for the finite size of the atomic model.

Fig. 1 also illustrates the experimental  $r^2G(r)$  curve for silica glass. The  $r^2G(r)$  functions may be compared by calculating a correlation function [12],  $F(\text{calc}, \text{exp})$  between the calculated and the experimental curves:

$$F(\text{calc}, \text{exp}) = \frac{\int [rG(r)]_{\text{calc}} [rG(r)]_{\text{exp}} dr}{\left( \int [rG(r)]_{\text{calc}}^2 dr \int [rG(r)]_{\text{exp}}^2 dr \right)^{1/2}} \quad (7)$$

This correlation function may range in value from 1.0 to  $-1.0$ . A value of 1.0 corresponds to perfect positive correlation, whereas a value of zero corresponds to no correlation. Table 1 lists the  $F(\text{calc}, \text{exp})$  values that relate the

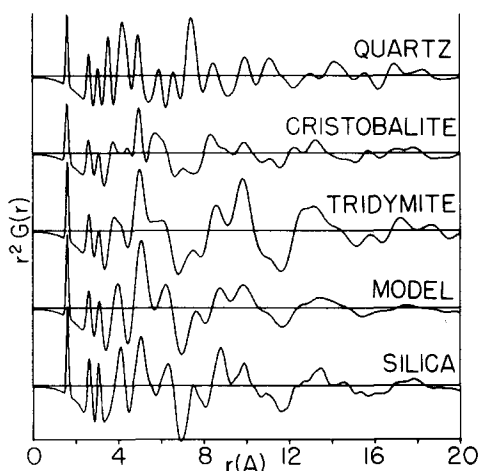


Fig. 1. The experimental RDF curve obtained for silica glass and the corresponding curves calculated from the atomic coordinates of a 1412 atom model and the crystal structures of tridymite, cristobalite and quartz. In order that the small details in  $G(r)$  eq. 5 at large  $r$  be evident on the same plot as the much larger details at small  $r$ , the function  $r^2G(r)$  is illustrated.

Table 1

Correlation coefficients comparing the silica glass radial distribution function with those for various bonding topologies defined in the text.

Range (Å)	1412 atom model	Trid.	Crist.	Quartz
0–20	0.91	0.82	0.69	0.26
0–10	0.91	0.83	0.68	0.28
10–20	0.87	0.90	0.76	0.10
0– 2	1.00	1.00	0.97	1.00
2– 4	0.95	0.89	0.87	0.46
4– 6	0.90	0.83	0.53	0.44
6– 8	0.96	0.83	0.65	–0.17
8–10	0.90	0.75	0.49	0.00
10–12	0.92	0.96	0.92	–0.32
12–14	0.80	0.86	0.82	0.31
14–16	0.86	0.69	–0.01	0.33
16–18	0.86	0.84	0.85	0.76
18–20	0.75	0.40	0.70	0.72

upper three curves in fig. 1 with the curve for silica glass. The correlation values calculated for the range  $0 < r < 20$  Å that compare the  $r^2G(r)$  functions computed from quartz, cristobalite, tridymite and the 1412 atom model with the corresponding function for silica glass are 0.26, 0.69, 0.82 and 0.91, respectively. Correlation functions are also presented for smaller ranges of interatomic distances.

Cristobalite and tridymite are composed entirely of six-membered rings of silicate tetrahedra. The 1412 atom model contains both six- and five-membered rings in a ratio of 2.6 : 1. The correlation coefficients suggest that the six-membered rings of the type present in tridymite play a dominant role in silica glass, that other ring sizes are important and result in the higher correlation coefficient for the 1412 atom model.

Although the correlation coefficient of 0.91 for the 1412 atom model is encouraging, a correct model should yield an RDF that agrees with the silica glass curve within the error limits (correlation coefficients of 0.97–1.00) throughout its entire range. Also, the correlation coefficient of 0.90 between the model and the silica glass curves in the range  $4 < r < 6$  Å suggests that the model does not have the correct proportion of the various ring sizes. In this connection, a much larger model, perhaps 200 Å in diameter, would be required to represent adequately, in a statistical fashion, the configuration present in a macroscopic sample.

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