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Monte Carlo studies show that an exclusion principle, based upon a minimum allowed O-O separation in adjacent tetrahedra, drastically restricts the relative orientations such tetrahedra can assume. This ad hoc criterion, with no energy considerations involved, reproduces the experimentally observed Si-O-Si angle distribution determined from the structural data of a large number of silicas and silicates. Similar results are obtained when Coulombic or nonbonded energy calculations are used. When extended structures are formed, this steric requirement alone causes additional and severe restrictions on the relative orientations of adjacent tetrahedra. In fact, it is not possible to have completely random orientations of tetrahedra beyond the first neighborhood shell, unless some nonrandomness is introduced to help formation of closed rings. Thus, the completely random continuous network model fails to produce extended structures in vitreous silica and defect models must be introduced to patch up the model. These considerations also apply to GeO_2 and SiS_2 structures.

INTRODUCTION

A variety of theoretical approaches have been applied to the modeling of vitreous silica: (a) "ball and spokes models" or the related computer versions,[1,2] (b) Monte Carlo studies similar to those reported for BeF_2 glasses,[3] (c) molecular dynamics studies,[4-6] and (d) molecular orbital calculations for small clusters.[7-9] In these approaches, the short-range structure, which preserves the average size and shape of the SiO_4 tetrahedra and the corner sharing of adjacent units, is mimicked by length constraints in (a) or by a suitable choice of parameters defining the attractive and repulsive forces or energies and then seeking the minimum energy configuration in (b) and (c). The aim of these approaches has been to produce a continuous random silica network,[2,10,11] the validity of which has been questioned by Phillips.[3]

A different approach to the modeling of vitreous silica was made by the present authors based on steric considerations.[12-14] Monte Carlo studies showed that an exclusion principle, based upon a minimum allowed O-O separation in adjacent tetrahedra, drastically restricted the relative orientations such tetrahedra can assume. This ad hoc criterion, involving no detailed energetic considerations, was applied to dimer units and found to reproduce the experimentally observed Si-O-Si angle distribution determined from the structural data of a large number of silicas and silicates.[12-14]

In the present paper, we extend the earlier work to trimers and rings as building blocks for extended structures and consider the variations caused by using either Lennard Jones or Coulombic forces as the restrictive criterion in place of the simple ad hoc $(O-O)_{min}$ exclusion distance. This procedure has been used to build a completely random network from a central tetrahedron and it is impossible even to complete the second nearest shell of tetrahedra without relaxing the assumption of complete randomness. Extension of these ideas is also made to GeO_2, SiS_2, and GeS_2 structures.

BUILDING SILICA STRUCTURE FROM THE MONOMERS

The Si-O length has an average value of $\simeq 1.60$ Å with a variation of $\simeq 0.05$ Å. The O-O edge length is on an average

$\simeq 2.61$ Å with a variation of $\simeq 0.1$ Å. The monomers are linked to form extended structures—most commonly by adjacent monomers sharing a corner. We will call the shared corner oxygen the bridging oxygen. The monomers can also be linked sometimes by the sharing of edges or faces of adjacent monomers. But we will restrict our discussions to corner-sharing tetrahedra. We will use the term "dimer" to refer to a pair of monomers sharing a corner. We will further assume that the term "dimer" is not used to refer to an isolated structure but to a part of a full three-dimensional network. Since the monomer is assumed to be relatively nondeformable, a dimer configuration is defined by three angular parameters that determine the relative orientations of the monomers in the dimer.[13] The description of a silica structure is thus equivalent to defining every unique dimer in the structure. In commonly found polymorphs of silica like quartz and cristobalite, only one or two unique monomers or dimers are found in their structures. In more complex structures like synthetic or meteoritic tridymites the unit cells are large and numerous nonidentical monomers and dimers are found in their structure.[7,8]

In building an extended structure, we can start with a reference monomer. It is then linked to four first neighbors. Each of these four monomers, in turn, is linked to three new monomers—leading to twelve second neighbors. If this process is continued, one would expect 36 third neighbors, 108 fourth neighbors, and so on. But there are spatial constraints and a scrutiny of known structures will show that closed rings are always formed which will lead to many fewer distant neighbors than the above predictions would indicate. In other words, often an N th neighbor would turn out to be a first neighbor—in which case we have a closed ring which we will call an N ring, i.e., a closed ring made up of N bridging oxygens and n monomers. When we speak of rings we speak of the smallest closed rings that are found in the structures being studied. In silicas and silicates most of the structures can be described in terms of 6 rings:e.g., quartz, cristobalite, tridymite, etc. A high-pressure silica polymorph—coesite—contains 4 rings. Though the mineral benitoite contains 3 rings, they are not further linked to form an extended network as in other silicas. In amorphous silica, x-ray dif-

fraction studies seem to suggest the existence of 5, 7, and 8 rings besides the 3, 4, and 6 rings.[2,10,15] We then ask: "How and why are the various structures formed? What is the origin of the observed variations in the size and shape of the monomers, the dimer types, the ring types and the way the rings are linked? Can we find restrictive criteria that will lead to the few observed structures as against the countless number of possible structures?" We sought answers to these questions and it seems many of them can be answered satisfactorily using simple concepts.

For Si-O = 1.60 Å in the monomer tetrahedron, the edge O-O distance is ≃2.61 Å and can be called the monomer O-O or contact distance. We can safely assume that no nonmonomer O-O distance will be less than this contact distance. This is definitely seen to be true in all known structures. So we used a single restrictive criterion that the O-O distances should not be less than this contact distance in any level of the structure. It is known from studies of numerous organic or polymeric structures that the nonbonded O-O separation is seldom below 2.9 Å. The optimum Van der Waals O-O separation is generally taken to be ≃3.04 Å.[16] One of the shortest O-O distances in known polymorphs of silica is 2.84 Å, the trimer O-O minimum in low quartz under a pressure of ≃68 kbar.[17] In our earlier work, we carried out Monte Carlo studies using each of the two values 2.61 and 2.90 Å for the O-O minimum.[13] In the following discussions we will use the term O-O short contact when the oxygen-oxygen separation is less than the assumed O-O minimum. What is the consequence of this single stipulation—a lower limit on O-O distances? We investigated this by Monte Carlo studies on dimers, trimers, larger clusters, and closed rings and determined the Si-O-Si angle distribution with and without this stipulation and compared the results with the experimentally known distributions.

Dimers

Keeping one monomer fixed, the orientation of the second monomer can be varied by specifying the three angular parameters α, β, and γ of the dimer.[13] Choosing random values for each of the three angles in the range 0–360° in each try, the nine dimer O-O distances and the Si-O-Si angles were calculated. If any distance was less than the preset O-O minimum (e.g., 2.61 Å, the contact distance) the dimer was rejected and a new one was selected with a different triad of angles. If there were no short contacts, the dimer was accepted. Out of a total of 2400 tries, ≃694 were accepted with O-O distances not less than 2.61 Å. About 520 were accepted when the preset O-O minimum was 2.90 Å. We would expect the smaller acceptance rate when the preset O-O minimum is larger. For each accepted dimer the minimum O-O distance was found. Obviously it will not be less than the preset O-O minimum.

Figure 1(a) shows the distribution of the Si-O-Si angle in the range 0–180°. When the condition is imposed that the O-O distances should not be less than 2.90 Å, the Si-O-Si angles below ≃114° are eliminated. On the higher side, practically all the dimers are accepted. The distribution has a maximum at ≃145°. There are two factors governing the observed distribution: (1) The probability that the angle is θ is propor-
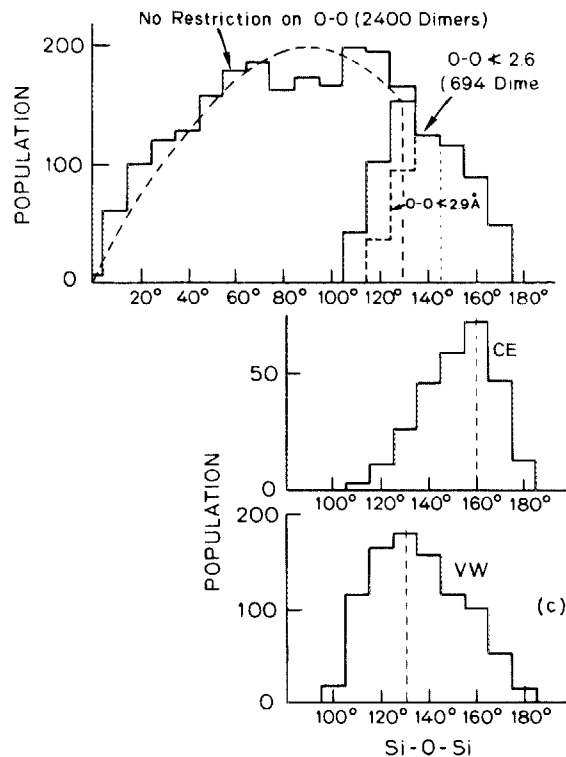

FIG. 1. Monte Carlo distributions of Si-O-Si angle for silica dimers: (a) using no restriction, and O-O$_{min}$ distance of 2.90 Å and O-O$_{min}$ distance of 2.61 Å; (b) using Coulombic energy interactions only and Boltzmann partitioning; (c) using nonbonded energy (van der Waals, VW) interactions only and Boltzmann partitioning (T = 300 °K).

tional to sin θ and is maximum at θ = 90° and 0 at θ = 0° and 180°. (2) The condition that O-O distances should not be less than the preset minimum of 2.90 Å eliminates much of the dimers with Si-O-Si angles below ≃120°. The experimentally observed Si-O-Si distribution and the distribution derived from Monte Carlo studies are very similar.

When the preset O-O minimum is 2.61 Å, there is more acceptance of dimers with Si-O-Si below 130° and a cut off near 106° is found [Fig. 1(a)]. The additional acceptance near low angles can be shown to be due largely to 3 rings because, when one of the dimer O-O distances is close to the contact distance, the conditions are favorable for the formation of 3 rings. The stipulation of a preset O-O minimum = 2.90 Å necessarily eliminates 3 rings.

No matter what model or parameters we choose for the interatomic forces, this limit on oxygen separation seems a realistic one. Ultimately one must find the preferred configurations from among those that have passed the initial test of no O-O short contacts, and this discrimination will be made on the basis of detailed energy considerations. To assess the energy approach, simple calculations of the Coulombic and nonbonded energies for silica clusters have been made in Appendix I to illustrate the broad trends. The energies are expressed in kilocalories per gram mole of SiO$_2$ [kcal (g mol)$^{-1}$]. The dimer results are given in Figs. 1(b) and 1(c) where the maxima are found to be ≃160° for Coulombic and ≃135° for nonbonded energies.

As expected, the nonbonded energy has a minimum of ≃ − 0.13 kcal (g mol)$^{-1}$ at O-O$_{min}$ = 2.8 Å and rises very

sharply below $O\text{-}O_{min} = 2.0$ Å. The variations in Coulombic energy are also of the same order in the range $O\text{-}O_{min} = 3.8$–4.6 Å and the Coulombic energy strongly discriminates against dimers with $O\text{-}O_{min} < 2.0$ Å. Avoiding intersecting oxygen spheres or tetrahedra in "ball and spokes models" is essentially what these findings represent. These estimates of the energy, crude as they may be, provide a useful perspective on the quantities involved and illuminate the general approach being taken.

Trimers

Similar Monte Carlo Studies were carried out on trimers—a central monomer linked to two adjacent monomers via bridging oxygens. The trimer is defined by the six angles associated with the two dimers in the cluster. Using a O-O minimum of 2.90 Å and choosing random values in the range 0–360° for the six angles, 2000 trimers were tried. Of them only 101 were accepted (a fraction of 0.042). The resulting distribution of the Si-O-Si angle was similar to that for the dimer. Since there should be no short contacts in each of the two dimers, we could expect the fraction of clusters accepted to be $(519/2400)^2 = 0.047$ considering only the restrictions at the dimer level. The additional restriction at the trimer level reduces the fraction of acceptance only very slightly—by a factor of $\simeq 0.90$. Evidently the above reasonings are statistical and apply to a large number of tries. For specific ranges of the dimer angles the relationships may be more complex.
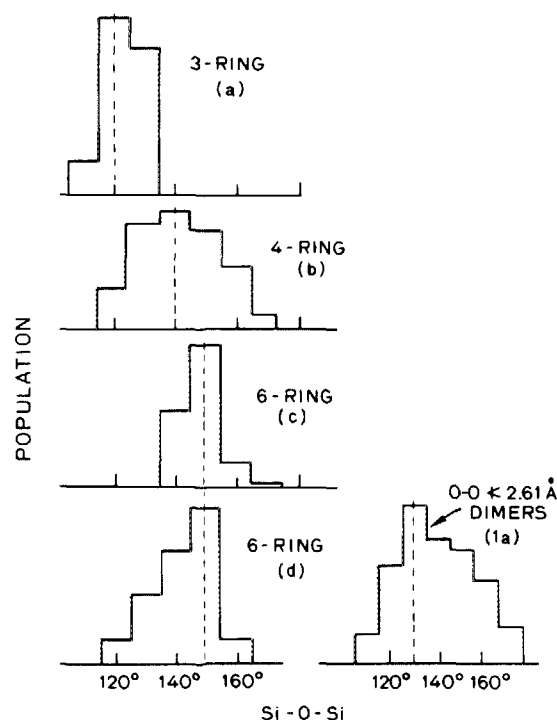
3 ring

The three bridging oxygens were assumed to form an equilateral triangle. Keeping one of the monomers fixed as before, the orientation of the other two are varied by varying three dihedral angles. A range of 0–360° for one of them and a range of 90–270° for the other two were found to be adequate by a preliminary calculation. Using random values of the three angles in these ranges, 3 rings were created and the restriction $O\text{-}O_{min} > 2.9$ Å was applied. 81 rings were accepted out of 880 tried—a fraction of $\simeq 0.092$ and an estimated fraction of $\simeq 0.01$ for the full range 0–360° for the angles. There are three dimers in the ring and the stipulation that each should satisfy the O-O minimum requirement leads to an expected value close to 0.01. The distribution of the Si-O-Si angle for the 3 ring is shown in Fig. 2(a). It has a maximum at $\simeq 120°$ and a cutoff at $\simeq 105°$.

4 ring

In 4 rings we need to specify 6 angles chosen as in Fig. 3. Again some preliminary calculations suggested the ranges for these angles and 4682 rings were tried by choosing random values for the six angles in the estimated ranges. Of them, only 75 rings satisfied the condition that the O-O distances should not be less than 2.90 Å, giving a fraction of 0.016. The accepted fraction is far less than what one would expect from the short contacts in the two dimers defined by the bridging oxygens 2 and 4 and two trimers which are responsible for the additional severe restrictions. Figure 2(b) shows the distribution of the Si-O-Si angle in the 4 ring. The maximum at 140° and the cutoff at 125° are both larger than those of the 3 ring. It is, however, to be recognized that the six angles defining the 4 ring cannot be chosen in a completely arbitrary fashion.

6 ring

To define a 6 ring, 12 angles must be specified. In order to save on computation, we chose three dimers at random

FIG. 2. Monte Carlo distribution of Si-O-Si angle for silica rings; (a) 3 rings; $O\text{-}O_{min} = 2.90$ Å (18 accepted rings out of 880 trials); (b) 4 rings; $O\text{-}O_{min} = 2.90$ Å (75 accepted out of 5000 trials); (c) 6 rings; Low Tridymite from experiment[18]; (d) 6 rings; $O\text{-}O_{min} = 2.90$ and 2.61 Å and the dimer $O\text{-}O_{min} = 2.61$ Å for comparison.
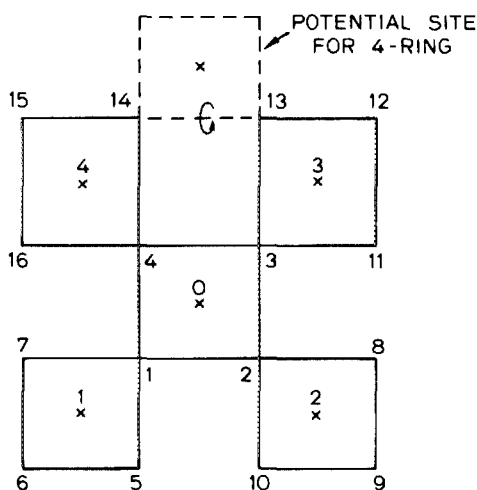
FIG. 3. Schematic representation of the first-neighbor shell of tetrahedra. Note the potential sites for the 4 ring where the dihedral angle of the added tetrahedron is fixed to within ± 12° by the dimers at 13 and 14.
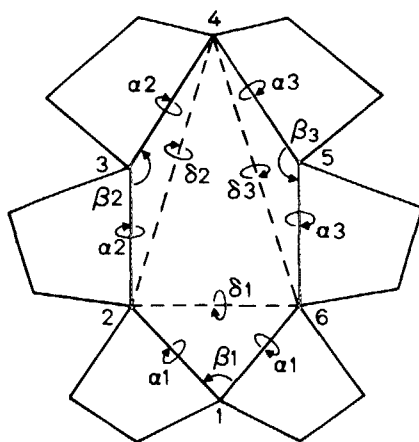
FIG. 4. Schematic representation of a 6 ring defined by 12 angles. 3 dimers at 1, 3, and 5, randomly selected from the dimer pool: $O-O_{min} = 2.90$ Å and δ_1, δ_2, δ_3 fully define the ring.

FIG. 5. Si-O-Si angle distributions for $O-O_{min} = 2.61$ Å: (a) dimers (pool of 695); (b) first-neighbor clusters (pool of 832 dimers); (c) second neighbor clusters (pool of 39 dimers).

from the accepted pool of 519 dimers free from 2.99-Å short contacts and connected them as in Fig. 4(b). The 9 dimer angles and the three dihedral angles δ define the ring fully. As in the case of the 4 rings, preliminary calculations estimated the ranges for the three δ. The short contacts would be too severe to warrant any search outside these ranges of the δ. Random values were chosen for the δ in the estimated ranges and the O-O distances were tested for each ring. Out of $\simeq 2000$ 6 rings tried, only 2 were free from short contacts, only $\simeq 0.2\%$. The very low acceptance fraction of 0.2% is caused by the three δ. Looking at Fig. 4 it is clear that besides the three dimers selected from the pool with bridging oxygens at 1, 3, and 5 and known to be free from short contacts, there are three more dimers at 2, 4, and 6 besides six trimers all of which should also be free of short contacts. The severity of rejction stems from this cause, i.e., additional dimers and trimers introduced by the linking of the three dimers to form the ring. The Si-O-Si angle distribution for the 12 dimers of the two accepted 6 rings is shown in Fig. 2(d). The maximum is at 145° and the cutoff at 125°. The Si-O-Si angle distribution of the dimers in the tridymites[18] is shown for comparison in Fig. 2(c).

To reduce the stringency of the selection process, subsequent cluster studies will assume an O-O minimum of 2.61 Å rather than 2.9 Å.

First-neighbor shell

As the next important step, we considered a cluster of five monomers—a central monomer sharing its four corners with four first neighbors. There are four dimers and six trimers in this cluster. We formed the clusters by forming acceptable dimers using a random selection of the dimer angles from the pool of 694 dimers free from 2.61 Å short contacts. We need only to ensure that there are no short contacts in the trimers. 208 first-neighbor clusters (FSTN) were accepted out of 455 tried—a fraction of $\simeq 0.46$. There is only a very small rejection of $\simeq 12\%$ at the trimer level. Since all the six trimers of the clusters should be free of short contacts simultaneously, we can expect that only $\simeq 0.88^8 = 46\%$ of the clusters tried would be accepted, as is indeed the case.
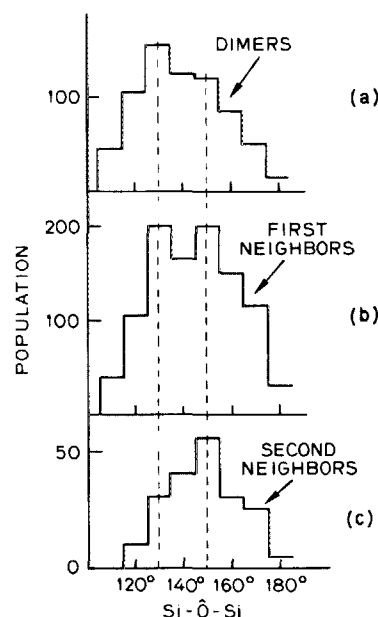
The Si-O-Si distribution for the 832 dimers of the 208 FSTN is shown in Fig. 5(b). Comparison with Fig. 5(a) (for dimers) shows that the maximum of Si-O-Si angle distribution noticeably shifts towards larger values in the FSTN—towards the observed distribution. In $\simeq 5\%$ of the FSTN tried, a trimer O-O distance was within 10% of the contact distance of 2.61 Å. These oxygen pairs can be potential edges of a monomer which can form 4 rings. For an actual ring to form the orientation of the monomer around this edge should be such as to avoid O-O short contacts. So we have additional restrictions if 4 rings are to be formed at this stage. Two additional dimers and trimers should be free of short contacts. The monomer completing the 4 ring could be defined by a dihedral angle around the edge we referred to. The estimated range of this angle would be $\simeq 12°$ on either side of a value to be determined from the other parameters. Again, we can see the severity of restriction imposed on the ring formation.

Second-neighbor shell

As the next step, we considered forming larger clusters from the pool of 208 FSTN clusters. Selecting 5 clusters at random from the FSTN pool, one was chosen as the central cluster: numbering the central monomer 0 and the first neighbors 1–4. The five monomers in each of the other four clusters are similarly identified with primed numbers. If, as explained in Fig. 6, 0′ is matched to 1, the monomers 4′, 1′, and 2′ form the second neighbors 5, 6, and 7. The monomer 3′ would not necessarily match the central monomer 0 and is dropped. Similarly, nine other second neighbors (8–16) are formed by matching 0″, 0‴, and 0⁗ with 2, 3, and 4, respectively. We now have a cluster of 17 monomers (0–16), composed of the central monomer (0), 4 first neighbors (1–4), and 12 second neighbors (5–16). We will divide the 12 second neighbors into four groups labelled SECN(j), $j = 1$–4. Each

CENTRAL 5-M CLUSTER

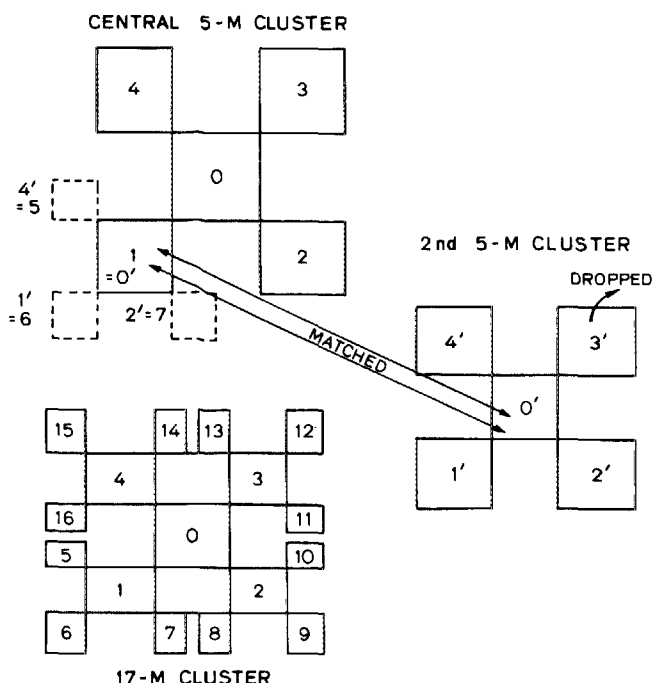2nd 5-M CLUSTER

17-M CLUSTER

FIG. 6. Schematic representation of second-neighbor cluster formation from members of the first-neighbor cluster pool. For arbitrary choice of the 5-monomer (5-M) clusters, 3' will not match O and is thus removed.

group contributes 3 new monomers to one of the four first neighbors (1–4). We will use the label 17-M for the 17-monomer cluster. 600 17-M clusters were thus formed from the FSTN pool. The FSTN distances are known to be free from short contacts because they are from the accepted pool. For each 17-M, all the 918 new O-O distances were calculated and those less than 3.0 Å were listed and the data analyzed. Out of $\simeq$600 17-Ms tried, none was totally free from O-O short contacts. Only three were accepted, if we relax the condition and allow short contacts in any one of the four SECNs: i.e., instead of 17-M clusters, we are satisfied with 14 monomer clusters free from short contacts. All other 597 17-M clusters had short contacts in two or more of the four SECNs. The following analysis explains why the selection process is so severe.

In the 17-M cluster there are 17 monomers, and 16 dimers which are known to be free from short contacts. There are 12 trimers—three from each of the four SECNs, e.g., the trimer defined by 5, 1, and 6 or by 11, 3, and 12. These are also free from short contacts as they are from the pool. However, there are 12 other trimers as well: e.g., those connecting 5, 1, and 0 or 15, 4, and 0. These trimers have to be tested for short contacts. Then there are 36 4-mers like those connecting 6, 1, 0, 2 or 9, 2, 0, 3. There are also 54 5-mers like those connecting 5, 1, 0, 2, 9 or 11, 3, 0, 4, 15. They should also be free from short contacts. The rejection of the 17-Ms therefore comes from short contacts within these 3-, 4-, and 5-mers. The short contacts due to the 12 trimers (e.g., the trimer linking 5, 1, and 0) can be eliminated if the monomer that was dropped, e.g., 3', could be matched to the central monomer 0. As explained earlier, this cannot be done for arbitrary choice of the 5 FSTNs. If certain symmetries

are present, this condition can be ensured and the short contacts due to these trimers can be removed.

It is now clear that, because of the steric restrictions, it will be extremely difficult to form large clusters—second neighbors and beyond—with completely arbitrary orientations of the linked monomers. However, the short contacts can be removed if closed rings can form and this requires nonrandom orientation of the tetrahedra. Formation of rings may still not allow further extension of the structure, unless some more nonnrandomness is imposed on the orientation of the tetrahedra.

Figure 5(c) shows the distribution of the 39 Si-O-Si angles of the three 14 monomer clusters free from short contacts. The minimum angle is $\simeq$118° and the maximum is at 150°. While this represents only a small sample, it at least illustrates the effect of the formation of extended structures—in pushing up the lower limits of the Si-O-Si angles to higher values.

COMPARISON WITH OTHER MODELS AND OTHER SYSTEMS

In most of the models of vitreous silica[1,10,11,19] the size and shape of the tetrahedra change slightly in different regions of the structure. But the most significant structural property associated with these models is the presence of sites with nonbridging oxygens. According to the arguments we presented, unless the orientations of adjacent monomers are highly correlated, there will be regions where the monomers cannot be linked by corner sharing owing to severe steric restrictions. In general, the short contacts cannot be removed by small changes in the orientations of the tetrahedra or by mild changes in their shape and dimensions. The network terminates, leaving monomers with nonbridging oxygens, unless conditions are favorable for the formation of closed rings.

In the continuous random network models (CRN) the nonbridging oxygens or voids are pushed to the surface.[1] We have not yet analyzed the CRN models exahaustively. However, some of the main features of the Bell–Dean Model[1] stand out clearly even in a preliminary analysis. In this, as well as the related computerized versions, the Si-O-Si angle is varied around a mean value of 153°.[1,2,10,11] According to our findings, this condition ensures that there are no O-O short contacts at the dimer level except at the few very low Si-O-Si angles (e.g., near 115°). The variations in the Si-O distances in the Bell–Dean model are perhaps a little larger than would be found in known structures of silica and silicates, e.g., some Si-O distances are as large as 1.75 Å. Mitra[6] has pointed out that the distribution of the O-Si-O angles is quite sharp in vitreous silica as deduced from ESR results and that in his own studies the distribution becomes sharper when the modeling was extended to larger volumes. Another point to remember is that even in these CRN models the orientations of adjacent monomers are not likely to be completely random. Sampling small regions of the Bell–Dean model do indicate short-range correlations in the orientations of adjacent monomers.

The question that we should ask is: "May the environments of monomers be significantly different in different re-

gions of the vitreous silica structure? If so, why should this happen? What are the constraints in nonequilibrium conditions that can trap the structures in different regions in quite dissimilar ways?" If, for instance, the environments of a monomer in different regions of the structure are not very different, symmetries are likely to be present and larger clusters can form as explained earlier. On the other hand, if a paracrystalline model is seriously considered,[3,23] we need a more precise spatial picture that could tell us why crystallization of these paracrystalline structures is hindered. Our approach, based on the local geometry of the structures in regions 2–6 monomers thick, focuses on the steric restrictions, the space available for the reorientation of the monomers and the rearrangements of rings giving valuable complementary information.

We made a preliminary analysis of the changes in the ring geometry of low quartz under high pressure using available crystal structure data.[17] The density of high-pressure low quartz differs by only $\simeq 10\%$ from that of coesite, a high-pressure polymorph of SiO_2. While low quartz can be described in terms of 6 rings and coesite in terms of 4 rings, the half 6 ring of high-pressure quartz is very similar to that of the coesite ring. The trimer O-O distance in low quartz at 68 kbar is 2.84 Å,[17] and can become the side of a 4 ring. In a very recent work, the trimer O-O distance in low quartz was found to be 2.79 Å at 102 kbar.[22]

Other structures with corner-sharing tetrahedra

Gaskell[20] and Gibbs[21] raised the following question concerning this approach to determining the structure of SiO_2: "If our explanation of the Si-O-Si angle distribution based on O-O short contacts is correct, can it explain why the Ge-O-Ge angle is only $\simeq 131°$ in quartzlike GeO_2 and the Si-S-Si angle $\simeq 109°$ in SiS_2?"

While answering this question, it is important to recall that there are several polymorphs of SiO_2 and several silicates containing corner-sharing tetrahedra and we have a distribution of Si-O-Si angles. On the other hand, only a single structure containing corner-sharing tetrahedra has been reported for GeO_2 and SiS_2, their other known structures being edge-sharing octahedra or edge-sharing tetrahedra. We have shown that O-O short contacts eliminate a large proportion of the dimers that could be formed by corner-sharing tetrahedra if their defining angles take completely random values. Further restrictions occur as extended structures are formed. These detailed considerations modify the Si-O-Si distributions as well as the minimum O-O in the extended structure. Moreover, in the energetics of the formation of a particular structure (given the conditions of formation), other factors will be involved as well: e.g., covalent, Coulombic and nonbonded energies. They are all interrelated parameters. The details of an actual structure will depend on the details of these energies and their variation with the relative orientations of the basic units in the extended structure.

Estimates of the Ge-O-Ge angle can be made using a simple approach. The Ge-O bond length is 1.73 Å as against the Si-O length of $\simeq 1.60$ Å. This means that, if we ignore all other considerations, the GeO_2 dimers should be identical to

the silica dimers, except for an increase in scale of $1.73/1.60 = 1.08$. So the distribution of the Ge-O-Ge angles should be identical to that of Si-O-Si, with this difference that a short contact of 2.61 Å in SiO_2 would mean a short contact of 2.82 Å in GeO_2. But if we stipulate that the O-O short contacts should be of the same magnitude in both the structures, the Ge-O-Ge peak will be shifted towards a lower value close to 131° as observed. Similarly, if we assume a minimum S-S separation of $\simeq 3.5$ Å and a Si-S bondlength of 2.13 Å, it can be shown that the Si-S-Si distribution has a maximum below 130°. Our approach thus predicts the shifting of the Ge-O-Ge or Si-S-Si angle peaks towards lower values as compared to Si-O-Si. However, extended structures and detailed energetics must be considered in order to estimate the actual bridging angles in specific structures. In passing, it should be pointed out that if the Si-Si distance in the SiS_2 dimer is assumed to be 3.04 Å (the same as in the SiO_2 dimers in quartz and cristobalite), the Si-S-Si angle drops to $\simeq 91°$ as against Si-O-Si$\simeq 144°$ for SiO_2.

Stipulating a lower limit for the cation separations may impose additional restrictions on the relative orientations of adjacent monomers. It should, however, be pointed out here that absence of anion-anion short contacts is not ensured by the absence of cation-cation short contacts. Our studies have shown that (a) the effect of stipulating a lower limit for the cation-cation separation (hard sphere model) will result merely in the sharp truncation of the sine curve below a cutoff angle; (b) when attractive terms are added and a simple Lennard Jones Potential is postulated for the cation-cation interactions, such a sharp truncation will be replaced by a smoother rise from a cutoff angle.

CONCLUSIONS

Oxygen-oxygen interactions are found to play an important role in the formation of silica structures in which adjacent tetrahedra are linked by corner sharing. If it is stipulated that the oxygen separations in the structure should not be less than their contact distance at 2.61 Å, a drastic restriction occurs in the relative orientations of adjacent tetrahedra. Much of the restriction occurs at the dimer level, which, in turn, forces a lower limit to the Si-O-Si bridging angle and affects their distribution in a variety of silicates. Simple calculations of Coulombic and O-O nonbonded energies confirm these findings. These energies, particularly the nonbonded energies, increase sharply at low separations— practically eliminating O-O distances significantly smaller than the contact distance.

When structures are extended beyond the first-neighbor tetrahedra, the orientations of adjacent tetrahedra can no longer be arbitrarily chosen. In fact, a completely random orientation of tetrahedra (in an absolute sense), is not possible even at the level of second neighbors. The orientations of adjacent tetrahedra should be highly correlated if closed rings are to be formed to eliminate the short contacts. The formation of closed rings is a prominent feature of known silica structures. The Si-O-Si angle distribution developed as a result of ring formation is in good accordance with experiment. Thus the completely random continuous network model is not exactly applicable for the formation of extended

structures in vitreous silica. Some type of defects must be introduced to allow extended structure formation to occur. In addition, the same type of steric arguments appear to apply to the GeO_2 and SiS_2 systems.

ACKNOWLEDGMENTS

APPENDIX: ENERGY CONSIDERATIONS
Coulombic energy (CE)

We assumed a weight of 1 for the silicons and the bridging oxygen of the dimer and 0.5 for the other six oxygens—preserving the stoichiometry of SiO_2. The Coulombic energy (to be referred to as CE) is given by

$$CE = \sum_i \sum_j 331 q_i q_j /(K r_{ij}),$$

where 331 is the conversion factor giving CE in kcal $(g\ mol)^{-1}$ of SiO_2. The summation is over the cluster. q is the charge on the atom in electron units. We assumed a value of -0.8 for oxygen and $+1.6$ for Si. r is the separation between the atoms. We treated k as a dielectric constant and used a value of 3.5. Purely dimer separations only were considered as the monomer contributions would be the same for all clusters according to our assumptions. If needed, we can scale the CE by a constant factor.

Nonbonded energy (VW)

Here we shall consider only the oxygen interaction in clusters and use a Lennard Jones 6, 12 potential:

$$VW = -2E_0(r_0/r)^6[1 - 0.5(r_0/r)^6],$$

with a minimum energy of $E_0 \simeq 0.2$ kcal$(g\ mol)^{-1}$, at $r = r_0 = 3.04$ Å.[16]

The following results give an indication of the change in dimer energy associated with changes in oxygen separation for both CE and VW. When $O-O_{min}$ increases from 3.0 to 4.0 Å, the CE decreases by 1.0 kcal$(g\ mol)^{-1}$ and the VW increases by 0.1 kcal$(g\ mol)^{-1}$. When $O-O_{min}$ decreases from 3.0 to 2.0 Å, the CE increases by 2.7 kcal$(g\ mol)^{-1}$ and the VW increases by 8.0 kcal$(g\ mol)^{-1}$.

To evaluate the effect of the CE and VW on the dimer Si-O-Si angle, we chose random values of the dimer angles for 2000 dimers and calculated the O-O distances. For each

dimer, the O-O minimum, the Si-O-Si angle, the CE and VW were calculated. The results were analyzed by collecting the dimers in boxes of $O-O_{min}$, of width 0.2 Å and centered at 2.0–4.6 Å in steps of 0.2 Å. The averages of the Si-O-Si angles, the CE and VW as well as their standard deviations, were calculated for each box. Similarly, the dimers were collected in boxes of Si-O-Si angles of width = 10° and centered at 80–180° in steps of 10°. For each box the average population and the standard deviation were calculated for CE and VW, using a Boltzmann weighting factor for each dimer equal to $\exp(-1.6774\ E)$, where E is either CE or VW expressed in kcal$(g\ mol)^{-1}$ and $1.6774 = 1/(kT)$ for $T = 300$ °K.

These results have been plotted in Figs. 1(b) and 1(c) for CE and VW, respectively.

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