

STRUCTURE OF STABLE AND METASTABLE WATER. ANALYSIS OF VORONOI
POLYHEDRA OF MOLECULAR DYNAMICS MODELSA. Geiger (~~Gaiger~~), N. N. Medvedev,
and Yu. I. Naberukhin

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A study has been made of various properties of Voronoi polyhedra and simplified Voronoi polyhedra (in which the indirect neighbors are excluded) for molecular-dynamic models of normal and "stretched" water. It has been shown that when the density is reduced from 1.0 to 0.8 g/cm³, the hydrogen bond network of the water becomes more nearly tetrahedral. When the density is further reduced, the network begins to break down, and large cavities appear. Whatever the density, the structure of the water is not like the structure of an ideal, random, tetrahedral network: the angles between the bonds in the network deviate considerably from tetrahedral.

INTRODUCTION

In many studies, particularly during the last few years, rather reliable support has been found for the view that a single, random network of hydrogen bonds is an adequate model of the structure of water [1-4]. Of course, such a network can be specifically realized only in a computer experiment. However, analysis of the properties of these networks has encountered a problem: in the modern versions of the molecular dynamics method or the Monte Carlo method, in application to water, there is no natural definition of a hydrogen bond. All that is assigned in these methods is the potential of complete interaction of water molecules, and the definition of a hydrogen bond must be added as a supplement. Therefore, different versions of the water network are obtained today by various investigators, depending on the definition of the hydrogen bond that they are using.

In the present work, we will use the Voronoi polyhedra method in an analysis of the structure of water. The properties of a Voronoi polyhedron of a given molecule are determined exclusively by the location of the nearest neighbors, without any need to know which of them are connected by hydrogen bonds. Herein lies the advantage of the method: it does not require construction of a network of hydrogen bonds in explicit form. However, it does have its own problems, which have prevented any application of the method to studies of the structure of water. (In [5], only the volumes of the Voronoi polyhedra were calculated, without any analysis of their geometric property; in [6, 7], they were not used in studying pure water, but rather in problems of hydration in aqueous solutions.) Voronoi polyhedra have been used extensively only in the analysis of close packing of spherical particles [8-12], beginning with the pioneering work of Bernal [13]. For loose systems, a class that includes water, Voronoi polyhedra are obtained in very complex form, since they are determined by the positions of not only the nearest neighbors but also comparatively distant molecules. Naturally, this is an obstacle to structural analysis. Such a situation is also illustrated by the data of the present work. However, we will show here that these difficulties can be overcome and that complete, unambiguous information on the structure of water can be obtained if we use, along with the conventional Voronoi polyhedra, simplified Voronoi polyhedra that we had introduced previously [14].

VORONOI POLYHEDRA

The Voronoi polyhedron (VP) of a given atom (or, more precisely, of the center of an atom) in a system of other atoms is defined as that region of space in which all points are closer to the given atom than to any of the other atoms in this system. Such a region is a convex polyhedron. Figure 1a is a two-dimensional illustration of a Voronoi polyhedron. The selected center O is connected by line segments to all other centers of the system.

Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences. Dortmund University, Germany. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 33, No. 2, pp. 79-87, March-April, 1992. Original article submitted May 20, 1991.

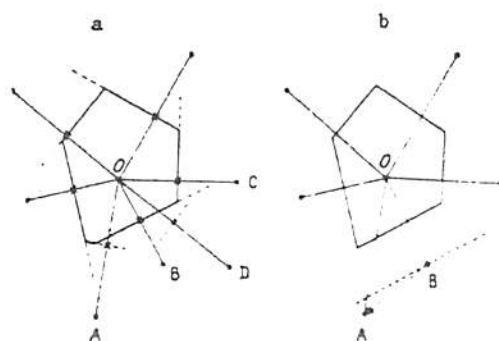


Fig. 1. a) Construction of Voronoi polyhedron for center O. Points marked as \times denote the middles of segments connecting center O to other centers of the system. b) Simplified Voronoi polyhedron for center O corresponding to Voronoi polyhedron in Fig. 1a. The face from the indirect neighbor A has been eliminated from this simplified polyhedron.

Through the center of each segment we pass a perpendicular line (or a plane in the three-dimensional case) that divides the space into two regions. All of the points of that region in which the center O is located lie closer to O than to the center located at the other end of the segment. The intersection of such half-spaces gives a region in which all points are closer to the given center O than to any other point.

Of course, not all centers of the system participate in forming faces of the Voronoi polyhedron. The more distant points are cut off by their nearer neighbors. For example, center D does not create a face of the polyhedron for center O, since the plane passing through the middle of the segment OD is "cut off" by planes passing through the centers of segments OB and OC. Thus, construction of the Voronoi polyhedron defines a certain number of "nearest" neighbors that give the faces of the VP. These points are called geometric neighbors of the particular center of the system.

Further, among the geometric neighbors we can perceive direct and indirect neighbors* [14, 15]. Thus, in Fig. 1a, center A is a geometric neighbor, but it is distinguished by the fact that the center of the segment OA lies outside the Voronoi polyhedron, whereas for the other neighbors, the centers lie on the faces. Such a situation occurs for the relatively distant geometric neighbors. The corresponding faces usually prove to be small, and hence they are called "nonbasic" - or "indirect" in the terminology of [15]. From this definition it is easy to see that the neighbor A is nonbasic if it is cut off by a plane passing through another geometric neighbor (for example, B) parallel to the corresponding face of the Voronoi polyhedron; in this case, the angle between segments OB and BA is obviously greater than 90° (Fig. 1b). Whence it follows, by the way, that in ideal tetrahedral networks, second neighbors with respect to bonds cannot be direct geometric neighbors (there the angle OBA = 109.5°).

In unordered systems, there is an enormous diversity of types of Voronoi polyhedra. Hence it is natural to desire to simplify the VP in some manner - to single out their primary properties after discarding the secondary properties. To this end, simplified Voronoi polyhedra (SVP) were proposed in [14]; these were obtained from the conventional VP after discarding the indirect neighbors. Thus, in constructing The SVP for the center O, we must ignore the neighbor A. The SVP obtained in this manner is shown in Fig. 1b.

MODELS

As models of water we have used computer models constructed by the molecular dynamics method with periodic boundary conditions for 216 molecules interacting with ST2 potential at a constant temperature of 273 K and densities that decrease from $\rho = 1.0$ to 0.7 g/cm^3 .

*These are the terms used in [15]; in the present article, the corresponding Russian terms can be translated literally as "basic" and "nonbasic" - Translator.

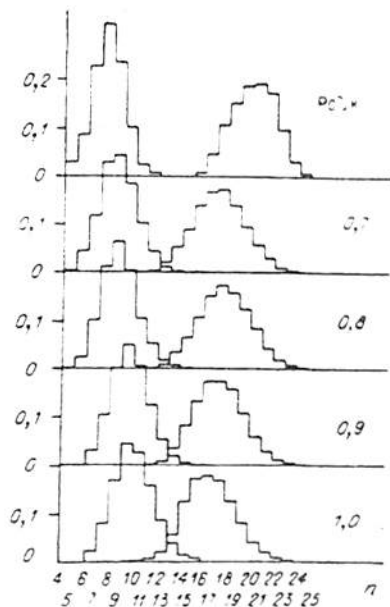


Fig. 2. Distribution of number of faces n in Voronoi polyhedra (on the right) and simplified Voronoi polyhedra (on the left) for models of water with densities $\rho = 1.0, 0.9, 0.8,$ and 0.7 g/cm³, and Polk model (from bottom to top).

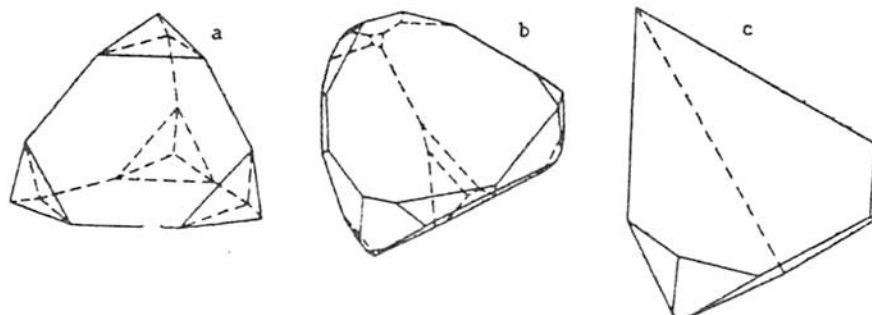


Fig. 3. Voronoi polyhedron for structure of diamond (a), typical Voronoi polyhedron ($n = 23$) for Polk model (b), and simplified Voronoi polyhedron ($n = 7$) corresponding to Polk model (c).

These models describe "stretched" metastable water along with "normal" water. The details of the procedures used in obtaining these models are given in [3]. Also reported in [3] were studies of various properties of the models, mainly by distribution function methods without the use of Voronoi polyhedra.

For comparison with the models of water, we will analyze a special model of a random tetrahedral network - the Polk model. This model was constructed mechanically [16] from randomly oriented units with tetrahedrally directed bonds in such a manner as to minimize the differences in bond lengths and the deviations from tetrahedral angles between the bonds. Then the Polk model was relaxed by minimizing the elastic energy of the network [17]. As a result, this random network deviates very little from ideal tetrahedral coordination: the standard deviation of the bond lengths is about 1%, angles 7%. Thus, the relaxed Polk model can be considered as the model of an ideal random tetrahedral network. The coordinates of the nodes of this model (consisting of 519 atoms) were very kindly furnished to us by Prof. P. Steinhardt, to whom we express our sincere appreciation. In the present article, we have used for analysis 377 central nodes of the model in order to avoid the influence of the boundary of the model on the VP characteristics.

DISCUSSION OF RESULTS

The probabilities of appearance of a given number of faces for the VP or SVP of water with densities from 1.0 to 0.7 g/cm³, along with the corresponding distribution for the Polk model, are shown in Fig. 2. In the Polk model we observe a large shift of the histograms when the VP is simplified, indicating a large number of indirect geometric neighbors that lead to a large number of faces for the VP. Elimination of these neighbors result in a substantial simplification of the polyhedron. The distribution becomes narrower, and the

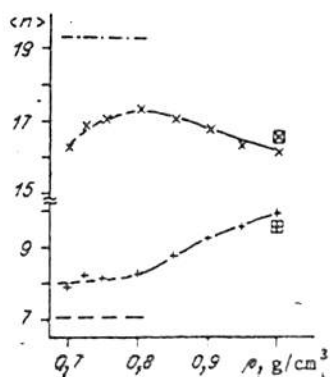


Fig. 4. Mean number of faces $\langle n \rangle$ on Voronoi polyhedra (upper curve) and simplified Voronoi polyhedra (lower curve) for water molecules, as a function of density ($T = 273$ K). The data plotted as squares correspond to a temperature of 224 K. The dashed curves show the values of $\langle n \rangle$ for the Polk model: 19.36 for the VP and 7.05 for the SVP.

most often encountered number of faces in the polyhedron is reduced from 20 to 7. The changes are so great that the two distributions do not overlap at all.

The source of such great changes is undoubtedly the well-defined tetrahedral directions of the bonds in the Polk model. In fact, in the ideal tetrahedral network of diamond, the Voronoi polyhedron is a hexadecahedron consisting of the fundamental tetrahedron (formed by the four nearest neighbors) with vertices cut off by the faces of a rhombododecahedron formed by 12 second neighbors (Fig. 3a). Here, the second neighbors are indirect geometric neighbors, and they give 12 comparatively small faces. Simplification of the VP in the ideal crystal of diamond would give as the SVP a regular tetrahedron. In a real crystal, however (I-structure of the crystal), this will be, of course, a more complex figure. A typical VP for the Polk model is shown in Fig. 3b. We see that here also there are four large faces corresponding to the first neighbors; they are speckled with a large number of small faces due to secondary neighbors and also neighbors that are more distant along the bonds. The simplified polyhedron (Fig. 3c) eliminates most of the small faces and restores the faces from the first neighbors, but not completely: certain vertices remain cut off by faces from more distant neighbors that have proved to be direct geometric neighbors.

An analogous picture should be observed for other networks with a predominantly tetrahedral direction of the bonds. For close packing of spherically symmetrical atoms (simple liquids), the situation is different. There, the participation of the indirect neighbors in constructing the VP is due mainly to thermal chaos, and the change in distribution when the transition is made from the VP to the SVP is less significant [14, 18]. For example, while the mean number of faces in the polyhedron $\langle n \rangle$ for water networks is greater than 16 for the VP and less than 10 for the SVP (Fig. 4), we find that in the case of simple liquids $\langle n \rangle$ is 14 for the VP and 12 for the SVP [18].

Thus, the distributions of the number of faces in Voronoi polyhedra for the models of water indicate the presence of a rather well defined tetrahedral order. It is interesting that when the density is reduced from 1.0 to 0.8 g/cm³, the distributions for the VP and SVP approach the distributions for the Polk model. With water densities below 0.8 g/cm³, this approach ends, so that the structure of water never becomes similar to this model. As shown in a previous study [3] and as can be seen from our subsequent discussion, breakdown of the system begins at 0.8 g/cm³, as manifested in the formation of large cavities. It was also noted in [3], on the basis of an investigation of various distribution functions, that before the water system begins to break down as the density is reduced, its network becomes more nearly tetrahedral. This is entirely consistent with the data presented in Figs. 2 and 4. One might think that the difference of the water structure from that of the Polk model is due to thermal excitations (the Polk model corresponds to a temperature of 0 K, the models of water to 273 K). However, it is fully evident that even after removing thermal

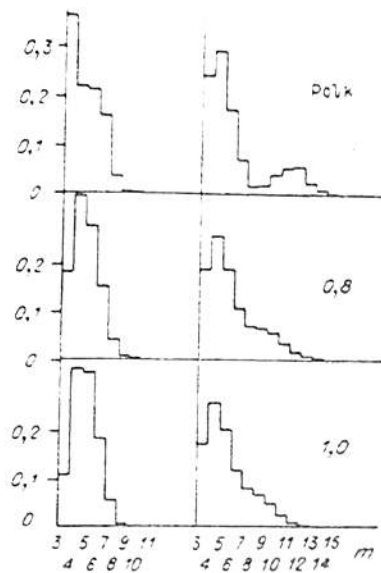


Fig. 5. Distribution of number of edges on faces of Voronoi polyhedra (on the right) and simplified Voronoi polyhedra (on the left) form models of water with densities $\rho = 1.0$ and 0.8 g/cm^3 , and Polk model.

excitation (upon transition from the I-structure of water to its intrinsic structures F or V [19, 20]), the structure of water will still differ from the structure of the Polk network, which is too nearly tetrahedral.

We have followed the influence of temperature on the structure of water by calculating the same distributions as in Fig. 2 with a density of 1.0 g/cm^3 and $T = 224 \text{ K}$. The data points plotted as squares in Fig. 4 show the mean number of faces in the VP and SVP for this state. As can be seen, the lowering of temperature with a constant density leads to an increase in the degree of "tetrahedrlicity" of the water network; the effect from lowering the temperature by some 50 K corresponds to a lowering of density by only 5%.

The observed dependence of the degree of ordering of the water structure on the density is exactly opposite to that for simple liquids, where an increase of density leads to a more highly ordered structure. The explanation for this opposite behavior is simple. In "ordinary" liquids, the structure is determined mainly by packing effects, whereas in water the structure is determined mainly by hydrogen bonds, with their very marked tendency toward local tetrahedral order. With large cavities corresponding to normal conditions, the water network is distorted under the influence of internal pressure. When this pressure is reduced, i.e., when the change is made to a lower density, we permit the water network to manifest its tetrahedral nature to a greater degree.

Figure 5 shows the distribution of the number of edges on the faces of the VP and SVP. We see that on the VP, some faces with 14 sides are encountered, but the faces are most often quadrilaterals. In simple liquids, these distributions were found to be somewhat narrower, with a maximum at $m = 5$ [11, 18]. The most interesting is the bimodal form of a distribution for the VP in the Polk model. The right-hand and lower part of this bimodal distribution pertains to residues of faces of the fundamental tetrahedron cut off by numerous faces from the second and third (etc.) neighbors through the network, which correspond to the left-hand part of the distribution. In the VP of diamond, the number of the latter relates to the number of the former as 12 to 4, which corresponds to a ratio of peak areas in the Polk model of approximately 3. When the tetrahedra are simplified, most of the small faces from the distant neighbors disappear, and certain faces of the fundamental tetrahedron recover their original triangular form; this explains the large maximum on the distribution for the SVP at $m = 3$. All of this is possible only as a consequence of small deviations from the tetrahedral configuration of the network in the Polk model. In the models of water, all of the distributions are more spread out; and upon simplification, the ideal tetrahedra are restored to a smaller degree (there is no maximum at $m = 3$).

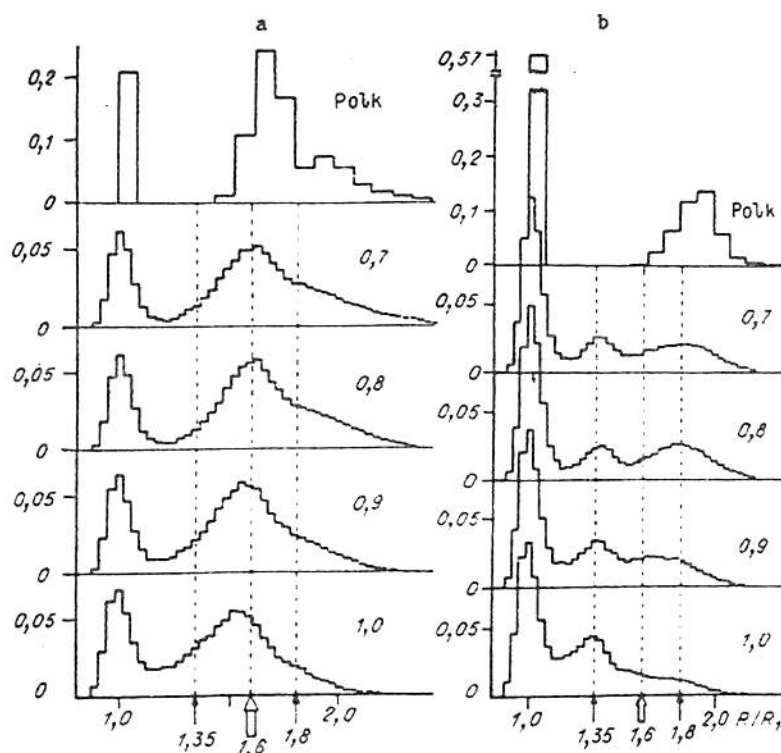


Fig. 6. Radial distributions of geometric neighbors for Voronoi polyhedra (a) and simplified Voronoi polyhedra (b) for models of water with density $\rho = 1.0, 0.9, 0.8,$ and 0.7 g/cm^3 and Polk model.

The role of the indirect neighbors in the structure of water can be followed well in the radial distributions of the geometric neighbors, i.e., the distributions of distances from the central atom to its geometric neighbors. In Fig. 6a these distributions are shown for the VP. The first peak on the distribution corresponds to the nearest neighbors. For the Polk model, there are exactly four nearest neighbors, and they are positioned at essentially identical distances (the first peak is isolated and narrow). For the models of water, the first peak is spread out, but the minimum that separates this peak from the distributions for the more distant neighbors becomes deeper as the density is reduced from 1.0 to 0.8 g/cm^3 . Here the coordination number (area under the first peak before the minimum) changes from 4.5 to 4.0. This part of the radial distributions of geometric neighbors coincides with the complete radial distribution for all molecules of water [3]; and just the noted facts, the same as there, must be interpreted as a consequence of an improvement of tetrahedral coordination of neighboring particles when the density is reduced.

The second, broad peak on the distributions corresponds to the next neighbors along the bonds. For the Polk model, its maximum is located between $R/R_1 = 1.6$ and 1.7 ; i.e., it corresponds to a distance to the second neighbors along the bonds in an ideal tetrahedral network, where $R/R_1 = (8/3)^{1/2} = 1.633$. In water, this peak is shifted from $R/R_1 = 1.52$ for dense water to $R/R_1 = 1.6$ for loose water; and this also demonstrates the rather high degree of tetrahedrality of the water networks.

The composition of the broad peak is disclosed in detail by analysis of the direct geometric neighbors as determined on the basis of the simplified Voronoi polyhedra (Fig. 6b). As we had mentioned, the second neighbors along the bonds cannot be direct neighbors in an ideal tetrahedral network. Therefore, the procedure of simplifying the VP effectively excludes the majority of the second neighbors in the distributions in Fig. 6b. In fact, we have essentially no neighbors at $R/R_1 \approx 1.6$ for the Polk network; and for the water models, a minimum is observed at this distance. Thus, the radial distributions for the simplified Voronoi polyhedra demonstrate the contributions of distant neighbors: third, fourth, and so on.

The distinctive feature of water that is disclosed by Fig. 6b is the behavior of the maximum on the distribution of distant neighbors at a distance $R/R_1 \approx 1.35$, which is less than the value for the second neighbors. In the model of Samoilov [21], this peak was as-

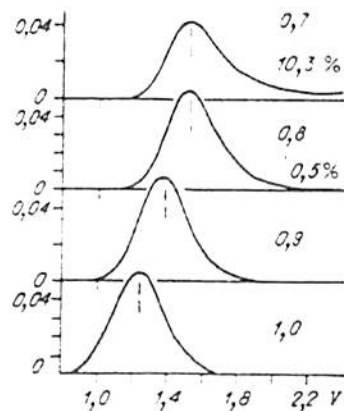


Fig. 7. Distribution of volumes of Voronoi polyhedra for models of water with density $\rho = 1.0, 0.9, 0.8,$ and 0.7 g/cm^3 . For the densities 0.8 and 0.7 , 0.5% and 10.3% (respectively) of the area under the curves is beyond the limits of the plots shown here.

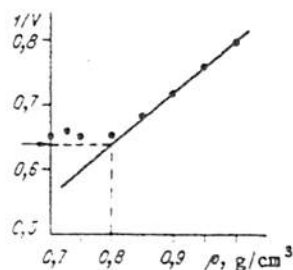


Fig. 8. Reciprocal of most probable volume of Voronoi polyhedron (position of maxima of distributions in Fig. 7) for models of water, as a function of density (data points). The straight line shows the reciprocal of the mean volume per molecule as a function of density. The arrow indicates the mean inverse volume of the Voronoi polyhedron for the Polk model. In calculating the volume, the unit of length was taken as the position of the first maximum on the radial distribution function R_1 .

cribed to molecules that do not enter into hydrogen bonds, molecules that are located in icelike cavities of the water structure. In computer models of water, however, we do not detect any such molecules or any such cavities [4]. Hence the peak under discussion must be assigned to distant neighbors (third and fourth) in the network of hydrogen bonds. Such distant neighbors may approach closer to the central molecule than the second neighbors if the network deviates sufficiently from tetrahedral. The possibility of realizing such a situation in networks of water hydrogen bonds is demonstrated by the structures of certain higher modifications of ice. Thus, in ice III, in which the angles between the hydrogen bonds differ appreciably from tetrahedral, certain third and fourth neighbors along the bonds are located closer than the second neighbors. In liquid water, apparently, an analogous situation exists. Therefore, the peak of the indirect neighbors as $R/R_1 \approx 1.35$ indicates strong deformation of the hydrogen bond network of liquid water, as well as substantial deviations of the bond angles from tetrahedral. The decrease of the area under this peak when the density is reduced to 0.8 g/cm^3 (see Fig. 6b) indicates an increase in tetrahedrality of the hydrogen bond network.

What is changed in the structure of water upon transition through the density 0.8 g/cm^3 ? An examination of the VP volume distributions will help to answer this question. From Fig.

7 we see that when the density is reduced from 1.0 to 0.8 g/cm³, the distribution is shifted toward larger volumes; i.e., on the average, the molecules acquire greater volumes of the surrounding space. This relationship is a trivial consequence of the inverse proportionality of the system density ρ to the mean volume per molecule (Fig. 8, straight line). A nontrivial result that we can see in Figs. 7 and 8 is that the maximum in the volume distribution remains in place as the density is reduced below 0.8 g/cm³, and the increase in mean volume of the VP with decreasing density in this case is a consequence of growth of the right-hand shoulder of the distribution - i.e., VP with anomalously large volumes appear. This fact indicates that, under these conditions, the sample contains cracks or pores that separate the molecules to great distances, whereas in the remaining volume, "normal" intermolecular distances are preserved. In other words, the unified network of hydrogen bonds in water begins to break up at densities below 0.8 g/cm³.

As we had mentioned previously, the Polk model can be considered as an ideal model of a random tetrahedral network in the sense that the maximum possible tetrahedral coordination in random networks is apparently realized in this model. Clearly, such a network has the minimum possible density and is the most open; any deformation of the ideal network (while its integrity is preserved) must lead to a decrease in the volume per particle. The reciprocal of the mean volume of one molecule ($\langle V \rangle^{-1}$) in the Polk network is 0.638 if we take R_1 as the unit of length. The value $\langle V \rangle^{-1} = 0.639$ in these units corresponds to a water density of 0.8 g/cm³. The closeness of these two values explains why the density of 0.8 g/cm³ is the limit of stability of the water network. At lower densities, the unified random tetrahedral network cannot be realized; and an increase of volumes can take place only through the formation of large pores in the network.

CONCLUSIONS

The basic results that we have obtained in regard to the structure of water, by an analysis of Voronoi polyhedra and simplified Voronoi polyhedra, are as follows: the network of hydrogen bonds in water is not similar to an ideal random tetrahedral network under any conditions; in the actual network, there are major deviations from the tetrahedral directions of the bonds, such that molecules that are distant with respect to the bonds may be located closer than the first molecules. When the density is reduced from 1.0 to 0.8 g/cm³, the tetrahedral coordination of the hydrogen bond network is improved: the angles between bonds approach tetrahedral. This can be interpreted as a consequence of a decrease in the internal pressure that had forced the network to be deformed under normal conditions. However, the capability for rectifying the random quasitetrahedral network by removing the pressure has a limit corresponding to a density of 0.8 g/cm³. When the density is further reduced, the network becomes unstable, forming discontinuities and cavities that are large on a molecular scale.

The results that we have set forth in this article give a rather clear demonstration of the possibilities of the Voronoi polyhedra method in analyzing the construction of the hydrogen bond networks that are the basis of water structure. An important feature of the method is that it does not depend on an exact definition of the hydrogen bond. This makes it possible to examine the properties of the network critically in terms of greater or lesser tetrahedrality without constructing the network itself. More detailed information, more convenient for interpretation, is obtained when the change is made from conventional to simplified Voronoi polyhedra in which no account is taken of most of the neighbors that are second along the bonds.*

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