Voronoi polyhedra analysis of MD simulated silicate glasses

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Voronoi polyhedra (VP) tessellation offers an alternative view at glass structure, stressing the topological and geometrical essence of glass. Although widely used for metal glass, its application in covalently bonded glass was mostly restricted to their phase transition changes or to the comparison with crystalline solids of similar composition. However, the presented contribution shows that VP space tessellation is constrained by the volume-surface relation that is typical for each VP of the glass constituent. Molecular dynamics simulation was used to obtain structures of some silicate glass, from which VP tessellations of the space were next performed. Anisotropy coefficient of each polyhedron was calculated and all polyhedra were statistically evaluated. A resulted frequency histogram reveals one-to-one correspondence of each element in the glass with the histogram peak, independently on the glass composition. However, some peaks in histogram can overlap. Therefore, two new parameters ξ, V_0, coming from the equation $V = \xi P^{1.5} + V_0$ (V, P are volume and surface of VP), were suggested as a more discriminating characteristics of elements' VP forming the glass. To better understand the meaning of ξ and V_0 coefficients, their temperature and structure dependences were studied. As expected ξ and V_0 tend to the relevant VP of higher isotropy with increasing temperature or loosen structure, i.e. V_0 decreases to zero and ξ reaches value corresponding to the regular polyhedron. Displaying (ξ, V_0) pairs for each VP in the Cartesian system, each glass element could be uniquely described by its (ξ, V_0) pair. Therefore, each substance can exist in its vitrified state only if the space tessellation made from the corresponding elements' VP, constrained by the volume-surface relation, expressed by their uniquely determined (ξ, V_0) pair, is possible.

Introduction

The Voronoi polyhedra (known also as Dirichlet-Voronoi polyhedra, Bernal polyhedra, or Wigner-Seitz cells) were developed in the frame of mathematics and solid-state physics. The Voronoi polyhedra analysis is a useful method to identify the near neighbour environment around atoms in condensed systems[1,2,3,4]. The most appealing feature of this method, describing the geometrical structure of multi-particle systems, is the orthogonal space tessellation in terms of Voronoi polyhedra (VP) attributed to each individual particle, so that any point within a polyhedron is closer to the central particle than to any other particle. This way, a definite part of a polyhedral-shaped space is unambiguously assigned to each particle.

The first applications of VP for description of MD simulated structures were confined to the one particle-type systems; typically to the study of MD (or Monte Carlo) simulated amorphous metals [5]. The method was later extended to the MD systems containing various types of particles. The main problem, discussed in connection with more kinds of particles, was how the various particles radii reflect in a construction of a Voronoi polyhedron. No simple objective method working without any adjustable parameters [6] was suggested until now. However, it was shown, that the simple procedure ignoring the differences in particle size is also applicable for systems containing various types of particles. Many quantitative characteristics can be enumerated for each VP. Among them, the most frequently used were: number of polygonal faces, distribution of polygonal faces with respect to the number of vertices (i.e. triangular, tetragonal, pentagonal, etc.) and with respect to their surfaces, total

surface, volume and number of edges, and various shape parameters (e.g. non-sphericity [7]; tetrahedricity, octahedricity, perfectness [8]).

For one particle-type systems, these parameters were advantageously used for determination of degree of ordering, the structural evolution of the system during nucleation [2], crystallization, melting [9] or other phase transformations. The distribution of VP with respect to the number of various polygonal faces (triangular, tetragonal, pentagonal, etc.) was used as a quantitative measure of the system "distance" from the particular crystalline state (e.g. hexagonal close packing) in which the above distribution has a sharp and simple shape. Application of various VP-parameters for structural analysis is studied in the work of Brostow [10] in detail. The direct polyhedra (i.e. the unambiguously defined polyhedra obtained in the course of geometrical construction of VP) are used for this purpose in our previous works [11,12]. However, other mentioned VP properties were not widely used for silicate glasses until now. To explain the situation we can realize, that contrary to the amorphous one-particle-type systems, the structure of silicate glass consists of two parts – the covalently bonded system of interconnected SiO_4 network and the modifier cations less-regularly coordinated by oxygen with mostly ionic bonds. Simultaneously, the prevailing role of covalent network was widely accepted. Therefore, from the topological point of view, the structure of silicate glass substantially differs from those of amorphous metals.

The aim of this paper is to bridge the different approaches to description of covalent and ionic species in glass, trying to suggest a common method for the geometrical description of the mixed covalent-ionic glass. VP tessellation is a starting point of our approach, showing the common features of VP of each species.

Method

The ensembles comprising 900 ions were simulated for the following compositions: 5%K2O+95%SiO2 (285 $Si4^+$, 585 $O2^-$, 30 K^+), 10%K2O+90%SiO2 (270 $Si4^+$, 570 $O2^-$, 60 K^+), 15%K2O+85%SiO2 (255 $Si4^+$, 555 $O2^-$, 90 K^+), 20%K2O+80%SiO2 (240 $Si4^+$, 540 $O2^-$, 120 K^+), denoted as K5, K10, K15 and K20, respectively. The effective pairwise interatomic potential of Born-Mayer type [13] was used to describe the interaction among the ions. Parameters of the potentials were taken from Garofalini[14,] Ewald summation [15] of the Coulomb force was performed in a cube with periodic boundaries, and leap-frog algorithm with time step of 10-15 s was used for numerical integration of Newton's equations of motion. MD simulation started from a random configuration at 6000 K and the system was equilibrated for 10 000 time steps (i.e. 10-11 s). The cooling procedure comprised a step-like decrease of the kinetic energy of all atoms followed by the numeric control of the reached temperature (2500 time steps), and equilibration (7500 time steps). Using this procedure, the system was cooled step-by-step from 6000 K to 4000 K, 3000 K, 2500 K, 2000 K, 1750 K, 1500 K, 1250 K, 1000 K, 750 K, 500 K, and finally to 300 K. At each temperature, the density of the system was adjusted to reach zero pressure (<5 kbar [16]). The all mentioned glasses were also simulated by using BKS [17] potentials (including the suggested parameters for Si-O and O-O). Moreover, glasses K30: 30%K2O+70%SiO2 (210 $Si4^+$, 510 $O2^-$, 180 K^+), Na30: (210 $Si4^+$, 510 $O2^-$, 180 Na^+) and Li30: (210 $Si4^+$, 510 $O2^-$, 180 Li^+) were simulated by BKS type of pairwaise potentials. Parameters of the BKS potentials for Li and K were taken from Teter [18], and that for Na from Yuan and Cormack [19]. The thermodynamic NVT ensembles (BKS potential simulated glasses) were continuously cooled to 300 K in 240 000 time steps of 1 fs, followed by 20 000 steps of relaxation (NVE ensembles). The data for lime-aluminium-silicate glasses 50%CaO+17%Al_2O_3+33%SiO_2

(100 Si^{4+}, 500 O^{2-}, 100 Al^{3+}, 150 Ca^{2+}), 25%CaO+25%Al_2O_3+ 50%SiO_2 (130 Si^{4+}, 520 O^{2-}, 130 Al^{3+}, 65 Ca^{2+}), 70%CaO+10%Al_2O_3+20%SiO_2 (68 Si^{4+}, 476 O^{2-}, 68 Al^{3+}, 238 Ca^{2+}), 62.5%CaO+12.5% Al_2O_3+25% SiO2 (80 Si^{4+}, 480 O^{2-}, 80Al^{3+}, 200Ca^{2+}) were taken from the formerly presented simulated glasses [20], from which those calculated for 400 K were processed. Moreover, data obtained for the simulation of sodium disilicate melt (1300 K)[21] were also processed and taken into account. Voronoi polyhedra were then constructed from all mentioned glass (and melt) structures following the algorithm of Brostow [22].

Results and discussion

Montoro et al[7] introduced the so-called non-sphericity, α, also referred to as anisotropy coefficient to characterise the structure of simple disordered systems. This quantity, derived from the scaled particle theory [23] is a suitable parameter for describing the shape of a general convex body. Higher anisotropy value means lower symmetry of VP, e.g. $\alpha = 2.23$, 1.50, 1.00 for regular tetrahedron, cube and sphere, respectively.

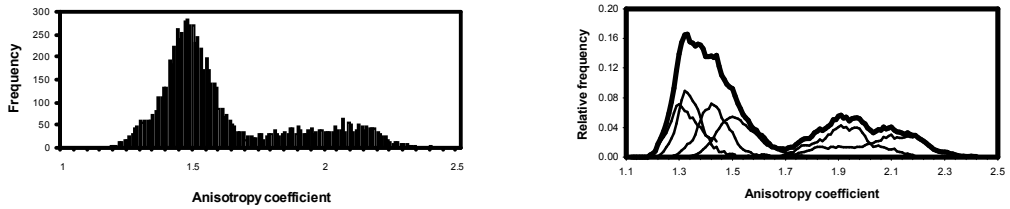

Fig. 1: Anisotropy coefficients a) histogram b) decomposed into the anisotropy coefficients of particular types of central atoms. Peaks correspond from left to right K, Na, Ca, O Al and Si central atoms.

As the first step of characterization of VP in glass, the anisotropy coefficients were evaluated for all mentioned glass and melt systems to have some idea about the distribution of α in the glass. Results obtained for all VP were summarised into one histogram, Fig. 1a). A complex shape of frequency function indicates the possibility of its deconvolution into more basic components. Indeed, partial histograms for distinct central atoms revealed several peaks. Those corresponding to network forming cations are situated at higher anisotropy values, while peaks corresponding to modifier cation are grouped in the well-separated low-anisotropy-coefficient region. Except for Si, all other cations reveal well-shaped nearly symmetric peaks. Si peak is rather diffuse, with significant low-anisotropy tail. Obtained result, that lower anisotropy corresponds to the network modifier cation, can be extended to the comparison among distinct modifiers. We can again see that the better modifying activity of alkaline cations (Na^+, K^+) results in a lower anisotropy compared with anisotropy of alkaline earth cations (Ca^{2+}). The more diffuse shape of Si peak was caused by higher amount of penta-coordinated of SiO_5 polyhedra in some studied glasses. The special structural position of O^{2-} anion excludes its categorization in terms of network forming/modifying activity. Position of O^{2-} is close to network modifiers anisotropy region, namely to Ca^{2+} cation. Formally, when only valency is taken into account, the anisotropy increases with increasing valency.

The former analysis resulting in one-to-one correspondence (independently on the glass

composition of the system) between the characteristic anisotropy value and the kind of central atom, i.e. the type of coordination polyhedron, pointed out the significance of the relation between the volume and the surface of VP of particular type of central atom. To avoid unit inconsistency, and to improve one-parameter characterization of the surface-volume relation with a more detailed two–parameters relation, we have decided to relate the volume of the VP with its surface powered to three halves:

$$V = \xi P^{3/2} + V_0 \qquad (1)$$

The ξ coefficient reflects anisotropy of VP ($\xi = 0.052,\ 0.068,\ 0.094$ for tetrahedron, cube and sphere, respectively), while V_0 is a minimal volume, formally corresponding to the VP with zero surface. The existence of the V_0 can be formally justified by statistics, but its physical meaning is not quite clear. It is suggested, (V-V_0) to be an extra volume determined by the surface of VP coming from the large versatility of shapes of VP in the non-crystalline structure. Then, V_0 should decrease with both increasing temperature and decreasing cooling rate, as the intermediate- and long-range interaction can play more important role in the relaxation processes.

In the first step, we have restricted the analysis to four compositions of the binary potassium-silicate glass at 300 K. The results of linear regressions obtained for Si, K and O central atoms are presented in Fig. 2, where points corresponding to individual polyhedra in each glass are plotted together with regression lines obtained from VP over all systems. The correlation coefficients close to unity together with small values of standard deviation indicate the high statistical significance in all studied cases. Similar results can be obtained for all other temperatures. It should be stressed that linear regressions over VP in each potassium-silicate glass yield ξ and V_0 coefficients falling into intervals statistically indistinguishable.

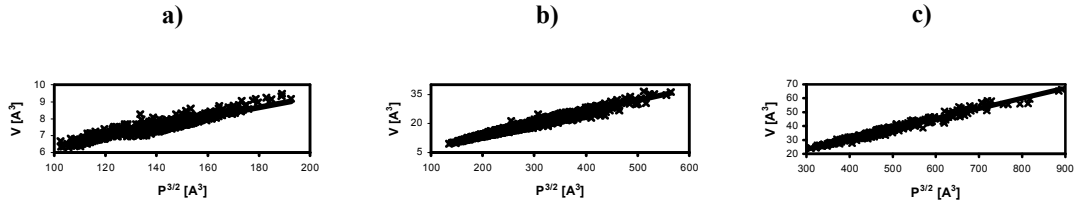

Fig. 2: Plot of volume versus properly powered surface of Voronoi polyhedra corresponding to the a) Si, b) O, c) K central atoms. The fitted line is determined by the least-square method over VP in all glasses. Atom species are taken over K05, K10, K15 and K20 glasses.

A natural question arises about the applicability of the performed analysis of VP to the real glasses, where the cooling rate can be about 10 orders lower. Moreover, it was shown, that microscopic quantities (radial distribution function, angle distribution, size of rings distribution) show a much stronger dependence on the cooling rate than macroscopic quantities [24,25]. Therefore, glasses with various compositions as well as with various structures (using different potentials and different cooling) were simulated. Results of these simulations are summed up in Fig. 3. VP of all types of central atoms clearly bear their own individualities, i.e. VP for each type of central atom and each structure contributes with a point in the (V_0, ξ) plot. The point corresponding for a room temperature can be shifted along the individual line as the structure is changed by the temperature increase. The (V_0, ξ)

points are shifted along the same line as the structure is changed by different composition or by different simulation conditions.

Moreover, some basic trends may be deduced from Fig. 3 straightforwardly. Moving from a network former to a network modifier, V_0 decreases and ξ increases, conserving the monotonous valency dependence. It worth mentioning, a value of oxygen anion is close to those of the two-valent central cation (Ca^{2+}). From the statistical point of view, slopes are determined with much better precision than corresponding intercepts. Both oxygen and silicon points are determined with relatively high precision in both directions. This fact reflects high geometric constrains put on the shapes of corresponding VP.

The above well-proved relationships may be generally summarized by the following statement. Each type of the central atom (including oxygen) has its own characteristic *iron line*, linearly relating the volume of VP to its properly powered surface. This result can be extended into some inverse task. Let us have a given composition of silicate melt. After its solidification to glass, the possible glass structure is restricted to tessellation of VP fulfilling the above *iron line* conditions. When such structure cannot be constructed, the phase separation (subliquidus unmixing or crystallization) probably takes place.

Gupta [26] formulated constrains for the glass forming ability based on the number of the degrees of freedom per vertex, while Marians & Burdett [27] underlined the importance of primitive 6-rings. These constrains are of topological origin, e.g. they describe the way, how the glass network is built-up from the elemental polyhedral building units. In contrary, constrains proposed on the bases of VP reflects mostly the geometry of the nearest neighbours surrounding different central atoms.

Conclusions

Analysis of anisotropy coefficients of VP from central atoms in various glasses and melt has revealed high correlation between surface and volume of VP. Linear relationship between volume and properly powered surface of VP has shown to be typical for each central ion; the structural changes shift this relation only in the well-defined direction determined by topological constraints. A hypothesis about the glass formation is formulated: the possible glass structure is constrained to the VP tessellation fulfilling the established volume-to-surface relation.

Acknowledgements

This work was supported by the Slovak Grant Agency for Science through the grant No. 1/7008/20. It was also part of the research project CEZ: MSM 223100002 Preparation and properties of advanced materials - modelling, characterization, technology.

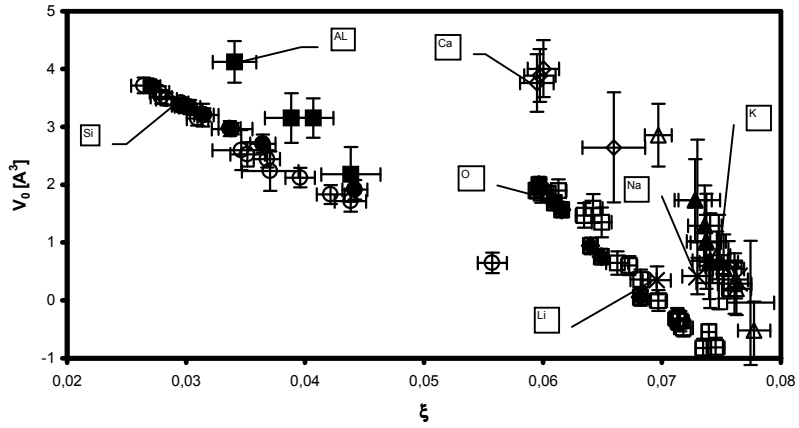

Fig. 3: Plot of coefficients ξ and V_0 (Eq. 1) corresponding to VP of different central atoms in various glasses. Error bars equals to the mean-square deviations. Si is labelled by circles (full in K15 glass), O by squares and full rhombi (in K15 glass), Al by full squares, Ca by open rhombi, K by triangles (full for K15 glass), and Na and Li by crosses

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