VOLUMES AND VOLUME FLUCTUATIONS OF VORONOI POLYHEDRA IN MD SIMULATED SILICATE GLASSES

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The method of Voronoi polyhedra analysis of silicate glass was suggested in terms of the averaged volumes and the volume fluctuations for each kind of the present particle; and demonstrated for $15K_2O{\cdot}85SiO_2$ *glass. The thermal expansion coefficient was separated into the partial molar contributions of the individual glass components. The calculated overall value of the thermal expansion coefficient was found in a reasonable agreement with the experimental value. The relative volume fluctuation of VP was used as a sensitive indicator of the structural changes induced by the temperature increase. The different positions of the well ordered* SiO_4 *sub-network manifest itself in lower but stronger temperature dependent values of the relative volume fluctuations of silicon Voronoi polyhedra.*

INTRODUCTION

Molecular dynamics (MD) is widely used method for the theoretical study of the structure and properties of various materials, including glasses and glass forming melts. Substantial part of any MD simulation consists in the tracing of trajectories of each particle in the simulated system. Hence, at every time step all information is available for the further structural analysis in the form of Cartesian coordinates of all particles. Despite of large spread of MD method, the structural analysis typically uses very simple aids like the snapshots, partial pair radial distribution functions, distributions of bond lengths and angles, coordination analysis, and cycle analysis. One of the more sophisticated but rarely used methods for the structural study is Voronoi polyhedra (VP) analysis.

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 was utilised as a useful method to identify the near neighbour environment around atoms in condensed systems [1-4]. VP can be introduced for each particle as the convex body within which any point is closer to the central particle than to any other one of the system. This way all system space is divided in a unique way into not-overlapping VP. Such way each particle is unambiguously assigned to the VP and vice versa each polyhedron represents a particular particle and hence one-to-one correspondence between particles and VP exists.

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 the determination of a 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.

Although VP is essentially a purely geometrical object, it contains information about the structure and chemical bonds present in the system (number of faces, their shape and surface, symmetry). From the physical point of view the system of VP volumes is directly represented in the equation of state. Volume, surface and shape of VP is not influenced only by the nearest neighbours but it can also reflect the medium range order and therefore VP analysis can be utilised in various theoretical studies of the relationships among the composition, structure and properties. For example, the tessellation of the system space offers a natural way for a study of the volume contributed by particles of the given kind in the dependence of the system temperature, and/or more generally in the course of the thermodynamics evolution of the system.

Obviously, the VP analysis offers a versatile tool for the study of multi-component systems. However, 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. Maybe, the features of VP ought to be used in some new manner to obtain valuable structural information for these more-particle-type systems. That is why the presented paper tries to propose a new type of application of VP parameters for the structural analysis of binary potassium-silicate glass, namely the dynamics of VP volumes.

METHOD

The ensembles comprising 900 ions were simulated for the following composition 15% K_2O + 85% SiO_2 (255 Si^{4+}, 555 O^{2-}, 90 K^+). This stoichiometry corresponds to the 35 mol % of Q^3 SiO_4-units and 65 mol % of Q^4 units. The effective pairwise interatomic potential of Born-Mayer type [11] was used to describe the interaction among the ions:

$$V_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho}\right) + \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}} \tag{1}$$

where r_{ij} is the distance between the i-th and j-th particles, z_i is the electronic charge, A_{ij} and ρ are constants. Parameters of the potentials were published in [12].

Ewald summation [13] of the Coulomb force was performed in a cube with periodic boundaries, and leapfrog algorithm with a time step of 10^{-15} s was used for the numerical integration of Newton's equations of motion. MD simulation started from a random configuration at 6000 K and the system was equilibrated for 12 500 time steps (i.e. 12.5 ps). 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 (10 000 time steps). During these 12 500 time steps the volume of the computational box was held constant. Using this procedure, the system was cooled step-by-step from 6000 K to 300 K with a temperature step of 100 K. At each temperature, the density of the system was adjusted to reach zero pressure (<5 kbar [14]).

Voronoi polyhedra were then constructed from 100 snapshots obtained during the 10 000 time steps, i.e. a snapshot was taken in every 0.1 ps. The construction of VP followed the algorithm of Brostow [15].

RESULTS AND DISCUSSION

Among all quantities describing VP, volume plays a special role. It is because one can intuitively well accept its straightforward connection with the structural positions of the individual atoms. The time evolutions of VP volumes were traced during 10 ps for each particle of the system. Figure 1 illustrates the evolution for six randomly chosen ions, two silicon, two oxygen, and two potassium atoms. The figure shows that the volume of VP increases significantly in the given order of ions. It reflects the tight regular tetra-coordination of Si by oxygen on one side and the looser potassium coordination reaching higher coordination numbers on the other side. The middle value of VP volume obtained for oxygen is a result of its bridging position in potassium silicate glass. The same structural arguments can be used to explain the different level of VP volume fluctuations increasing in the same order, i.e. from silicon to potassium (see figure 5). The magnitude of volume fluctuations is directly connected with kinetic energy of the individual particle, i.e. the fluctuation is mainly determined by the temperature of the system. This is shown for two randomly chosen silicon atoms in figure 2, where the fluctuation levels for 300 K and 4000 K are compared.

To reach the possibility of the comparison between the experimental macroscopic properties like density or thermal expansion coefficient on one side and the microscopic picture of glass structure obtained by MD on the other side, averages of VP characteristics over the ions of the same type were calculated. In case of VP volume, the relative change, $\Delta_{rel}V(X)$, was calculated according to the following equation

$$\Delta_{rel} V(X;T) = \frac{V_{ave}(X;T) - V_{ave}(X;T=300\ K)}{V_{ave}(X;T=300\ K)} \qquad (2)$$

where X stands for the particle type, i.e. X = Si, O, K; T is thermodynamic temperature and $V_{ave}(X;T)$ is the average VP volume for X-type particle at temperature T. The temperature dependence of $V_{ave}(X;T)$ for each species is plotted in figure 3. The common zero value for 300 K is obviously given by the definition of $\Delta_{rel}V(X;T)$. The most striking feature of the figure is the significant temperature dependence of $\Delta_{rel}V(Si;T)$ in comparison with the temperature course for O and K. Moreover, the statistically insignificant oscillating behaviour of $\Delta_{rel}V(K;T)$ is observed, what results in the sign changes of its temperature derivative, which is directly the partial thermal expansion coefficient at the temperature T. It must be distinguished from the mean partial thermal expansion coefficient, $\beta_{mean}(X;T)$, defined in the temperature range from 300 K to T

$$\beta_{mean}(X;T) = \frac{\Delta_{rel} V(X;T)}{(T-300\ K)} \qquad (3)$$

This statistically more robust quantity was used for the further study as it is not sensitive to the small oscillations of $\Delta_{rel}V(X;T)$ temperature dependence.

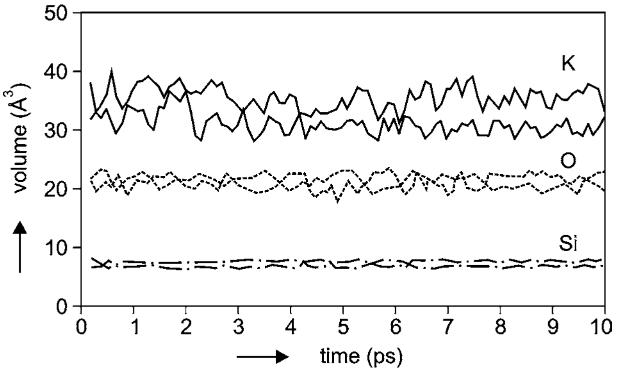

Figure 1. Evolutions of the VP volumes for arbitrary chosen particles at 4000 K. Two particles of each kind are presented.

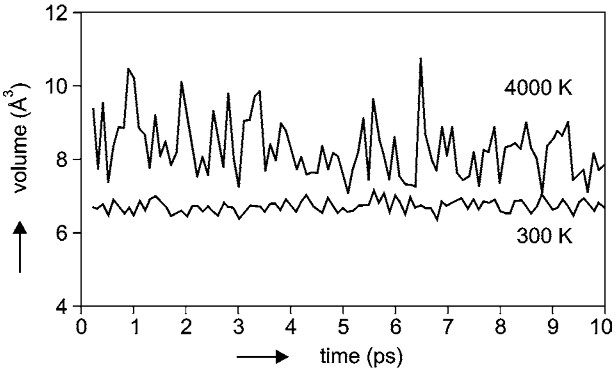

Figure 2. VP volume evolutions for two arbitrary chosen silicon atoms; the VP volume of the first silicon atom shows its volume changes at 300 K, and the second one at 4000 K.

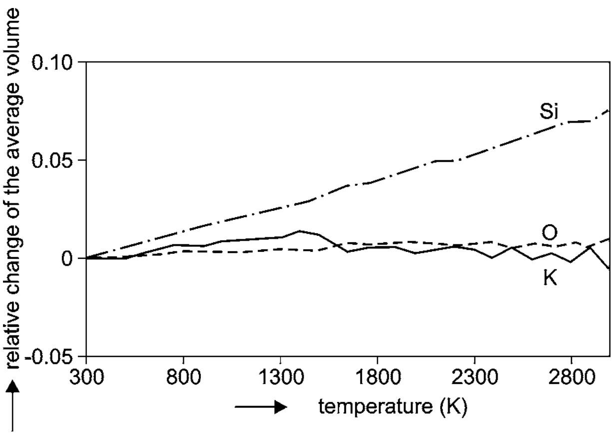

Figure 3. Relative changes of the VP volumes averaged over Si- (dot-dashed line), O- (dashed line), and K- (solid line) atoms.

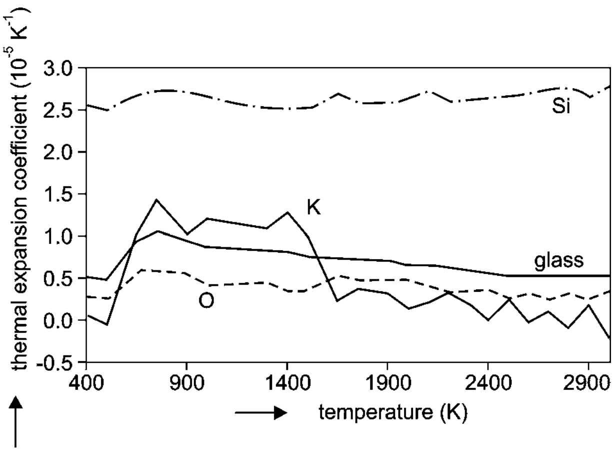

Figure 4. Partial thermal expansion coefficients calculated from the partial VP volumes, $V_{ave}(X;T)$. The overall thermal expansion coefficient of glass is yielded from equation 4.

The temperature dependences of the mean partial thermal expansion coefficients are presented in figure 4 together with the mean thermal expansion coefficient, $\beta_{\mathrm{mean}}(T)$, of the simulated glass

$$\beta_{\mathrm{mean}}(T) = \frac{\sum_{\mathrm{X}} n(\mathrm{X})\,\beta_{\mathrm{mean}}(\mathrm{X};T)\,V_{\mathrm{ave}}(\mathrm{X};T = 300\ \mathrm{K})}{\sum_{\mathrm{X}} n(\mathrm{X})\,V_{\mathrm{ave}}(\mathrm{X};T = 300\ \mathrm{K})} \quad (4)$$

where $n(\mathrm{X})$ is the number of X particles.

The experimental value of the thermal expansion coefficient of the real glass equals approximately to $2.4\ 10^{-5}\ \mathrm{K}^{-1}$ [16]. The value is in a reasonable agreement with the result of our calculation, which is about $0.4\ 10^{-5}\ \mathrm{K}^{-1}$. The lower calculated value can be plausibly explained by the higher glass transition temperature of the simulated glass and the lower extent of the structure relaxation during the very fast MD cooling procedure. The most regular part of the structure relax very quickly because only small changes of the mutual particle arrangement take place and the significant part of the relaxation consists of bond length changes caused by the anharmonicity of the vibration potential energy. This is the case of the small and relatively regular SiO_4 tetrahedra. Thus, smooth and nearly constant value of $\beta_{\mathrm{mean}}(\mathrm{Si};T)$ was found, which is practically identical with the experimental value of $\beta_{\mathrm{mean}}(T)$. The small absolute values of $\beta_{\mathrm{mean}}(\mathrm{O};T)$ and $\beta_{\mathrm{mean}}(\mathrm{K};T)$ are then a result of the necessity of the significant rearrangement of the structure needed during the temperature change, embracing the cycles of silicate network.

The more illustrative picture about the dynamics of the studied system is obtained when the information about the averaged volume fluctuations are complemented to average volumes. These quantities were calculated for each kind of the particle from the full set of VP volumes obtained from the snapshots recorded during the isothermal time evolution:

$$s_V(\mathrm{X};T) = \sqrt{\frac{1}{n(\mathrm{X})}\sum_{i\in \mathrm{X}}[V_i(\mathrm{X};T) - V_{\mathrm{ave}}(\mathrm{X};T)]^2} \quad (5)$$

The figure 5 presents averaged volume fluctuations for all kinds of particles. In the scale of the figure, the temperature dependence seems to be relatively insignificant. On the other hand, the absolute fluctuation values follow the order of the corresponding VP volumes. Hence, the relative fluctuations related to averaged VP volume at the given temperature, displayed in figure 6, were calculated. The strong separation between silicon on one side and oxygen and potassium on the other one was unveiled. The low values for Si directly follows from the strong and regular nearest-neighbour structure arrangement in SiO_4 network-forming tetrahedra. The structurally looser (but geometrically more regular) VP(K) and VP(O) give approximately 2-4 times greater relative volume fluctuations with respect to those of VP(Si). In addition, the linear temperature dependence is emphasised in this representation for all kinds of particles. The linearity is nearly ideal in case of Si ($R^2 = 0.98$) and very strong in case of oxygen ($R^2 = 0.84$). It is worth noticing that the linear temperature dependence of relative volume fluctuation was predicted in the frame of statistical physics [17]. Comparing the slopes, we can see that relative volume fluctuation of Si increases approximately twice in comparison with O and K because the temperature increase causes higher disorder among originally well ordered SiO_4 sub-network in comparison with the looser structure around potassium and oxygen atoms.

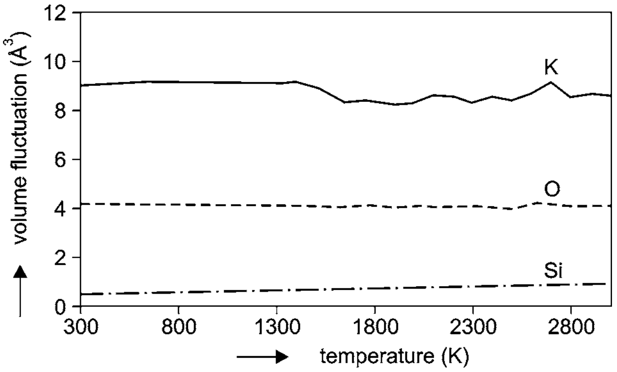

Figure 5. VP volume fluctuations of the glass constituents presented in the temperature range from 300 K to 3000 K: Si- (dot-dashed line), O- (dashed line), and K- (solid line) atoms.

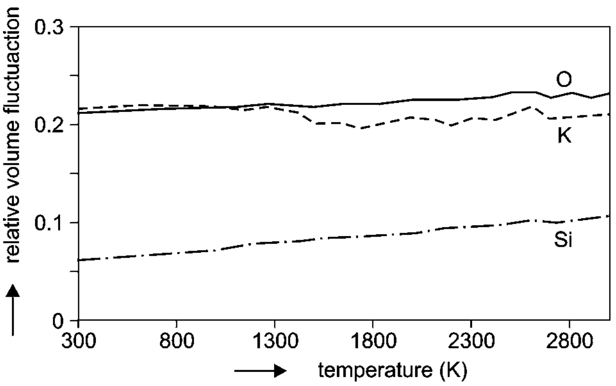

Figure 6. Relative VP volume fluctuations (averaged fluctuations related to the averaged VP volumes) of the glass constituents: Si- (dot-dashed line), O- (dashed line), and K- (solid line) atoms.

CONCLUSION

The method of Voronoi polyhedra analysis of silicate glass was suggested in terms of averaged volumes and volume fluctuations for each kind of the present particle. The method was demonstrated for $15K_2O{\cdot}85SiO_2$ glass. The thermal expansion coefficient can be effectively separated into partial molar contributions of individual glass components. The calculated overall value of the thermal expansion coefficient was found in a reasonable agreement with the experimental value. Moreover, the partial contribution of silicon fits this value almost exactly. The influence of the lower relaxation extent inherent for the MD cooling procedure explained the differences between the calculated and observed values. It was found that the relative volume fluctuations of VP can be used as a sensitive indicator of structural changes induced by the temperature increase. The different positions of the well ordered SiO_4 sub-network manifest itself in lower but stronger temperature dependent values of relative volume fluctuations of silicon Voronoi polyhedra.

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OBJEM A FLUKTUACE VORONOIHO MNOHOSTĚNŮ V SILIKÁTOVÝCH SKLECH SIMULOVANÝCH METODOU MD

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Byla navržena metoda analýzy Voronoiho mnohostěnů pomocí průměrných objemů a fluktuací jednotlivých složek křemičitého skla. Metoda je demonstrována na příkladu skla se složením $15K_2O{\cdot}85SiO_2$. Koeficient teplotní roztažnosti skla byl separován na parciální příspěvky jeho složek. Vypočtený koeficient teplotní roztažnosti skla je v rozumné shodě s experimentální hodnotou. Bylo zjištěno, že relativní fluktuace objemů VP jsou citlivým indikátorem strukturních změn vnesených růstem teploty. Posice křemíkových atomů v rámci dobře uspořádané subsítě SiO_4 se projevují v nižších hodnotách jejich relativních objemových fluktuací a současně v silné závislosti na teplotě.