# Group connectivity in binary silicate glasses: A quasi-chemical approach and molecular dynamics simulation

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## Abstract

The medium-range order of molecular dynamics (MD) simulated binary alkali silicate glass with 5, 10, 15, 20, 25, and 33.3 mol% of $Na_2O$ is studied in terms of the connectivity groups $Q^{n,a_1,\ldots,a_n}$, where $n$ stands for the number of bridging oxygen atoms, and $a_1,\ldots,a_n$ indicate the type of the connected $Q^n$ units. MD structure significantly deviates from the random connectivity model. The deviations were quantified by means of the quasi-chemical approach. The interchange energy between $Q^3$ and $Q^4$ units was found to be negative, indicating preferential formation of $Q^3$–$Q^4$ connections. This means that no tendency to phase separation was observed. Although alkali cations were apparently non-homogeneously distributed in space, regions abounding in $Q^3$–$Q^3$ and $Q^4$–$Q^4$ connections were not formed. It was suggested that grouping of alkali cations can be also mediated by the $Q^{4,4433}$ groups.
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## 1. Introduction

If someone is interested in structural investigations of alkali silicate glasses, he/she usually wants to know whether the proposed model reveals something more about the medium-range ordering in silicate glass, e.g. about miscibility, a spatial distribution of alkalis, and/or glass transition behavior. Molecular dynamics (MD) simulations should be in principle the prime tool for answering such questions.

Distributions of $Q^n$ units in binary sodium silicate glasses simulated by molecular dynamics are close to the random bonding model mentioned previously by Gurman [1], Araujo [2], and Bechstedt and Hübner [3] for up to 33 mol% of $Na_2O$. The simple stoichiometric model predicting presence of only $Q^4$ and $Q^3$ units in the glass structure is much closer to experimental results of $^{29}Si$ MAS-NMR [4–6]. However, this model does not contain $Q^2$ units which are inherently present in the MD simulated glass. A remarkable improvement is offered by both Gurman's quasi-chemical model [1] and Shakhmatkin's thermochemical model [7] which connect thermodynamic and structural approaches to silicate glass. These models introduce additional parameters achieving this way quantitative agreement with both experiments and MD simulations.

Q-species reflect the second nearest neighbor ordering around Si. On the other hand, $Q^{n,a_1,\ldots,a_n}$ connectivity groups ($n$ stands for the number of bridging oxygen atoms, and $a_1,\ldots,a_n$ indicate a type of the connected $Q^n$ units) carry a piece of structural information about the fourth nearest neighbors [4,8].

The random connectivity model for the distribution of $Q^{n,a_1,\ldots,a_n}$ units might give meaningful hints for experimental glasses probed by the multiple quantum NMR technique as well as molecular dynamics [4,9]. Unfortunately, high quality experimental results are not available till

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now, therefore any deeper discussions in this field would be premature. On the other hand, $Q^{n,a_1,\ldots,a_n}$ units distributions are easily extracted from MD simulations; hence a direct comparison is possible and straightforward.

This work is a follow-up to our previous paper [9]. In that paper, an attempt to interpret the experimental multiple quantum $^{29}$Si NMR results with help of the random connectivity model (RCM) was made. Regrettably, it was found that $Q^{n,a_1,\ldots,a_n}$ distributions extracted from NMR data did not fulfil the basic connectivity requirement $N_{34} = N_{43}$ which says that number of connections from $Q^3$ to $Q^4$ must be the same as from $Q^4$ to $Q^3$. On the other hand, that paper indicated that the concept of RCM model can be further developed in connection with a molecular dynamics (MD) simulation. The presented work analyzes $Q^{n,a_1,\ldots,a_n}$ distributions in MD simulated sodium silicate glasses containing 5, 10, 15, 20, 25, 33.3 mol% of $Na_2O$ with help of the RCM model and the quasi-chemical approach (QCA) [10], which considerably simplifies the problem by introducing the concept of interchange energies, $\Delta E_{ij}$. It also tries to address the questions of miscibility and the spatial distribution of alkalis in terms of silica sub-network connectivity.

## 2. Theory and simulation

### 2.1. The random connectivity model (RCM)

The random connectivity model was already described in paper [9] and to the large extent also in Araujo's paper [2]. RCM enhances the models predicting $Q^n$ distribution by incorporating the connections among silicon tetrahedra $(SiO_4)$ into the model. The tetrahedra ($Q^n$ units) are linked fully on the random base. The probability, $\pi_i$, that the randomly chosen bond between two adjacent tetrahedral units includes a $Q^i$ unit, is given by

$$\pi_i = \frac{i y(Q^i)}{\sum_{j=1}^n j y(Q^j)}, \tag{1}$$

where $i$ is the number of bridging oxygens (BO) $(i = 1,\ldots,n)$ and $y(Q^i)$ is a fraction of $Q^i$ units out of total Q-species. The probability of finding a certain connectivity group $Q^{n,a_1,\ldots,a_n}$ has to obey the multinomial distribution, which generalizes the binomial one to experiments with more than two outcomes. Multinomial probabilities are computed as follows:

$$P(x_1, x_2, \ldots x_n) = \frac{n!}{x_1! x_2! \ldots x_n!} \times \pi_1^{x_1} \pi_2^{x_2} \ldots \pi_n^{x_n}, \tag{2}$$

where $x_i$ are constrained by the number of trials (number of BO), $n$,

$$x_1 + x_2 + \ldots + x_n = n, \tag{3}$$

and $x_i$ stands for the number of the $Q^i$-units connected to the central Q-unit. Instead of using the statistical notation $P(x_1, x_2, \ldots, x_n)$ we introduce the structurally related notation $y(Q^{n,a_1,\ldots,a_n})$ as was already used in papers [8,4]

$$y(Q^{n,a_1,\ldots,a_n}) = y(Q^n) \times P(x_1, x_2, \ldots x_n). \tag{4}$$

Number of connections between $Q^i$ and $Q^j$ units, $N_{ij}$, is given by the following sum

$$N_{ij} = \sum_{\{x_1,\ldots,x_i\}} x_j P(x_1, x_2, \ldots x_i) \times y(Q^i). \tag{5}$$

$N_{ij}$ contributes to the overall connectivity, $N$, of a silicate system

$$N = \sum_{i,j} N_{ij} = \frac{N(BO)}{N(Si)}. \tag{6}$$

This sum equals two for silica glass where only $Q^4$ units are found and 1.5 for disilicate glass containing only $Q^3$ units.

### 2.2. Quasi-chemical approach to group connectivity (QCA)

The lattice model developed by Guggenheim in 1952 [10,11] is well suited for the description of liquid structures. The fundamental assumption is the division of the liquid volume into cells (sites) so that each molecule occupies one site of a lattice. This construction introduces the equilibrium distance between the molecules, which provides the basis for a corresponding coordination number. In the zeroth approximation the contact surfaces of pairs (representing bonds) are proportional to the general geometrical surfaces of the molecules. This is equivalent to a completely random distribution of molecules. Orientational effects conditioned by the energy differences and molecular inhomogeneities can be accounted for by a quasi-chemical equilibrium. In this equilibrium the contact surfaces are weighted by Boltzmann factors, which consider the interchange energies of the contact pairs. In the following only the basic assumptions and some important equations are summarized. It is assumed that each $Q^n$ unit has the coordination number, $n$, in a well-defined lattice. A distinction is made between connections of like ($ii$) and unlike ($ij$) units. Calculating the numbers of connections $N_{ii}$ and $N_{ij}$ for the unit of type $i$, $n$ condition equations are obtained:

$$i y(Q^i) = 2 N_{ii} + \sum_{j \neq i} N_{ij} \quad \text{for} \quad i = 1, \ldots, n. \tag{7}$$

We now introduce the quasi-chemical equilibrium for the connections, i.e.

$$N_{ii} + N_{jj} \overset{\Delta E_{ij}}{\leftrightarrow} 2 N_{ij} \quad \text{for} \quad i \neq j, \tag{8}$$

$$\frac{N_{ij}^2}{N_{ii} N_{jj}} = \exp\left(\frac{-2\Delta E_{ij}}{RT}\right) \quad \text{for} \quad i \neq j, \tag{9}$$

where the quantities

$$\Delta E_{ij} = E_{ij} - (E_{ii} + E_{jj})/2, \tag{10}$$

are by definition the free interchange energies per connection. In general, the $\Delta E_{ij}$, are functions of temperature. However, in the following we consider the special case