Structure and transport properties of amorphous aluminium silicates: computer simulation studies

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Abstract

The structure and transport properties of SiO$_2$–Al$_2$O$_3$ melts containing 13 mol% and 47 mol% Al$_2$O$_3$ are investigated by means of large scale molecular dynamics computer simulations. The interactions between the atoms are modelled by a pair potential which is a modified version of the one proposed by Kramer et al. [J. Am. Chem. Soc. 64, 6435 (1991)]. Fully equilibrated melts in the temperature range $6000 \, \text{K} \geq T > 2000 \, \text{K}$ are considered as well as glass configurations, that were obtained by a rapid quench from the lowest melt temperatures. Each system is simulated at two different densities in order to study the effect of pressure on structural and dynamic properties. We find that the Al atoms are, like the Si atoms, mainly four–fold coordinated by oxygen. However, the packing of the AlO$_4$ tetrahedra is very different from that of the SiO$_4$ tetrahedra, which is reflected by the presence of triclusters (O atoms surrounded by three cations) and edge–sharing AlO$_4$ tetrahedra. On larger length scales, a micro–segregation occurs, resulting in an Al–rich network percolating through the Si–O network. This is reflected in a prepeak of concentration–concentration structure factors around $0.5 \, \text{Å}^{-1}$ (both in the system with 47 mol% and 13 mol% Al$_2$O$_3$!). We also address the interplay between structure and mass transport. To this end, the behavior of the selfdiffusion constants for the different compositions and densities is studied.
I. INTRODUCTION

One of the most abundant oxides in natural silicates and technological silicate glasses is Al$_2$O$_3$. Although alumino silicates are therefore of central interest in geosciences and materials science, the structure even of the binary system SiO$_2$–Al$_2$O$_3$ is far from being well-understood. However, the knowledge of the chemical ordering in the latter system provides also the basis for a better understanding of the structure of more geologically relevant alkali or alkaline earth alumino–silicates.

The chemical ordering of aluminium is very complicated when built into the tetrahedral Si–O network. In order to achieve local charge neutrality, Al$^{3+}$ ions need a different environment of O$^{2-}$ ions than Si$^{4+}$ ions. Thus, unlike SiO$_2$, Al$^{3+}$ ions do not form a network of AlO$_4$ tetrahedra that are connected with each other via the O atoms at the corners. Instead, different experimental techniques such as nuclear magnetic resonance (NMR) [Lee and Stebbins, 2000; Schmucker et al., 1999; Sen and Youngman, 2004; Stebbins et al., 2005; Stebbins and Xu, 1997; Xue and Kanzaki, 1999] as well as IR and Raman spectroscopy and X–ray scattering [Morikawa et al., 1982; Okuno et al., 2005] found evidence for structural units such as three–fold coordinated oxygen atoms and five– and six–fold coordinated aluminium atoms that are not found in pure silica, unless one considers amorphous silica at very high temperatures, say above 4000 K (see Horbach and Kob, 1999).

At low Al$_2$O$_3$ concentrations, the Al atoms are mainly four–fold coordinated by oxygens, but, as proposed in NMR studies, these AlO$_4$ units are accompanied by so–called triclusters, i.e. structural units where an oxygen atom is surrounded by three cations (where at least one of them is an Al atom). Recently, molecular orbital calculations confirmed the possibility of such triclusters (Kubicki and Toplis, 2002). Moreover, a combination of molecular dynamics computer simulations and Hartree–Fock calculations (Tossell and Cohen, 2001; Winkler et al., 2004; Tossell and Horbach, 2005) found evidence that O tricluster atoms participate typically in two–fold rings (i.e. edge–sharing geometries) of composition Al$_2$O$_2$ or AlSiO$_2$. Certainly, further experimental studies are necessary to clarify to what extent triclusters and edge–sharing tetrahedra exist in real aluminium silicates.

As shown by recent NMR studies, five– and six–fold coordinated Al atoms are also important structural units in the system SiO$_2$–Al$_2$O$_3$. The fraction of these highly coordinated Al atoms tends to increase with increasing Al$_2$O$_3$ concentration (Sen and Youngman, 2004;
Stebbins et al., 2005). All these experimental findings show that, in alumino silicates, the local chemical ordering of Al atoms is very different from that of Si atoms.

In a recent MD simulation study of the system (Al₂O₃)₂(SiO₂) [abbreviated in the following as AS2], we have shown that the different chemical ordering of Al and Si on local length scales also leads to structural ordering on intermediate length scales of the order of 1 nm (Winkler et al., 2004). This intermediate range order (IRO) can be described by a microphase separation where the Al–rich network structure percolates through the Si–O network. The IRO gives rise to a prepeak in partial static structure factors at a wave number \( q = 0.5 \text{ Å}^{-1} \). It can be seen as a precursor of the metastable liquid–liquid phase separation below \( \approx 1900 \text{ K} \) that is found experimentally (MacDowell and Beall, 1969) between about 10 mol% and 50 mol% (AS2, with 33 mol% Al₂O₃, lies approximately in the center of the demixing region).

The formation of IRO seems to be quite a general feature of multicomponent silicate melts. Similar IRO as the one found in AS2 has also been seen in neutron scattering experiments of a calcium silicate (Gaskell et al., 1991), sodium silicates (Meyer et al., 2002; Meyer et al., 2004), and alkali aluminosilicates (Cormier et al., 2001; Kargl and Meyer, 2005). For the example of sodium silicates, the IRO is reflected in a prepeak around 0.9 Å⁻¹ in static structure factors. It has its origin in the formation of sodium–rich channels in the static structure. These channels serve as preferential pathways in an immobile Si–O matrix and thus provide an explanation for the high mobility of sodium in ion–conducting sodium silicate melts (Horbach et al., 2002; Meyer et al., 2004). The presence of diffusion channels in sodium silicates is a nice example for the interplay between structure and mass transport in glassforming melts.

The structure–transport relation is also a central issue of the present study. We have extended our previous simulations of AS2 to aluminium silicates with 13 mol% Al₂O₃ and 47 mol% Al₂O₃. These systems are simulated at different densities to see how pressure affects the structural and dynamic properties of aluminium silicates. Furthermore, we aim to understand how the interplay between local structural features (triclusters, two–fold rings, five– and six–fold coordinated Al ions) and IRO changes with composition. This is in turn will allow us to elucidate the interplay between structural features and transport processes, when we investigate the temperature dependence of the selfdiffusion constants for the different systems under consideration.
II. MODEL AND DETAILS OF THE SIMULATIONS

As in our recent study of AS2, we use a potential proposed by Kramer et al. (1991) to model the interactions between the atoms. It is based on the so-called BKS potential (van Beest et al., 1990) for pure silica that has been extensively applied in recent studies (see, e.g., Horbach and Kob, 1999, and references therein). Apart from mixtures of SiO$_2$ with Al$_2$O$_3$, the Kramer potential allows also the consideration of sodium silicates. As shown recently, it provides quite a realistic description of sodium di-, tri- and tetra-silicate (Ispas et al., 2002; Meyer et al., 2004) as well as of AS2 (as far as comparison with experimental data is possible, see also below) [Winkler et al., 2004; Tossell and Horbach, 2005].

The potential has the following functional form:

$$\phi_{\alpha\beta}(r) = \frac{q_\alpha q_\beta e^2}{r} + A_{\alpha\beta} \exp \left( -B_{\alpha\beta} r \right) - \frac{C_{\alpha\beta}}{r^6}$$  \hspace{1cm} (1)

with $\alpha, \beta = \text{Si}, \text{Al}, \text{O}$. Here $r$ is the distance between an ion of type $\alpha$ and an ion of type $\beta$. The values of the parameters $\{A_{\alpha\beta}, B_{\alpha\beta}, C_{\alpha\beta}\}$ that were calculated by $ab$ initio methods are $A_{\text{SiO}} = 18003.7572$ eV, $A_{\text{AlO}} = 8566.5434$ eV, $A_{\text{OO}} = 1388.7730$ eV, $B_{\text{SiO}} = 4.87318$ Å$^{-1}$, $B_{\text{AlO}} = 4.66222$ Å$^{-1}$, $B_{\text{OO}} = 2.76$ Å$^{-1}$, $C_{\text{SiO}} = 133.5381$ eVÅ$^6$, $C_{\text{AlO}} = 73.0913$ eVÅ$^6$, and $C_{\text{OO}} = 175.0$ eVÅ$^6$ (for the Si–Si, Si–Al and Al–Al interactions the latter parameters are all set to zero) [Kramer et al. (1991)].

The Buckingham part of the potential,

$$\phi_B(r) = A_{\alpha\beta} \exp \left( -B_{\alpha\beta} r \right) - \frac{C_{\alpha\beta}}{r^6}$$\hspace{1cm} (2)

has been truncated and shifted to zero at $r_B^c = 5.5$ Å. In order to make the truncated potential, $\phi_{B}^{\text{trunc}}(r)$, differentiable at $r_B^c$ it has been multiplied by a smoothing function of exponential form:

$$\phi_{B}^{\text{trunc}}(r) = \begin{cases} 
\left[ \phi_B(r) - \phi_B(r_B^c) \right] \exp \left( -\frac{d_B}{(r-r_B^c)^2} \right) & r < r_B^c \\
0 & r \geq r_B^c 
\end{cases}$$\hspace{1cm} (3)

with $d_B = 0.05$ Å$^2$. The parameter $d_B$ is chosen such that the exponential in Eq. (3) does not affect the system’s properties. But it smoothens out the cusp at $r_B^c$ which would lead to a discontinuous force at $r_B^c$ and thus to a drift in the total energy in microcanonical MD runs [Allen and Tildesley, 1987]. By the systematic use of smoothing functions as in Eq. (3)
(see also below), we have not encountered an energy drift in any of the microcanonical runs that we have performed in this work.

In the long–ranged Coulomb–part the charges \( q_\alpha e \) (\( e \): charge of an electron) are not the bare ionic charges of ions of type \( \alpha \) but are considered to be effective charges. The charges for silicon and oxygen are set to \( q_{Si} = 2.4 \) and \( q_{O} = -1.2 \), respectively. With the original charge for aluminium, \( q_{Al} = 1.9 \), the unphysical situation of a non–zero net charge results. Only with the additional component phosphorus the system recovers charge neutrality according to the parameter sets in Kramer et al. (1991). We have therefore modified the Kramer potential by using a distance–dependent Al charge as follows:

\[
q_{Al}(r) = \begin{cases} 
\tilde{q}_{Al} [1 + \ln \left( C_{Al} \frac{(r-r_{Al})^2}{1+(r-r_{Al})^2} + 1 \right) ] \exp \left( -\frac{d_{Al}}{(r-r_{Al})^2} \right) & r < r_{Al} \\
\tilde{q}_{Al} & r \geq r_{Al}
\end{cases}
\tag{4}
\]

with \( \tilde{q}_{Al} = 1.8 \). The concept of a “distance–dependent Al charge” should not be taken too literally. We just introduce an additional short–ranged potential to the original one, with a cut–off at \( r = r_{Al} \).

The exponential function in Eq. (4) serves again as a smoothing factor. The parameters in Eq. (4) are adjusted such that the potential is very close to the original one at short distances. At distances \( r \geq r_{Al} \) the Al charge is \( \tilde{q}_{Al} = 1.8 \), thereby producing charge neutrality. For the cut–off radius \( r_{Al} \), the value \( r_{Al} = 6 \, \text{Å} \) is chosen. The parameter \( d_{Al} \) is set to \( 2 \, \text{Å}^2 \) for \( q_{Al}(r) \) in the Al–O interactions and to \( 1.47 \, \text{Å}^2 \) for \( q_{Al}(r) \) in the Al–Al and the Al–Si interactions. Finally, we have chosen \( C_{Al} = 0.0653609 \) for the Al–O interactions and \( C_{Al} = 0.0637977 \) for the Al–Al and Al–Si interactions. The parameters for \( d_{Al} \) and \( C_{Al} \) are slightly different from those reported in Winkler et al. (2004). However, these slight differences are not relevant with respect to the resulting structural and dynamic properties.

From Eq. (4) it becomes obvious that at small distances the potential between the Al (or Si) and the O atoms goes to minus infinity (since the coefficients \( C_{\alpha\beta} \) are positive), i.e. it becomes unphysical. Therefore we have modified the potential at short distances by substituting it by a polynomial continuation that makes the potential repulsive at very short distances:

\[
\phi_{\alpha O}(r) = a_{1,\alpha} + a_{2,\alpha} r + \frac{1}{3} a_{3,\alpha} (r - a_{4,\alpha})^3 \quad r < r_{\text{poly}}^\alpha
\tag{5}
\]

with \( \alpha = \text{Si, Al, O} \). The values for \( a_{1,\alpha} \), \( a_{2,\alpha} \), \( a_{3,\alpha} \), \( a_{4,\alpha} \), and the cut–off radius \( r_{\text{poly}}^\alpha \) are listed in Table II. One may wonder why the polynomial terms in Eq. (5) are appropriate to
describe the interactions at small distances accurately. But even at the highest considered
temperature, \( T = 6000 \text{ K} \), only a negligible number of ion pairs approach each other at
distances \( r < r_{\text{poly}}^{\text{c}} \). Thus, the potentials as given by Eq. (5) are only of technical impor-
tance and do not affect at all the physical properties in the temperature range considered in this
study.

Having described in detail the model potential, we give now the main details of
the simulation runs. Molecular dynamics simulations were done for the two com-
positions 29(Al\(_2\)O\(_3\))197(SiO\(_2\)) (with about 13 mol% Al\(_2\)O\(_3\)) and 65(Al\(_2\)O\(_3\))73(SiO\(_2\)) (with about
47 mol% Al\(_2\)O\(_3\)). In the following, we will abbreviate these compositions as A29S197 and
A65S73, respectively. Both systems were simulated at two different mass densities \( \rho \) to
study how pressure affects structural and dynamic properties. For A29S197, the densities
\( \rho = 2.29 \text{ g/cm}^3 \) and \( \rho = 2.4 \text{ g/cm}^3 \) were chosen, which are slightly below and above the
experimental value at room temperature, \( \rho = 2.36 \text{ g/cm}^3 \) (Morikawa et al., 1982). In the
case of A65S73, the densities \( \rho = 2.35 \text{ g/cm}^3 \) and \( \rho = 2.65 \text{ g/cm}^3 \) were chosen, both of which
are below the experimental value \( \rho = 2.74 \text{ g/cm}^3 \) (Morikawa et al., 1982). In the following,
we refer to runs at low and high density by the abbreviations LD and HD, respectively.

The simulated systems consist of 2208 and 2176 atoms for A29S197 and A65S73, re-
spectively, that sit in a cubic simulation box with periodic boundary conditions in all three
Cartesian directions. The equations of motion were integrated with the velocity form of the
Verlet algorithm, and the Coulombic contributions to the potential and the forces were calcu-
lated via Ewald summation (Binder et al., 2004). The time step of the integration was 1.6 fs.
For each of the four systems (i.e. A29S197 and A65S73 at two different densities each), 13
temperatures were considered in the interval \( 6000 \text{ K} \geq T > 2000 \text{ K} \) (the lowest temperatures
were 2470 K and 2390 K for the LD and HD runs of A29S197, respectively, and 2190 K and
2060 K for the LD and HD runs of A65S73, respectively). The temperature of the systems
was controlled by coupling them to a stochastic heat bath, i.e. by periodically substituting
the velocities of the particles with the ones from a Maxwell–Boltzmann distribution with
the desired temperature. This thermostat has been first proposed by Andersen (1980) who
has shown also that it generates a canonical distribution in phase space. After the system
was equilibrated at the target temperature, we continued the run in the microcanonical
ensemble, i.e. the heat bath was switched off. In order to improve the statistics we have
done eight independent runs at each temperature. At the lowest temperatures, equilibration
runs between 23.4 ns and 42.3 ns real time were done, followed by production runs of the same length. The longest simulations were done for the HD A29S197 system at $T = 2390$ K, where the total simulation time was $2 \times 42.3$ ns (equilibration+production) $\times 8 = 676.8$ ns, corresponding to about 416 million time steps. In addition to the simulations of fully equilibrated melts, we produced glass structures by quenching the systems from the melt to 300 K, followed by relaxation runs of 10,000 time steps at that temperature. Note that the total simulation time of the present study was 48.2 CPU years on an IBM Regatta at the NIC Jülich.

Fig. 1 displays the temperature dependence of the pressure $p$ for the different systems. In the case of the HD samples, $p(T)$ exhibits a minimum which moves to lower temperatures with increasing Al$_2$O$_3$ concentration, namely from about 4300 K in A29S197 to about 2400 K in A65S73. This feature is less pronounced in the LD samples, and it is even absent in the LD sample of A65S73. In agreement with density measurements of aluminium silicate melts around 2000 K, the pressure of the A29S197 model exhibits a relatively weak dependence on temperature. From Fig. 1 one can infer that around 2000 K, the density at ambient pressure is about 2.3 g/cm$^3$. This value is in good agreement with the experimental value of 2.32 g/cm$^3$ at 2000 K for an aluminium silicate melt with 14.82 mol% Al$_2$O$_3$ (Aksay et al., 1979). However, for the Al$_2$O$_3$-SiO$_2$ melt with 47 mol% Al$_2$O$_3$ (which is similar to our A65S73 model), Aksay et al. (1979) obtained a value of 2.62 g/cm$^3$ at 2200 K. At this temperature, one can estimate an ambient pressure density around 2.45 g/cm$^3$ for our simulation model and thus, in the case of the A65S73 model, the density is about 10% smaller than in the corresponding real system.

III. RESULTS

A. Structural properties

In this section, structural properties of the models of A29S197 and A65S73 are investigated. The central issue is to elucidate the interplay between the local chemical ordering around the Al atoms and the IRO that we have recently encountered in a simulation study of AS2 (Winkler et al., 2004).

As we have already mentioned in the Introduction, the local structure of amorphous alu-
In particular, NMR experiments yield detailed information about the Al–O coordination and the occurrence of triclusters. All these experiments have been done at room temperature, i.e., well below the experimental glass transition temperature $T_g$. Therefore, a direct comparison of, e.g., NMR results with those from a computer simulation is not very meaningful, since the glass structures from a MD simulation have a very different thermal history than the experimental ones (which is due to the much shorter time scale that is accessible in a simulation). All one can do is to extrapolate the properties of fully–equilibrated samples at high temperatures (in this study above 2000 K) to temperatures at which the system would fall out of equilibrium on the typical experimental time scale.

Keeping this issue in mind, we discuss now the temperature dependence of the Al–O coordination in the A29S197 and A65S73 models for different coordination numbers $z_{\text{Al–O}}$. The coordination number $z_{\text{Al–O}}$ is defined as the number of O atoms surrounding an aluminium atom within a distance $r \leq r_{\text{cut}}$. For $r_{\text{cut}}$, we have chosen 2.32 Å, which corresponds to the location of the first minimum in the partial pair correlation function of the Al–O correlations. Note that $r_{\text{cut}}$ is significantly larger than the mean distance between an Al and an O atom which is $r_{\text{Al–O}} = 1.67$ Å for our model system. But this difference between $r_{\text{cut}}$ and $r_{\text{Al–O}}$ is normal for a melt structure where the relatively large width of the first peaks in the pair correlation function is due to structural disorder and the thermal motion of the atoms.

Fig. 2 shows the coordination number distribution $P_{\text{Al–O}}(z)$ in a semi–logarithmic plot as a function of inverse temperature for $z_{\text{Al–O}} = 3, 4, 5$. We have not included the results for $z_{\text{Al–O}} = 6$ since six–fold coordinated aluminium atoms are quite rare, i.e., not more than 2% of them are found in each of the considered systems. From our data it is hard to extrapolate to lower temperatures since none of the curves can be described by an Arrhenius law (a straight line in Fig. 2) over a large temperature range. It might even be that, e.g., the curves for $z = 4$ exhibit a maximum at large values of $1/T$, or those for $z = 5$ a minimum. At least it seems that three–fold coordinated Al atoms disappear at low temperature whereas one may expect a significant fraction of five–fold coordinated Al atoms also at low temperature, in particular in the HD A65S73 system. However, Fig. 2 shows that for A29S197, as well as for A65S73, most of the Al atoms are four–fold coordinated by O atoms.

Since five– and six–fold coordinated Al atoms are relatively rare, we expect a large num-
ber of triclusters of the form O–3(Si,Al) in order to yield charge neutrality in the local environment of Al atoms. And indeed, as can be seen in Fig. 3a, the number of triclusters O–3(Si,Al) per Al atom is of the order of one in the whole temperature range that is considered for the different systems. The minimum in the curves for A29S197 around 3000 K can be easily explained by a closer inspection of the data. At high temperature, triclusters with only one or no Al atom are the most frequent ones. But their number strongly decreases with decreasing temperature, whereas the number of triclusters with two or three Al atoms increases with decreasing temperature, thus leading to the minima in Fig. 3a. Fig. 3b displays the number of two–fold rings (i.e. edge–sharing tetrahedra) as a function of temperature. Clearly, there are about 0.4 two–fold rings per Al atom at low temperature. Most of the two–fold rings contain two Al atoms (about 60–80%) or one Al and one Si atom (about 20–40%). The fraction of edge–sharing SiO$_4$ tetrahedra is for all the considered systems of the order of 1% or smaller (of course, this holds only at low temperatures). The O atoms of the two–fold rings are most likely also triclusters, in agreement with our previous study (Winkler et al., 2004 and Tossell and Horbach, 2005).

In our recent work on AS2, we have demonstrated that the different chemical ordering of aluminium and silicon leads to a microphase separation on intermediate length scales of the order of 10–12 Å whereby an Al–O rich network percolates through the Si–O network. These structural correlations are reflected by a prepeak in partial static structure factors at a wavenumber around $q = 0.5 \text{ Å}^{-1}$. Appropriate quantities to study the latter feature are the static concentration–concentration structure factors $S_{c\alpha,c\alpha}(q)$. In the following, we define these quantities and we discuss their behavior in the case of the aluminium silicates considered here.

For the definition of the $S_{c\alpha,c\alpha}(q)$ we follow a paper by Blétry (1976) that generalizes the Bhatia–Thornton formalism for two–component systems to arbitrarily many components. Consider a mixture of $n$ chemical species that contains a total number of $N = \sum_{\alpha=1}^{n} N_{\alpha}$ particles, where $N_{\alpha}$ denotes the number of particles of species $\alpha$. The local number density in reciprocal space for particles of type $\alpha$ is defined as follows (Hansen, 1986):

$$\rho_{\alpha}(\mathbf{q}) = \sum_{k=1}^{N_{\alpha}} \exp(i\mathbf{q} \cdot \mathbf{r}_k)$$

with $\mathbf{q}$ the wavevector and $\mathbf{r}_k$ the position of the $k$'th particle of type $\alpha$. The partial static
structure factors are then given by (Hansen, 1986)

$$S_{\alpha\beta}(q) = \frac{1}{N} \langle \rho_\alpha(q)\rho_\beta(-q) \rangle . \quad (7)$$

Here we assume that the system is isotropic and thus, each of the $S_{\alpha\beta}(q)$ depends only on the magnitude of the wavevector $q$. The functions $S_{\alpha\beta}(q)$ are obviously symmetric, i.e. $S_{\alpha\beta}(q) = S_{\beta\alpha}(q)$, and therefore, there are $n(n+1)/2$ independent partial structure factors. With this definition, Eq. (7), the $S_{\alpha\beta}(q)$ approach in the limit $q \to \infty$ the mean concentration $x_\alpha = N_\alpha/N$ for $\alpha = \beta$ and zero for $\alpha \neq \beta$. We show below that the concentration–concentration structure factors can be written as linear combinations of the partial structure factors $S_{\alpha\beta}(q)$.

The local concentration variables for particles of type $\alpha$ are given by

$$c_\alpha(q) = \rho_\alpha(q) - x_\alpha \sum_{\beta=1}^{n} \rho_\beta(q) . \quad (8)$$

The densities $c_\alpha(q)$ express the local deviation from a homogeneous density distribution of particles of type $\alpha$ and thus, if $\rho_\alpha$ is equal to $N_\alpha/N$ for $\alpha = 1, ..., n$, the variables $c_\alpha$ vanish. The partial structure factors that correspond to the concentration densities $c_\alpha(q)$ are defined in a similar way as the partial structure factors for the number densities:

$$S_{c_\alpha c_\beta}(q) = \frac{1}{N} \langle c_\alpha(q)c_\beta(-q) \rangle . \quad (9)$$

In this case $S_{c_\alpha c_\beta}(q) = S_{c_\beta c_\alpha}(q)$ also holds. Moreover, the functions $S_{c_\alpha c_\beta}(q)$ obey the sum rule

$$\sum_{\beta=1}^{n} S_{c_\alpha c_\beta}(q) = 0 \quad (10)$$

which follows directly from the definition, Eq. (9).

In the case of $n=2$ one has $c_1 = -c_2$, and thus $S_{c_1 c_1}(q) = S_{c_2 c_2}(q)$. Furthermore, Eq. (10) yields $S_{cc} \equiv S_{c_1 c_1}(q) = -S_{c_1 c_2}(q)$. This means that for $n=2$ there is only one relevant structure factor $S_{cc}(q)$ for the concentration density correlations, and this quantity can be written as a linear combination of the partial structure factors as given by Eq. (7),

$$S_{cc}(q) = x_2^2 S_{11}(q) + x_1^2 S_{22}(q) - 2x_1x_2 S_{12}(q) . \quad (11)$$

For $q \to \infty$ this function approaches $x_1x_2$, which is expected for an ideal mixture.
Slightly more complicated is the case $n = 3$. Now the functions $S_{ca,c3}(q)$ with $\alpha = \beta$ are related to the partial number density structure factors as follows:

$$S_{c1c1}(q) = (x_2 + x_3)^2S_{11}(q) - 2x_1(x_2 + x_3) [S_{12}(q) + S_{13}(q)] + x_1^2 [S_{22}(q) + 2S_{23}(q) + S_{33}(q)] ,$$  \hfill (12)

$$S_{c2c2}(q) = (x_1 + x_3)^2S_{22}(q) - 2x_2(x_1 + x_3) [S_{12}(q) + S_{23}(q)] + x_2^2 [S_{11}(q) + 2S_{13}(q) + S_{33}(q)] ,$$  \hfill (13)

$$S_{c3c3}(q) = (x_1 + x_2)^2S_{33}(q) - 2x_3(x_1 + x_2) [S_{13}(q) + S_{23}(q)] + x_3^2 [S_{11}(q) + 2S_{12}(q) + S_{22}(q)] .$$  \hfill (14)

Each of the $S_{ca,c3}(q)$ with $\alpha \neq \beta$ can be written as a linear combination of the three $S_{ca,ca}(q)$,

$$S_{c1c2}(q) = \frac{1}{2} [S_{c3c3}(q) - S_{c1c1}(q) - S_{c2c2}(q)] ,$$  \hfill (15)

$$S_{c1c3}(q) = \frac{1}{2} [S_{c2c2}(q) - S_{c1c1}(q) - S_{c3c3}(q)] ,$$  \hfill (16)

$$S_{c2c3}(q) = \frac{1}{2} [S_{c1c1}(q) - S_{c2c2}(q) - S_{c3c3}(q)] .$$  \hfill (17)

Thus, the latter functions do not contain any additional information, and so we consider only the correlation functions as given by Eqs. (12)–(14) in the following.

The three functions $S_{ca,ca}(q)$ are shown in Fig. 4 for A29S197 and in Fig. 5 for A65S73. Their behavior is qualitatively very similar in the two systems: In both cases, the functions exhibit a pronounced peak around $q_1 = 2.72$ Å$^{-1}$. This peak indicates the chemical ordering on local length scales: Between nearest cation neighbors there is always a shell of oxygen atoms, i.e. strong fluctuations occur on length scales of the order of the nearest cation–oxygen distance (note that $2\pi/q_1 = 2.3$ Å corresponds approximately to the location of the first minima in the partial pair correlation function of Si–O and Al–O correlations). Apart from the peak at $q_1$, in $S_{cAcAl}(q)$ and $S_{cScS}(q)$, a pronounced prepeak is found around $q_p = 0.5$ Å$^{-1}$, whereas in $S_{cOcO}(q)$, such a prepeak is absent. This behavior of the different concentration–concentration functions is similar to our recent result for AS2. There, we have related the prepeak to a microsegregation into Al–O rich and Si–O rich regions on the length scale of about 1 nm. Indeed, in the snapshots of Figs. 4 and 5 one can clearly identify Al–O rich percolating regions in the Si–O network. It is remarkable that the location of the prepeak at $q_p$ seems to depend neither on the Al–O concentration nor on the pressure (at least for the pressures that are observed at the two densities considered for each system).
This finding is contrary to the behavior of structural features on local length scales where we have found a strong dependence on temperature, pressure, and Al$_2$O$_3$ concentration (see above).

The determination of $S_{\text{csc}}(q)$ from scattering experiments is very difficult since it requires the measurement of partial structure factors $S_{\alpha\beta}(q)$. For silicates, this has been possible only for a few examples, e.g. a calcium silicate glass (Gaskell et al., 1992). In the case of aluminium silicate glasses, total structure factors have been measured for different compositions using X–ray scattering by Morikawa et al. (1982) and by Okuno et al. (2005). Their results can be directly compared to simulation data. To this end, an X–ray scattering structure factor $S_X(q)$ has to be calculated from the partial structure factors, $S_{\alpha\beta}(q)$, by weighting them with X–ray form factors,

$$S_X(q) = \frac{N}{\sum_{\alpha} N_{\alpha} f_{\alpha}^2(s)} \sum_{\alpha\beta} f_{\alpha}(s) f_{\beta}(s) S_{\alpha\beta}(s)$$

with $\alpha, \beta = \{\text{Si, Al, O}\}$. The form factors $f_{\alpha}(s)$ depend on the wavenumber $q$ via $s = q/(4\pi)$. Note that the $f_{\alpha}(s)$ are taken from the literature (International Tables, 1974). Fig. 6 shows the “reduced” X–ray structure factor $q(S_X(q) - 1)$ in comparison to experimental results. As we recognize from the figures a good agreement is obtained between simulation and experiment both for A29S197 and A65S73. For the latter system, two experimental data sets are available and, as we see in Fig. 6b, the simulation curve is closer to the more recent result of Okuno et al. (2005).

As we can infer from Fig. 6 no prepeak is visible around 0.5 Å$^{-1}$ in the reduced X–ray structure factor. Note that this is also the case for $S_X(q)$ itself. This is due to the fact that the main contribution to $S_X(q)$ comes from $S_{\text{O–O}}(q)$ which does not exhibit a prepeak at 0.5 Å$^{-1}$. Also in neutron scattering experiments, one has no access to partial structure factors for aluminium silicates (due to the lack of appropriate isotopes). Thus, the accessible total structure factor is dominated by the O–O correlations and will hardly show a prepeak. It remains a challenge to the experimentalists to verify the presence of the latter prepeak in aluminium silicates.
B. Dynamical properties

We have seen that the considered aluminium silicates exhibit a chemical ordering on length scales of about 1 nm which can be described by a microphase separation into an Al rich and a Si rich network structure. In our recent study of AS2 (Winkler et al., 2004), we have shown that the addition of Al₂O₃ to a silica melt enables a much faster selfdiffusion of all components compared to pure SiO₂. This is also the case for A29S197 and A65S73 which we consider here. In Fig. 7a, the selfdiffusion constants of our systems (for the LD samples) are displayed on a semilogarithmic scale as a function of inverse temperature. Clearly, the diffusion constants increase with increasing Al₂O₃ concentration (note that the diffusion constants of AS2 fall between the curves shown in Fig. 7a, as expected; see Winkler et al., 2004). In Fig. 7b, the oxygen diffusion constants D₀ are shown, now also with the results for the HD systems. We can infer from this figure that an anomalous behavior of D₀ with respect to pressure emerges: The diffusion becomes faster with increasing pressure. This anomaly is well–known in many different “simple” network forming glasses such as SiO₂, H₂O, etc. (see, e.g., Shell et al., 2002 and references therein). For SiO₂, this anomaly has been related to structural changes that occur with increasing pressure (Angell et al., 1982; Kubicki and Lasaga, 1988; Rustad et al., 1990; Barrat et al., 1997): The network structure changes gradually from a four–fold coordination of silicon atoms at low pressure to an imperfect five–fold coordination at intermediate pressure and eventually to a six–fold coordination at very high pressure (note that in the latter regime the selfdiffusion constants decrease with increasing pressure). Intuitively, the anomalous diffusion can be understood as follows: In the tetrahedral network structure there are not as many possibilities for the formation of local defects as in a higher–coordinated network. Since these defects facilitate diffusion in a network structure (see, e.g., Horbach and Kob, 1999), the particles in a higher–coordinated network tend to exhibit a faster diffusion than in a tetrahedral network.

But what are the defects that facilitate the diffusion in the Al₂O₃–SiO₂ networks? Important structural units might be triclusters and five–fold coordinated silicon atoms, both of which are more frequent in the HD systems (see above). Thus, they might be responsible for the higher diffusion constants, as compared to the LD systems.

As we see in Fig. 7a, silicon is the slowest component and aluminium the fastest component of the diffusing species. In order to quantify the temperature dependence of the
different diffusion constants, we show in Fig. 8 the ratios $D_{Si}/D_{O}$ and $D_{Al}/D_{O}$ as a function of temperature for the different systems. It is remarkable that $D_{Si}/D_{O}$ depends only weakly on density and composition (note that also $D_{Si}/D_{O}$ for BKS–SiO$_2$ would fall roughly on top of the corresponding curves in Fig. 8, see Winkler et al., 2004). This shows that the diffusion of silicon and oxygen is intimately connected with each other. On the other hand, $D_{Al}/D_{O}$ nearly approaches the constant value of one in A65S73 in the considered temperature range (at least for the HD system). This might be due to the fact that in the Al$_2$O$_3$ rich system, A65S73, oxygen diffusion steps occur mainly in the vicinity of Al rich regions, in particular near triclusters, whereas in A29S197, also the O diffusion in the slow Si rich regions is important. This issue has to be clarified in future studies.

IV. SUMMARY

Large scale molecular dynamics computer simulations were used to study the structure and diffusion dynamics of the aluminium silicates A29S197 and A65S73. The microscopic interactions between the ions were described by a simple pair potential proposed by Kramer et al. (1991). In this work, we have demonstrated that this model potential yields good agreement with available experimental data such as the mass density and the X–ray structure factor. However, recent NMR experiments (Sen and Youngman, 2004; Stebbins et al., 2005) observed a significant number of six–fold coordinated Al atoms already at small Al$_2$O$_3$ concentrations. By contrast, our simulation model predicts a vanishing number of AlO$_6$ units in the glass structure. This might be realistic for A29S197 but not for the Al–rich A65S73 system. In the case of five–fold coordinated Al atoms, an extrapolation from the melt data to the experimental glass transition temperature is not easy (see above). However, as a typical local structure, we find tricluster O atoms in conjunction with two–fold rings. Recent Hartree–Fock calculations that used small clusters from our recent MD simulation of AS2, found evidence that the combination of triclusters with two–fold rings is indeed realistic (Tossell and Horbach, 2005). It should be emphasized that this finding refers only to binary alumino silicates. The local structure may be very different in ternary alumino silicates that contain also charge–balancing cations such as calcium or alkali ion species.

The different local ordering of Al and Si atoms leads to a microsegregation on length scales of about 1 nm. This structural feature is reflected in a prepeak in static concentration–
concentration correlation functions (and also in partial static structure factors). The location of the prepeak is around 0.5 Å⁻¹, independent of Al₂O₃ concentration, pressure, and the details of the local structure in the considered systems. This remarkable result shows that according to our simulation model, the formation of Al rich channels that percolate through the Si–O network is a central feature of the chemical ordering in the system Al₂O₃–SiO₂. This is a prediction of our simulation that could be tested by scattering experiments. Prepeaks in other silicates, that have a similar origin as the one found in our aluminium silicate models, have been successfully identified in recent neutron scattering experiments (see Gaskell et al., 1991; Meyer et al., 2002; Meyer et al., 2004; Kargl and Meyer, 2005).

Our analysis of the diffusion dynamics suggests that triclusters are important for the mass transport in aluminium silicates. Moreover, we have found subtle differences in the dependence of the three diffusion constants on temperature (e.g. the ratio $D_{Al}/D_O$ is essentially one for the HD A65S73 system, while it increases in the case of the A29S197 systems). It would be interesting to see whether these features can be understood in the framework of mode coupling theory. Work in this direction is in progress.

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Fig. 1: Pressure as a function of temperature at the indicated compositions and densities. Note that the points at 300 K are far below the glass transition temperature of the simulations, which is around 2000 K (see text).

Fig. 2: Temperature dependence of $P_{Al-O}(z)$ for $z = 3, 4, 5$ as indicated, for a) A29S197 and b) A65S73.

Fig. 3: This plot shows the amount of triclusters, O–3(Si,Al), and 2–fold rings as a function of temperature: a) Number of triclusters and b) number of 2–fold rings per Al atom for the different systems as indicated.

Fig. 4: Structure factors $S_{c_{a}c_{a}}(q)$ for A29S197 at the temperature $T = 2470$ K and the different densities as indicated, a) $S_{c_{Si}c_{Sl}}(q)$, b) $S_{c_{Co}c_{O}}(q)$, and c) $S_{c_{Al}c_{Al}}(q)$ [see Eqs. (12–(14)) for the definition of $S_{c_{a}c_{a}}(q)$]. Also shown is a snapshot at $T = 300$ K which illustrates the intermediate range order as reflected in the prepeak around $q = 0.5 \AA^{-1}$. The large white spheres are the silicon atoms, the large black spheres are the aluminium atoms, and the small black spheres are the oxygen atoms. Note that the size of the spheres does not correspond to the actual size of the atoms.

Fig. 5: The same as in Fig. 4 but now for A65S73. The temperatures are $T = 2190$ K and $T = 2060$ K for the low and the high density, respectively.

Fig. 6: Reduced X–ray scattering structure factor $q(S_{X}(q) − 1)$ as calculated from the simulation using Eq. (18) in comparison to experimental results by Morikawa et al. (1982) and Okuno et al. (2005) (dashed lines), for a) A29S197 and b) A65S73.

Fig. 7: Arrhenius plots of the selfdiffusion constants $D_{a}$, a) for Si, Al, and O for the different compositions at low densities and b) for O for all considered systems as indicated.

Fig. 8: Temperature dependence of the ratios of the diffusion constants, $D_{a}/D_{b}$ ($\alpha, \beta = Si, Al, O$), for the different systems as indicated.
VII. LIST OF TABLES

| α − O | $a_{1,\alpha}$ [eV] | $a_{2,\alpha}$ [eV/Å] | $a_{3,\alpha}$ [eV/Å$^3$] | $a_{4,\alpha}$ [Å] | $r_{\text{poly}}$ [Å] |
|-------|------------------|------------------|------------------|------------------|------------------|
| Si–O  | -23.96027        | -2.85441         | -50.0            | 1.41590          | 1.276            |
| Al–O  | -87.62405        | 26.72474         | -3.0             | 4.49012          | 1.28             |
| O–O   | -30590.38        | 90.38499         | -0.1             | 97.25877         | 1.9547           |

TABLE I: Parameters for the polynomial continuation at small $r$ that prevents the potentials from going to minus infinity for $r \to 0$. 
VIII. LIST OF FIGURES
FIG. 1:

FIG. 2:
FIG. 3:

FIG. 4:
FIG. 5:

FIG. 6:
FIG. 7:

FIG. 8:
-2.0 -1.0 0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0

A29S197, $\rho = 2.29\text{g/cm}^3$

A29S197, $\rho = 2.40\text{g/cm}^3$

A65S73, $\rho = 2.35\text{g/cm}^3$

A65S73, $\rho = 2.65\text{g/cm}^3$