Structure of Liquid and Glassy Oxides and Silicates up to Extreme Conditions

S. Jahn, J. Stefanski, C. Prescher

published in

NIC Symposium 2018
K. Binder, M. Müller, A. Trautmann (Editors)

Forschungszentrum Jülich GmbH,
John von Neumann Institute for Computing (NIC),
Schriften des Forschungszentrums Jülich, NIC Series, Vol. 49,
ISBN 978-3-95806-285-6, pp. 333.
http://hdl.handle.net/2128/17544

Structure of Liquid and Glassy Oxides and Silicates up to Extreme Conditions

Sandro Jahn, Johannes Stefanski, and Clemens Prescher

Institut für Geologie und Mineralogie, Universität zu Köln,
Zülpicher Str. 49b, 50674 Köln, Germany
E-mail: s.jahn@uni-koeln.de

Melts and glasses are important geological and technological materials. Knowledge of their structure is the key to understand their physical and thermodynamic properties from an atomic-scale perspective. However, the development of structure models for melts and glasses is still challenging due to the complex dependence on pressure, temperature and chemical composition. Combined experimental and computational investigations are a promising approach to achieve progress in this field. Here, we present results of some recent molecular modelling studies of complex oxide and silicate melts and glasses. The first example is concerned with the structural origin of the glass-forming ability of calcium aluminate melts. Next, we discuss the structural evolution of SiO_2 glass up to very high pressures. Finally, a computational method to predict trace element partitioning between two immiscible melts is critically assessed. All of these computational studies are motivated by experiments and require high performance computing resources.

1 Introduction

The structure of oxide and silicate melts and glasses is of great interest in physics, materials and Earth sciences but also for industrial applications. Their physical properties strongly influence magmatic processes ranging from the Earth's surface to its deep interior and from its early history to the present day. Glassy materials have a wide range of applications from window glasses to the immobilisation of radioactive waste. The relation between the atomic structure of a melt or glass and its physical or chemical properties has been subject to intense research for decades but it is still a challenging task. In contrast to crystalline materials, glasses and melts do not possess a long-range structural order and the local or short-range order is much more diverse and determined by statistics. The addition of chemical components even increases the structural complexity. Variation in pressure and temperature leads to a continuous change in the structure, which is also different from crystals where structural transitions occur at discrete state points.

Experimentally, the structure of melts and glasses is often studied using x-ray or neutron diffraction methods. The Fourier transformation of the measured structure factor yields the radial distribution function $g(r)$, a radially averaged function of atomic density fluctuations as a function of distance r from a central atom. For systems consisting of more than one chemical element $g(r)$ is an average of partial radial distribution functions $g_{ij}(r)$ weighted by the scattering length and the concentration c of elements i and j. $g_{ij}(r)$ is defined as

$$g_{ij}(r) = \frac{1}{c_i c_j \rho_0 N} \left\langle \sum_{a=1}^{N_i} \sum_{b=1}^{N_j} \delta(\mathbf{r} - (\mathbf{r}_a - \mathbf{r}_b)) \right\rangle \tag{1}$$

where N is the total number of atoms, N_i is the number of atoms of element i and ρ_0 is the atomic number density. $\mathbf{r}_a$ and $\mathbf{r}_b$ are atomic position vectors of atoms a and b, $\mathbf{r}$ is a distance vector with length r. δ is the Kronecker delta.

For chemically simple systems (not more than two to four different elements) the integration over the first peaks of $g(r)$ provides information about average nearest neighbour distances and coordination numbers. However, the three-dimensional structure of the melt or glass cannot be reconstructed from the experiment. Furthermore, the x-ray scattering power for the light major elements of natural silicate melts (Si, Al, Mg, O) is very similar and interpretation of the total scattering function is complicated due to the overlap of the contributions from different ion pairs, e.g. Al-O and Mg-O. Hence, diffraction methods are often not element specific enough and other experimental approaches such as x-ray absorption spectroscopy, Raman spectroscopy or NMR spectroscopy may have to be employed in addition to obtain a comprehensible information about the glass or melt structure. Finally, experiments at high temperature and/or high pressure add additional challenges.

Molecular modelling, e.g. using molecular dynamics simulations, in combination with supercomputing power has become a powerful approach to complement and interpret experimental data to resolve the structure of disordered materials. The accuracy of the predicted structure depends on the atomic interaction potential and on the ability of the simulation to reach an equilibrium state (or in the case of glasses a relaxation state similar to the experiment) with a finite simulation cell (typically 10^2 to 10^4 atoms) and in a finite simulation time (typically 10^{-11} to 10^{-8} seconds). While classical interaction potentials are computationally cheap and allow simulations of larger systems over longer times, they generally have a more limited range of applicability in the description of chemical bonding than computationally much more expensive quantum-mechanical (*ab initio*) methods. In our research on melts and glasses we perform *ab initio* molecular dynamics simulations on high performance supercomputers such as JUQUEEN or JURECA. In parallel we develop advanced classical interaction potentials for classical molecular dynamics simulations. Subsequently, the structure models obtained from both approaches are assessed by comparison to experimental data. Having obtained confidence in the predicted simulation model we extend the simulations to experimentally unexplored conditions and/or derive physical and thermodynamic properties. In the following we present some details about the computational approach and discuss a few examples of our recent research on melts and glasses using high performance computing resources.

2 Methods

Ab initio simulations were performed in the framework of density-functional theory (DFT) using a planewave basis set as implemented in the CPMD[1] or CP2K[2] codes. The exchange-correlation functional was treated in the generalised gradient approximation according to Perdew *et al.*[3] and norm-conserving pseudopotentials were employed. The planewave cut-off was chosen between 80-160 Ry depending on the specific configuration. Car-Parrinello or Born-Oppenheimer molecular dynamics simulations were performed with time steps between 0.1 and 1.0 fs. Typical system sizes ranged from 100 to 300 atoms and production runs between 10 and 50 picoseconds. For simulations of the melts at ambient pressure, temperatures of at least 2500 K were chosen to allow for breaking and formation of strong bonds, e.g. Si-O[4], on the timescale of the simulation. Glasses or melts of SiO_2 at very

high pressures were equilibrated at 4000 K to allow for sufficient dynamics and assuming that the structural difference between the melt and the glass was small compared to the pressure-induced changes. *Ab initio* molecular dynamics simulations are computationally very demanding and require the use of high performance supercomputers such as JUQUEEN, where the CPMD code shows reasonable scaling up to bg_size = 1024 (16384 cores). CP2K scales reasonably well up to a bg_size = 512 if the farming option is employed. On JURECA both codes scale well up to a few hundred cores.

Classical molecular dynamics simulations were made on JURECA using advanced polarisable ion potentials[5,6] as implemented in the CP2K code[2]. The interaction potentials were optimised by fitting forces, ionic dipoles and quadrupoles as well stress tensors predicted by the classical force field to corresponding DFT data for a number of reference structures[5]. The molecular dynamics simulation cells representing the oxide and silicate melts and glasses contained typically between 1000 and 2000 ions. Production runs lasted for at least 50 to 100 picoseconds with a time step of 1.0 fs. Glasses were produced from the melts (equilibrated at 2500 K) by slow cooling with a quench rate of 4×10^{12} K s^{-1}. CP2K simulations using the classical potential show a good scaling behaviour on JURECA of up to at least 72 cores.

3 Structure of Calcium Aluminate Melts and Glasses

The glass-forming ability of silicate and oxide melts depends on the amount of network-forming anions. While pure alumina (Al_2O_3) melts are not glass-forming, the addition of Ca increases the O:Al ratio and facilitates the formation of an AlO_4 network. Recently, we finished a combined experimental and simulation study of the structure of $Ca_3Al_2O_6$ melt[7]. $Ca_3Al_2O_6$ is at the Ca-rich end of the glass-forming composition range such that glasses are only formed in container-less levitation experiments. The method of isotopic substitution in conjunction with neutron diffraction experiments were used to elucidate specifically the Ca coordination environment in the melt.

Complementary to the experiment we performed both classical and first-principles molecular dynamics simulations of this liquid. Structural models from the molecular dynamics simulations were refined using reverse Monte Carlo simulations. The latter did not change the structure significantly, which provided confidence in the molecular dynamics results. Also, classical and first principles simulations yielded a consistent structural model. Our simulation results show that, although significantly depolymerised, liquid $Ca_3Al_2O_6$ is largely composed of AlO_4 tetrahedra forming an infinite network with a slightly higher fraction of bridging oxygen atoms than expected for the composition (Fig. 1, left). With increasing Ca concentration, the AlO_4 tetrahedral network gets less connected. From the simulation results we concluded that the glass-forming ability is closely related to a percolation threshold at which the glass can no longer support the formation of an infinitely connected AlO_4 network. Calcium-centred polyhedra exhibit a wide distribution of four- to sevenfold coordinated sites, with higher coordinated calcium preferentially bonding to bridging oxygens (Fig. 1, right).

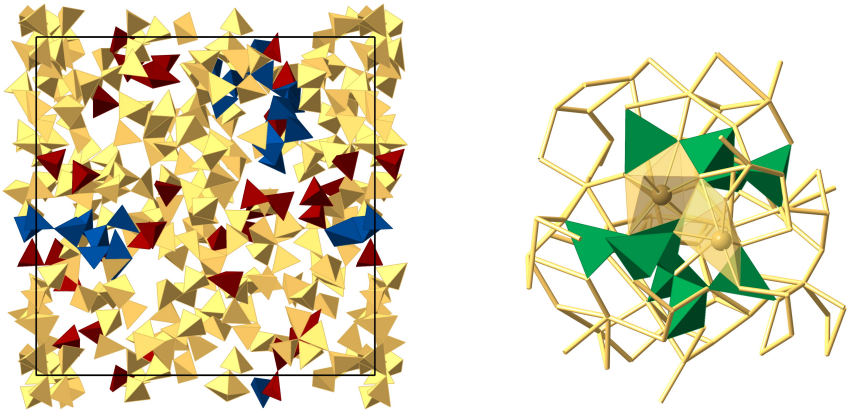

Figure 1. Snapshots from classical molecular dynamics simulations of $Ca_3Al_2O_6$ melt at 2500 K. The left figure shows the infinite network of corner-sharing AlO_4 tetrahedra (yellow) from which small clusters (blue) and isolated tetrahedra (red) are excluded. The right figure shows a typical Ca environment in 5- and 6-fold coordination (yellow) connected to AlO_4 tetrahedra (green). Figures were modified from Drewitt *et al.*[7].

4 SiO_2 Glass at Very High Pressures

Silicate melts have played an important role on Earth throughout its entire history. Magmatism and volcanic activity are well known phenomena but even today it is suspected that silicate melt pockets exist at the core-mantle boundary, i.e. at almost 3000 km depth . Due to the high pressure (about 136 GPa) the structures of these melts must be very different from those of ambient pressure melts. Even higher pressures are expected in the interior of larger planetary bodies. From high pressure phase transitions of crystalline silicates it is known that the coordination of Si changes from tetrahedral to octahedral between 10 and 25 GPa. In melts and glasses a continuous transition from 4-fold to 6-fold is observed in the pressure range from 15 to 40 GPa. The evolution of silicate melt structures at pressures above 100 GPa has remained elusive for a long time.

Very recently, we succeeded to perform the first successful x-ray diffraction study of SiO_2 glass up to pressures of 172 GPa[8]. The experiments showed that above 50 GPa the coordination of Si increases continuously above 6-fold to reach an average of 6.8 at the highest experimental pressure. *Ab initio* molecular dynamics simulations support this observation and predict a further increase in Si coordination upon further compression. In Fig. 2 (left) we show the evolution of the Si-O radial distribution function with increasing mass density. It is interesting to note that the Si-O nearest neighbour distance initially increases with increasing pressure up to about 30 to 40 GPa, which indicates that compression is mainly driven by increasing the coordination number. At higher pressures compression is also accompanied by shortening of Si-O bonds. A snapshot of the SiO_2 glass structure at a density of 7.0 g/cm^3 with a mean Si coordination of 7.3 is shown in Fig. 2 (right).

To rationalise the structural change beyond 6-fold coordinated Si we use the concept of oxygen-packing fraction[9]. The maximum packing fraction of a close packed structure

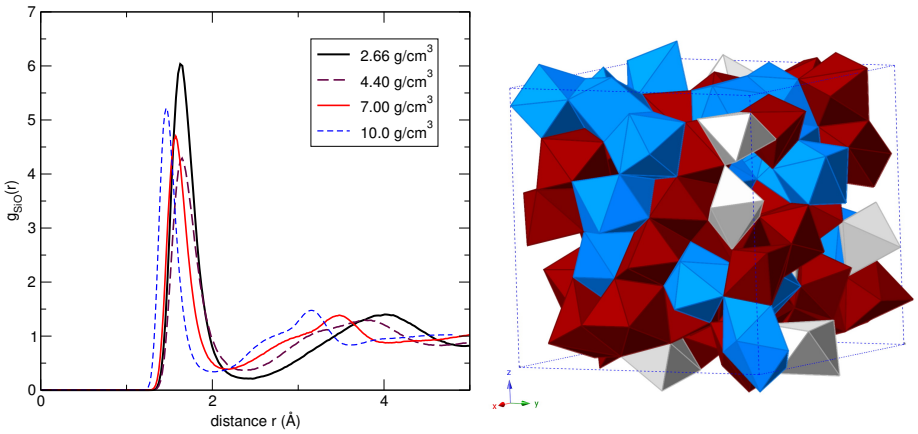

Figure 2. Si-O radial distribution functions of SiO_2 glass/melt at 4000 K as a function of density from *ab initio* molecular dynamics simulations (left). The lowest two densities correspond to those of the crystalline polymorphs quartz and stishovite. Increasing pressure first leads to a small increase of the nearest neighbour Si-O distance while at very high pressures (above 40 GPa) the Si-O distance decreases. The figure on the right shows a snapshot of the SiO_2 glass with a density of 7.00 g/cm^3 and a mean Si coordination of 7.3. Coordination polyhedra are coloured grey for SiO_6, red for SiO_7 and blue for SiO_8.

of spheres is about 0.74. Assuming oxygens are close packed the Si atoms have to occupy tetrahedral or octahedral interstitial sites, the latter being larger and thus preferred at high pressure. At very high pressure, the oxygen ions are increasingly compressed and the size of the much less compressible Si becomes significant. In a limiting scenario both ions reach the same size and form a close packed structure of Si and O atoms with a oxygen-packing fraction of only 2/3 of 0.74 ($= 0.49$). Thus, increasing the Si coordination above 6-fold leads to a decrease in oxygen-packing fraction. This picture has been confirmed by both our experiments and our simulations[8].

5 Prediction of Trace Element Partitioning between Silicate Melts

The (re-)distribution of chemical elements, which happens in the course of many geological processes, is determined by thermodynamics, i.e. by small differences in the Gibbs free energy due to different coordination environments in different phases. A measure of the element distribution between two phases is the partition coefficient $D_X^{\alpha/\beta}$ that is expressed as the ratio of concentrations of the element X in one phase (α) relative to another phase (β). For a quantitative understanding of this problem, a relation is sought between the measured partition coefficients and the molecular structure and energetics of the different phases. While the structure of the crystalline phases is usually well known and respective partition coefficients are well described by the empirical lattice strain model[10], the treatment of the energetics in disordered materials (melts, glasses, fluids) is much less obvious. So far, very simple approximations were made to account for the influence of the fluid or the melt on partitioning, or the latter was ignored at all. However, some experimental studies show a strong dependence of the partition coefficient of some trace elements (especially rare earth elements) between mineral and melts on the melt composition[11,12].

Our goal is to develop an efficient computational method to predict from first principles element partition coefficients at geologically relevant conditions including disordered phases. We combine electronic structure calculations with less expensive classical potential simulations to establish the technique and to explore the accuracy needed to obtain reliable results. Energetic differences of element exchange between different phases are obtained using the method of thermodynamic integration. The major goal of this project is to understand (and predict) why the partition coefficients of some elements depend strongly on melt composition whereas for other elements they do not. Results of our pilot studies have just been published[13,6] but there remains a lot to do to make such predictions more accurate. Here, we summarise our recent work on trace element partitioning between different (immiscible) silicate melts.

For the study of trace element partitioning a single trace element atom, e.g. of yttrium, was introduced into the classical or the *ab initio* melt. The alchemical transmutation method of thermodynamic integration was used to evaluate the equilibrium constant of an exchange reaction between two melt phases whereby a trace element cation (e.g. Y^{3+}) was exchanged with a main element cation (e.g. Al^{3+}). An exemplary reaction would be the exchange of Al and Y between a gabbro and granite melt:

$$Y^{3+}_{granite} + Al^{3+}_{gabbro} \rightleftharpoons Al^{3+}_{granite} + Y^{3+}_{gabbro} \tag{2}$$

This reaction was split into two separate sub-reactions. In each melt the trace element atom was transmuted into the main element atom (or vice versa) along the reaction path λ with typically three intermediate steps ($\lambda = 0.25, 0.5, 0.75$) to obtain the free energy difference ΔF

$$\Delta F = \int_0^1 \left\langle \frac{\partial V_\lambda}{\partial \lambda} \right\rangle_\lambda d\lambda = \int_0^1 \langle V_{Al} - V_Y \rangle_\lambda d\lambda \tag{3}$$

$V_{Al} - V_Y$ is the difference in total energy when occupying the exchange site with one element or the other . The angular brackets indicate the average over time (see example in Fig. 3).

At room pressure the Gibbs energy difference ΔG is well approximated by ΔF and thus the Gibbs energy difference of the exchange reaction is then readily obtained by

$$\Delta G_{exchange} = \Delta F^{Y \rightarrow Al}_{granite} - \Delta F^{Y \rightarrow Al}_{gabbro} \tag{4}$$

The equilibrium constant is defined as

$$K_{exchange} = exp\left(-\frac{\Delta G_{exchange}}{RT}\right) \tag{5}$$

Assuming similar activities of the elements in both melts and insignificant partitioning of the main element, $K_{exchange}$ is a good approximate of the trace element partition coefficient $D_Y^{gabbro/granite}$. In the example shown in Fig. 3, we determined an yttrium partition coefficient of four between a gabbro and a granite melt, i.e. yttrium prefers to partition into the less polymerised melt. This result from classical simulations is in good agreement with an experimental value of 9.3, which was measured at a lower temperature (1450 K)[12]. So far, the *ab initio* simulations yield a lower partition coefficient of about one at a temperature of 3000 K. Further systematic studies of the various parameters (interaction potential, pressure, temperature, finite size and simulation time effects, etc.) are needed to understand

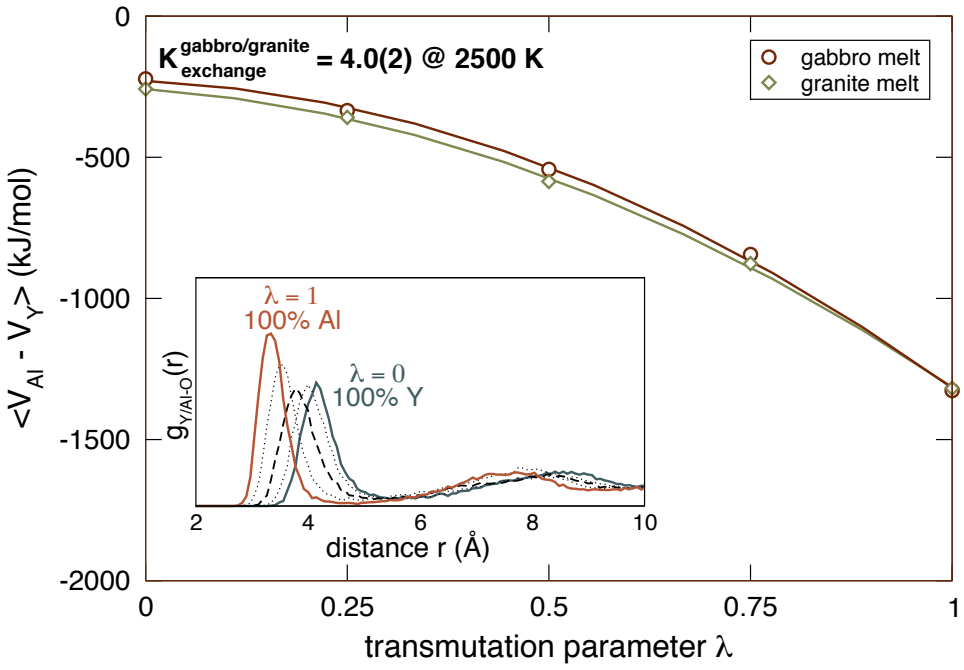

Figure 3. Average energy difference for different transmutation states during exchange of Y and Al in two different melts based on classical molecular dynamics simulations. The area between the two curves corresponds to the free (or Gibbs) energy difference of the exchange reaction as explained in the text. The inset shows the evolution of the radial distribution function between the exchanged atom and oxygen atoms during transmutation (figure modified from Wagner *et al.*[6]).

this difference and to evaluate the predictive power and possible accuracy of our modelling approach.

6 Concluding Remarks

Ab initio and classical molecular dynamics simulations provide unique insight into the structure of complex oxide and silicate melts and glasses. Furthermore, they open new perspectives for linking structural to physical and thermodynamic properties of these materials. Understanding these relations is extremely useful for designing materials with desired properties but also to interpret observations in nature and from experiments. In the Earth science context these computational approaches, which are only possible thanks to the availability of high performance computing facilities, have the potential to reveal the atomic-scale mechanisms for many geological processes that happen on different time and length scales and that are still insufficiently understood. Furthermore, they are capable to predict properties at conditions that are not (yet) accessible by experiments.

Acknowledgements

We would like to thank former group members and experimental collaborators, especially Johannes Wagner and James Drewitt for their contributions to this work. We acknowledge the Gauss Centre for Supercomputing (GCS) and the John von Neumann Institute for Computing (NIC) for providing computing time on the supercomputers JUQUEEN and JURECA at Jülich Supercomputing Centre (JSC). Part of this work was supported by the Helmholtz graduate school GEOSIM.

References

1. D. Marx and J. Hutter, *Ab initio molecular dynamics: Theory and implementation*, in: Modern Methods and Algorithms of Quantum Chemistry, NIC Series Vol. 1, J. Grotendorst (Ed.), 301–449, 2000.
2. CP2K, `http://cp2k.berlios.de/`.
3. J. P. Perdew, K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple*, Phys. Rev. Lett., **77**, 3865–3868, 1996.
4. G. Spiekermann, M. Wilke, and S. Jahn, *Structural and dynamical properties of supercritical H_2O-SiO_2 fluids studied by ab initio molecular dynamics*, Chem. Geol., **426**, 85–94, 2016.
5. S. Jahn and P. A. Madden, *Modeling Earth materials from crustal to lower mantle conditions: A transferable set of interaction potentials for the CMAS system*, Phys. Earth Planet. Int., **162**, 129–139, 2007.
6. J. Wagner, D. Künzel, V. Haigis, and S. Jahn, *Trace element partitioning between silicate melts - a molecular dynamics approach*, Geochim. Cosmochim. Acta, **205**, 245–255, 2017.
7. J. W. E. Drewitt, A. C. Barnes, S. Jahn, S. C. Kohn, M. J. Walter, A. N. Novikov, D. R. Neuville, H. E. Fischer, and L. Hennet, *Structure of liquid tri-calcium aluminate*, Phys. Rev. B, **95**, 064203, 2017.
8. C. Prescher, V. B. Prakapenka, J. Stefanski, S. Jahn, L. B. Skinner, and Y. Wang, *Beyond 6-fold coordinated Si in SiO_2 glass at ultrahigh pressures*, PNAS, 2017, doi:10.1073/pnas.1708882114.
9. A. Zeidler, P. S. Salmon, and L. B. Skinner, *Packing and the structural transformations in liquid and amorphous oxides from ambient to extreme conditions*, PNAS, **111**, 10045–10048, 2014.
10. J. Blundy and B. Wood, *Prediction of crystal-melt partition coefficients from elastic moduli*, Nature, **372**, 452–454, 1994.
11. S. Prowatke and S. Klemme, *Effect of melt composition in the partitioning of trace elements between titanite and silicate melt*, Geochim. Cosmochim. Acta, **69**, 695–709, 2005.
12. M. W. Schmidt, J. A. D. Connolly, D. Günther, and M. Bogaerts, *Element Partitioning: The Role of Melt Structure and Composition*, Science, **312**, 1646–1650, 2006.
13. D. Künzel, J. Wagner, and S. Jahn, *Ni partitioning between metal and silicate melts: An exploratory ab initio molecular dynamics simulation study*, Chem. Geol., **461**, 47–53, 2017.