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A comparative numerical analysis of liquid silica and germania^{\ddagger}

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Abstract

A two-body interatomic potential is used to describe the structural properties of liquid germania and silica by Molecular Dynamics simulation. The results show that the short-range order is identical in the liquid and the glass phase, made of a tetrahedrally connected network while longer range order displays differences with temperature. The most striking difference in thermodynamical behaviour appears to be driven by pressure as illustrated from the simulation of the pressurized amorphous systems.

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1. Introduction

Research into the properties of amorphous systems is of both fundamental and technological importance. Among these amorphous systems, silica plays a key role because of its important role in geosciences. Its structural transitions are known to take place under various geological conditions (Chemical Fundamentals of Geology, 1996; Spera, 1989) because of the number of potential polymorphs under high pressure or high temperature, it is a particularly challenging task to undertake computer simulations of this system. Numerous studies on this subject have been reported, focusing either on the structure of the silica glasses and melts (Horbach and Kob, 1999; Della Valle and Andersen, 1992) and on the dynamics of the material (Trachenko et al., 2000), or on related systems such as silicates and alumino-silicates (Horbach et al., 2001; Sunver et al., 2002) which represent the archetypal geological systems. It has been found that melts can change their local structure causing strong density modifications (Brueckner, 1970) in magmas and silicon can exhibit a change of its coordination number from four to six (Guissani and Guillot, 1996). Most of these results have been first initiated with computer simulations but more and more in situ high pressure and high temperature experiments become now available (Sugai and Onodera, 1996).

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However, while a majority of studies have been devoted to the silica and the silicate chemistry, little has been done to elucidate the corresponding behavior in germanium dioxide (GeO₂) even though this material bears a certain number of similarities with silica: both systems exhibit at ordinary conditions a tetrahedral local structure, they can also exist in α as well as β quartz (Laubengayer and Morton, 1932) and pressure induced structural transformations are also occuring in germania (Itié et al., 1989). On the latter issue, it seems that the change of coordination from four to six is much more sensitive in germania than in silica.

Compared to the analogous silica system, potentials offering the description of chemical and physical properties of GeO₂ have not received considerable attention so far. Various potentials have been used to describe the physics of silica (Van Beest et al., 1990; Tsunuyecki et al., 1988). For instance, potentials trying to handle three-body interactions between the O-Si-O bonds have been derived for studies of the glassy state (Susman et al., 1991) by different authors but we are not aware of any published work on this issue for germania. Note however that tetrahedral structures present in both of the investigated systems can be reproduced simply in dealing with O^{2-} and Ge^{4+} (or Si^{4+}) ions interacting with a simple two-body spherically symmetric potential (Woodcock et al., 1976). Surprisingly, no numerical study has been undertaken to understand the structure of vitreous and liquid germania, although several authors have reported on the simulation of the crystalline polymorphs of GeO₂ and their behaviour with pressure (Tsuchiya et al., 1998; Oeffner and Elliot, 1998).

In this article, we present some results about the simulation of vitreous and liquid germania. All along, we compare the results with simulated silica using the same kind of two-body potential. The results show that there are weak differences in the local structure, both systems exhibiting a progressive loss of the tetrahedral character with increasing temperature in the liquid phase. The major difference is found in the first sharp diffraction peaks appearing in the $S_{X-X}(Q)$ structure factor (X=Ge,Si). Much more sensitive is the effect of pressure which applies earlier on the local environment of the germanium atom. As a consequence, the number of oxygen neighbors in the

vicinity of a germanium atom grows faster than in silica.

2. Numerical details

The system consists of 256 germanium (silicon) and 512 oxygen. In the present calculations have been used ab-initio potentials developed by Tsunuyecki et al. (1988) for SiO_2 and Oeffner and Elliot (1998) for GeO_2 . The models employ pairwise additive interatomic potentials of Born-Huggins-Mayer type:

$$\Phi_{ij} = \frac{q_i q_j}{r_{ij}} + a_{ij} \exp\left(-b_{ij} r_{ij}\right) - \frac{c_{ij}}{r_{ij}^6} \tag{1}$$

consisting of a coulombic interaction term, a Born-Mayer repulsion and an attractive interaction. No three-body or many body interaction is included. Due to the divergence of the last term, the potentials for O-O, Si-O and Si-Si become unphysically attractive at short distances which can produce some spurious effects at high temperatures (Belonoshko, 1994) when the $1/r^6$ term overwhelms the short-range repulsion at atomic separation. An additional Lennard-Jones potential overcomes such problems for silica (Guissani and Guillot, 1996). In the case of germanium, the shortrange repulsion barrier is one order of magnitude greater as compared to silica which makes the overwhelming of the $1/r^6$ unlikely and there is in general no need to provide the additional potential in the calculation (Oeffner and Elliot, 1998). q_i and q_j are the reduced charges of the atoms *i* and *j*, r_{ij} is the interatomic distance, and a_{ii} , b_{ii} and c_{ii} are the forcefield parameters corresponding to the repulsiondispersion terms (see Tsunuyecki et al., 1988; Oeffner and Elliot, 1998).

The atoms have been first confined in a cubic box of respective length L=23.044 Å and L=22.644 Å in order to recover the experimental value of the density $\rho_g=3.66$ g cm⁻³ for GeO₂ and $\rho_g=2.2$ g cm⁻³ for SiO₂. For the latter, it is well known that the fixed density ρ_g in MD simulation does not yield the correct bond distances (Della Valle and Andersen, 1992). To overcome this disagreement, a slightly higher density $\rho=2.5$ g cm⁻³ is generally preferred if one wishes to undertake structural studies (Guissani and Guillot,

1996). After having thermalized the system at T_i =4000 K for 20000 time steps (20 ps) the system has been cooled to 300 K with a linear cooling schedule at a quench rate of 2.5×10^{12} K s⁻¹. Integration has been done using a leap-frog Verlet algorithm (Verlet, 1967). Various configurations (positions and velocities) have been saved at different temperatures (down to 300 K or up to 10000 K) which have been used as starting configurations for production runs of 10⁴ steps. Densification has been realized by simulating the experimental procedure, i.e. increasing the density at room temperature (for comparison with in situ easurements) and eventually decompressing the system to investigate the permanently densified glasses (Micoulaut, 2004). At the density $\rho_{\rm g}$, the glass transition temperature was about 1070 K for GeO₂, and as expected, the T_{g} shifts to the higher temperatures with increasing density (1100 K at $\rho=3.8$ g cm⁻³). In the case of silica, the glass transition temperature at the density ρ =2.5 g cm⁻³ is about 1800 K (and $T_g^{exp}=1450$ K (Elliot, 1989)). We note that the simulated value in the germania glass is very close to the experimental one (Elliot, 1989) (850 K) while the very notable discrepancies between simulated and experimental T_{g} 's (like in the present silica case) are usually attributed to the non-realstic quenching rates to form the glass. We are only aware

of a similar situation in vitreous selenium (Caprion and Schober, 2000).

3. The system at 300 K

Before investigating the structure of the liquids, it is of interest to study germania and silica at ambient temperature in the glassy state for which numerous experimental data are available allowing a preliminary check for the validity of the models. We first focus on the atomic distances obtained from the computation of the pair correlation functions $g_{ii}(R)$ (Figs. 1 and 2).

The atomic distances obtained for germania for the numerical results are in fair agreement with experimental data obtained from inelastic neutron scattering by Price and Saboungi (1998). The numerical results give $r_{\text{Ge-Ge}}=3.32\pm0.04$ Å, $r_{\text{Ge-O}}=1.72\pm0.02$ Å and $r_{\text{O-O}}=2.81\pm0.02$ Å to be respectively compared with the experimental values of 3.16 ± 0.03 , 1.73 ± 0.03 and 2.83 ± 0.05 Å. We assume that the roughness of the Ge–Ge pair correlation function arises from the absence of an interatomic potential (except the Coulombic term) for this particular pair in the Oeffner–Elliot model (Oeffner and Elliot, 1998) and note that the corresponding behaviour does not appear in an alternative GeO₂ potential that contains pairwise



Fig. 1. Pair correlation function $g_{ij}(R)$ of vitreous and liquid silica for different temperatures, ranging from 300 K up to 6000 K. The solid lines represent the system at ρ =2.5 g cm⁻³ while the dotted lines correspond to ρ =2.2 g cm⁻³.



Fig. 2. Pair correlation function $g_{ii}(R)$ of vitreous and liquid germania for different temperatures, ranging from 300 up to 6000 K.

Ge-Ge interactions (Tsuchiya et al., 1998). The secondary peaks in the Ge-Ge correlator are also found to be in reasonable agreement with experimental observation (Price and Saboungi, 1998), i.e. 5.10 Å versus 5.21 Å from diffraction data, and 7.39 Å versus 7.53 Å. The somewhat higher simulated Ge–Ge distance as compared to experimental findings does not seem to have much incidence on the forthcoming structure factors, neither on the simulated bond angles (Gutierrez and Rogan, 2004). The best agreement for the silica system is found at a density of 2.5 g cm⁻³ slightly higher than the experimental value of ρ_g =2.2 $g \text{ cm}^{-3}$. The choice of a higher density (mentioned previously and questioned (Guissani and Guillot, 1996) allows however to describe not only the structure but also the saturation of the silica liquid and several thermal coefficients (α_{V_2} , χ_T) over a reasonable temperature range. Therefore, $\rho=2.5$ g cm^{-3} will be used as the silica glass density. We stress however that there are only weak differences on the global trend of the partial radial distribution functions with density change (see Fig. 1). Furthermore, as we will compare both germania and silica pattern on a rescaled x-axis (see below, Fig. 3), the effect of the density misfit is not a matter of concern, at least in real space. The obtained distances are here: $r_{\text{Si}-\text{Si}}=3.20$ Å, $r_{\text{Si-O}}=1.62$ Å and $r_{\text{O-O}}=2.61$ Å which are comparable to the experimental findings (Grimley et al., 1990) (3.184, 1.608, 2.626 Å). It should also be noted that the second and third shells of the pair correlation functions $g_{ij}(r)$ are very pronounced in the glass but become less intense with increasing temperature thus suggesting a breakdown of the intermediate range order for the liquid.

It is also useful to calculate the running coordination number $n_{ii}(R)$ which gives the number of atoms of type *i* surrounding an atom of type *i* with distance. Of special interest is the distance R', which corresponds to the typical distance at which the pair correlation function is a minimum. This means also that $n_{ii}(R)$ is obtained by computing the integral from 0 to R=R' over the pair correlation function for *ij* correlations. Fig. 4 gives running coordination number $n_{ii}(R)$ for silica and germania at T=300 K and clearly suggests that the local environment of the silicon and germanium is fourfold coordinated $(n_{X-O} \simeq 4)$. Indeed, the existence of a plateau at the value 4 means that most of the silicon and germanium atoms are surrounded by four oxygen atoms thus forming a tetrahedron. Also, it is worth mentioning that four tetrahedra exist in the first shell surrounding a central $XO_{4/2}$ unit $(n_{X-X} \simeq 4)$ signifying that the oxygen atoms are bridging oxygens between two tetrahedra. One can also note that $n_{Si-Si} > n_{Ge-Ge}$ at the distance R', an effect which arises from the larger density (as compared to the experimental value) that has been



Fig. 3. Pair correlation functions in vitreous and liquid XO_2 with X=Ge (solid line) or Si (dashed line) as a function of the distance in reduced units (see text for details) for different temperatures, ranging from 300 to 10^4 K.

used in silica (for $\rho=2.2 \text{ g cm}^{-3}$, it is found $n_{\text{Si}-\text{Si}} \approx n_{\text{Ge-Ge}}$) (Fig. 5).

The next task consists of investigating the structure at larger length scales by use of partial static structure factors:

$$S_{ij}(Q) = \frac{\left(1 + \delta_{ij}\right)}{2N} \sum_{k=1}^{N_i} \sum_{l=1}^{N_j} \left\langle \exp(i\mathbf{Q}.(\mathbf{r}_k - \mathbf{r}_l)) \right\rangle \quad (2)$$

which depend on the magnitude of the wave-vector \mathbf{Q} . N_i and N_j are the number of atoms of species *i* and *j*. Fig. 3 (upper panels) shows the structure factors $S_{ij}(Q)$ for vitreous germania compared to experimental results obtained from a combination of X-ray and neutron scattering data (Price and Saboungi, 1998). These measurements have been refined recently but without a complete resolution of all the partials (Sampath et al., 2003). The main features in the structure factors are the peaks occurring at Q_P =1.5–2 Å⁻¹ (the first sharp diffraction peak, FSDP corresponding to a correlation length L_1 =2 π/Q_P =4.1 Å) while the pronounced peaks at 2.6 and 4 Å⁻¹



Fig. 4. Partial structure factors in GeO_2 (solid line) and SiO_2 (dashed line) compared to experiments from neutron diffraction in germania. The dots represent experimental data from Price et al. (1989).



Fig. 5. Running coordination number $n_{X-X}(R)$ and $n_{X-O}(R)$ in vitreous silica and germania at 300 K.

appearing in the partial Ge-O and O-O structure factors can be attributed to chemical short range order and topological short range order as derived from scaling considerations (Price et al., 1989). We note that the position of the simulated peak at Q=2.8 Å⁻¹ in the partial structure factor $S_{\text{Ge-Ge}}$ is somewhat lower as compared to experiment, a situation that has been also obtained in simulated silica for the global structure factor (Rino et al., 1993). Furthermore, the presence of prepeaks in both S_{Ge-Ge} and S_{Ge-O} are generally thought to be related to atomic-density fluctuations. These fluctuations have been modeled in terms of voids (Elliot, 1995a,b) and a direct relationship between the the amount of voids and the production of prepeaks has been demonstrated numerically (Cervinka et al., 1985). In the present GeO₂ system, the voids may arise from the one appearing inside m-membered rings containg more than m=3 germanium atoms, which produce a structural correlation distance between Ge-Ge or Ge-O pairs. Specifically, in four-membered rings, the correlation distance associated with next to nearest neighbour Ge-Ge pairs inside a planar ring is $\sqrt{2d_{\text{Ge-Ge}}} = 4.46\text{\AA}$, a distance which is even lower for the more realistic conformations of the m=4 ring (boats or chairs) (Elliot, 1995a,b). Finally, oscillation in Q space is mostly observed for the Ge-Ge correlation due to the tetrahedral character of the network structure. On the same figure has been represented the corresponding results for silica which show similar trends with Q (Fig. 4).

4. The liquid state

We now turn to the liquid state of GeO_2 and SiO_2 , starting in the simulation from the configuration at $T=T_i$ and changing smoothly the temperature according to the procedure describe above.

One has already seen from Figs. 1 and 2 that with increasing temperature the primary and secondary peaks in $g_{ii}(R)$ become less intense, accompanied by a global broadening. Fig. 3 represents the same pair correlation functions of germania and silica for different temperatures ranging from the ambient T=300 K up to the very high temperature (here T=6000 K), but with a different scale. In order to highlight the differences between both systems, the horizontal axis has been represented in reduced units, i.e. in units of r_{ii} where r_{ii} is the atomic distance at the corresponding given temperature. Note that there is a slight variation of the bond distances with increasing temperature. The X-O bond distance decreases from 1.72 Å (X=Ge) and 1.62 Å (X=Si) at 300 K to 1.68 and 1.60 Å at 6000 K. For the X-X and O-O bond distances, the change is even more abrupt since it is respectively found in GeO₂ 3.20 Å (3.25 Å for silica) and 2.72 Å (2.70Å for silica).

With the applied scaling, it appears that no major differences are found between both systems in the local structure. Furthermore, the global broadening of the first peak with increasing temperature and the progressive loss of longer range correlations as seen from the decrease of the secondary peaks appear to be very similar. The only difference is observable from the first peak in the X-X pair correlation function at T=300K. The mapping (i.e. following our described procedure using reduced units) of silica radial distribution functions onto germania radial distribution functions has been reported in the glass phase by Price (Price and Saboungi, 1998), who used a properly rescaled radial distribution function of simulated silica to understand experimental data on GeO₂. At very high temperatures (6000 K), the broadening of the first peak in g_{X-O} and g_{X-X} leads to the loss of the n = 4 plateau in the running coordination number $n_{ij}(\mathbf{R})$ thus signaling that the tetrahedral character has disappeared. Furthermore, the high temperature favours the occurence of an increased number of supplementary tetrahedra in the first shell of a basic $XO_{4/2}$ tetrahedron. It is found at 6000 K that $n_{Ge-O}(r')=4.76$ and $n_{Si-O}(r')=4.61$ while $n_{Ge-Ge}(r')=7.24$ and $n_{Si-Si}(r')=7.40$.

The same kind of study can be performed for the larger length scale, by computing the partial static structure factors in the liquid phase. Here it is shown (Fig. 6) that in contrast with the short-range order, differences in longer range correlations can exist at all temperatures, from 300 K up to 6000 K. The most striking are found in the X-X (X=Ge,Si) structure factors illustrated by the existence of a pre-diffraction peak in germania at 1.8 $Å^{-1}$ which is not found in silica at low temperature. For both systems is found the peak at around 2.5 \AA^{-1} . On the other hand, when temperature comes up, both $S_{ii}(Q)$ map more or less onto each other, a feature which is particularly obvious for T=6000 K. A similar global trend is observed for the two other structure factors (S_{X-O} and S_{O-O}) at each temperature, especially for the main peaks related to chemical short range order and topological short range order (Price et al., 1989). With increasing temperature, the small oscillations at very low Q in silica disappear and both systems exhibit almost the same $S_{X-O}(Q)$ and $S_{O-O}(Q)$ distribution at very high temperature. One can therefore conclude that the major differences between SiO_2 and GeO_2 are found in the X–X correlations at long distances and mostly at low temperatures.

The longer range structure of germania and silica in the glassy state appears to be rather different and the present results deserve some more general comments. One usual tool which serves to characterize intermediate and medium range order in glasses is the ring statistics or ring distribution (Rino et al., 1993) which attempts to quantify the number of closed loops in the network structure. Theses rings are generally determined from Raman spectroscopy (Galeener et al., 1983) or NMR (in the case of edge-sharing tetrahedra; Eckert et al., 1989) because they can have some very significative breathing modes (such as e.g. the 3- and 4-membered ring modes in silica, corresponding to typical lines in the Raman spectra; Geissberger and Galeener, 1983). Silica has been found to have a majority of (m=6) six-membered rings having six silicon atoms and six oxygen atoms and some amount of smaller rings such as the aforementioned ones (Hobbs et al., 1998). The number of these rings has been quantified by Geissberger and Galeener (1983). Computer simulations have been also able to calculate efficiently such ring statistics in the more recent years (Yuan and Cormack, 2002) and have found a distribution centered around m=6. On the other hand, it has been suggested by Henderson and Fleet that germania could consist of four-membered (m=4) rings (which have a particular stretching Raman mode at



Fig. 6. Partial structure factors $S_{ij}(Q)$ in vitreous and liquid XO₂ with X=Ge (solid line) or Si (dashed line) as a function of Q) for different temperatures, ranging from 300 to 6000 K.

515 cm⁻¹) and some three membered rings (Henderson and Fleet, 1991). The intermediate range order appears therefore to be rather different, which may explain the differences on the computed S_{X-X} (*Q*) functions. The number of rings obviously decreases with increasing temperature as suggested from Raman studies on the boroxol ring concentration in vitreous and liquid B₂O₃ (Walrafen et al., 1983). For the systems of interest, we are only aware of a study on the fictive temperature effects on the ring modes in silica (Geissberger and Galeener, 1983), which found that the fraction of 3- and 4-membered rings decreases with temperature.

5. Effect of pressure

Using the present simulation, it is possible to explore for further differences between germania and silica by investigating the effect of an applied pressure. From the obtained structures, one can determine the degree of tetrahedral distorsion by calculating a distorsion parameter defined by $\delta = d_{X-O}/d_{O-O}$ [X=Si,Ge]. This parameter should be equal to $\sqrt{3/8}$ for an ideal tetrahedron and any deviation from this value therefore provides a direct measure of the effect of the pressure on the local structure of the network. In Fig. 7 is displayed the variation of δ with



Fig. 7. The distorsion parameter of a regular XO_{4/2} as a function of applied pressure (X=Ge open circles, X=Si, filled circles). The dashed horizontal line represents the value $\sqrt{3/8}$. The right axis represents the $n_{X-O}(R')$ coordination number (X=Ge open squares, X=Si filled squares).

applied pressure for silica and germania. Clearly differences emerge from the simulation. While at low pressure the local environment of the tetrahadron is preserved due the constant value of δ (slightly higher however than $\sqrt{3/8}$, distortion sets in at a lower pressure for germania. Specifically, the increasing distortion of the germanium tetrahedron is found to occur for a "distortion" pressure P=2.8 GPa, whereas the latter value is shifted by about 2.2 GPa for silica. The distortion mechanism appears also to be radically different. In germania it is a stepwise increase (most noticable from the jump of δ at around 3 GPa), compared with a smooth increase for SiO_2 . Furthermore, the "distortion" pressure in silica correlates well with the calculated pressure where loss of rigid units modes (RUM) occurs (Trachenko and Dove, 2002), signaling that for greater pressures the structure densifies by static RUM-type distortions thus leading to pressure induced rigidity (Trachenko et al., 1998).

The evolution of the coordination number n_{X-O} (*R'*) with pressure is more sensitive in the case of germania and grows from $n_{Ge-O} = 4$ at zero pressure up to 5.2 at 18 GPa, whereas $n_{Si-O}(R')=4.7$ at the same pressure. The conversion from four-fold to higher coordinated atoms under pressure is therefore more dramatic in GeO₂. A recent report (Majerus, 2003) has shown that such effects could be more deeply investigated by studying the system $(1-x)GeO_2-xSiO_2$. Here there is a way to switch continuously from the high germanium sensitivity to pressure to the weaker one of silica. As a consequence, the onset pressure is shifted with concentration as well as with the corresponding hysteresis appearing upon decompression.

6. Conclusion

It has been shown that a simple two-body potential could describe accurately the glass and liquid phase of both the germania and silica systems. The local structure is almost the same at all temperatures with some slight differences at 6000 K, while more pronounced differences emerge in the intermediate range order, which is seen from the static structure factors at low Q. The application of pressure seems to produce non-similar changes as it

is found that the average germanium coordination number increases more rapidly than for SiO_2 and is accompnied by increased distortion of the basic tetrahedron.

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