ELSEVIER

Ceramics International 31 (2005) 713–717

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Modeling glass materials

Kurt Binder[a,*], Jürgen Horbach[a], Anke Winkler[a], Walter Kob[b]

[a]*Institut für Physik, Johannes Gutenberg–Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany*
[b]*Laboratoire des Verres, Université Montpellier II, Place E. Bataillon, Case 069, 34095 Montpellier, France*

Received 23 June 2004; received in revised form 25 June 2004; accepted 10 July 2004

Abstract

Structural and dynamic properties of silicate melts and glasses (SiO_2 and its mixtures with Na_2O and Al_2O_3) are derived from Molecular Dynamics simulations and compared to pertinent experimental data. It is shown that these mixtures exhibit additional intermediate order as compared to pure silica, where the characteristic length scales stem from the tetrahedral network structure. While sodium ions show much faster diffusion through percolating channels than the silicon and oxygen ions forming the surrounding network, aluminium ions are incorporated into the network (leading to tricluster formation) and do not show such an enhanced mobility.

Keywords: C. Diffusion; D. SiO_2; D. Al_2O_3; D. Alkali oxides

1. Introduction

Molten silica and its mixtures with various oxides are of basic interest both in materials science, for the glass and ceramics industry, and for the earth sciences, since most minerals and rocks have been formed from such melts underneath the earth crust. Despite intense research for decades, structure–property relations on the atomistic level still involve many challenging problems. This paper describes some progress obtained recently via Molecular Dynamics simulations [1–15].

The Molecular Dynamics (MD) method [16] reduces the statistical mechanics of a condensed matter system to averages along trajectories through the phase space of the chosen model system generated via classical mechanics. Thus, Newton's equations of motion are integrated (e.g. using the Verlet algorithm [16]) relying on simple effective potentials that describe the interactions between the ions. In the work described here, the well-known BKS potential [17] for silica and a (modified) [11,15] extension due to Kramer et al. [18] is used.

It is important to realize that this approach ignores all quantum-mechanical effects: while quantum effects associated with the delocalization of the ions are normally very small at the high temperatures of interest, the fact that all effects associated with the electrons are incorporated in effective potentials clearly involves a serious approximation: effects such as charge transfer between ions, induced dipole moments, change of the character of the bonding from covalent to ionic depending on the local environment, etc., cannot be accounted for. In fact, more accurate methods that take effects from the electrons to some extent into account, such as the Car-Parrinello "ab initio Molecular Dynamics" (CPMD) [19], when applied to the present problem do reveal small but systematic differences in the local structure and in the corresponding forces [20–22]. However, it must be emphasized that for the simulation of such viscous melts and glasses it strongly depends on the context whether or not the chemically more realistic simulations using CPMD [19–22] are "better" than simple MD: while MD can easily deal with rather large systems of the order of 10^4 ions [2–15] or more, CPMD is restricted to the use of the order of 10^2 ions only. Such small systems are clearly unsuitable to study problems such as intermediate range order [14] or microphase separation [15] in melts and glasses. Also one needs to be very careful in the judgement

---

[*] Tel.: +49 6131 3923348; fax: 49 6131 3925441.
E-mail address: kurt.binder@uni-mainz.de (K. Binder).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2004.07.011

whether finite size effects are a problem or not. For pure silica it has been demonstrated [2] that important size effects are found (for systems containing 10^3 ions or less) in dynamic properties, such as the intermediate scattering functions $F_s(q,t)$, q being the wavenumber and t the time, while the partial structure factors $S_{\alpha\beta}(q)$ and other static properties show no size effect at all. In addition it must be noted that CPMD needs many orders of magnitude more computational effort than classical MD. Already the latter method requires a very small time step (δt =1.6 fs is appropriate [1–5] if the BKS potential [17] is used), and hence equilibrating a melt for a real time of about 20 ns is already a major calculation (note that the treatment of pseudo-Coulomb interactions in the BKS potential [17] via Ewald summation methods is very time consuming [5]). Such a time span just suffices to equilibrate a pure SiO_2 melt at temperatures as high as $T = 2750$ K [5], SiO_2–Al_2O_3 mixtures [15] at $T = 2300$ K, and SiO_2–Na_2O mixtures at 2100 K [11–14]. In contrast, CPMD runs can explore only the picosecond time ranges and hence can equilibrate melts only at much higher temperatures than classical MD. Unfortunately, if one ignores the need to perform very long runs to properly equilibrate the melts and simply cools down very fast to the temperatures of interest, one finds a strong dependence of many properties on the cooling rate [1]. These differences between properties predicted for different cooling rates, which in the simulations are in the range from 10^{12} K/s to 10^{15} K/s while in the experiments they are many orders of magnitude smaller, i.e. they are of the same order as differences between properties predicted from distinct parametrizations for pair potentials, or differences between MD and CPMD results. Thus, the judgement of small differences in detail obtained from different calculations is subtle.

2. Summary of results for pure silica

Since the model and the simulation method are well documented in the literature [1–10], we here recall very briefly the main results of these studies only. Several quantities have been compared to corresponding experiments in order to check the quality of the BKS potential, which originally was validated for crystalline phases of SiO_2 only. For example, using the simulated partial structure factors and the known neutron scattering lengths, a comparison with experiment [23] could be performed without invoking any adjustable parameter whatsoever. The striking agreement between experiment and simulation is a first indication that the BKS potential is good enough for the present purposes.

However, it is not enough to consider the static structure only if one wishes to make sure that the potential is reasonable—also dynamic properties need to be tested. The temperature dependence of the sound velocities, in the glass as well as in the melt, characterizes fast collective length scales in the system, and is readily extracted from an analysis of suitable dynamic correlation functions in the simulation [9]. Again impressive agreement with corresponding data [24] was found, without adjusting any fit parameters. Very slow collective motions in the melt are characterized by the shear viscosity. This quantity could be obtained from the simulations only at very high temperatures [5], $T \geq$ 3000 K, complementing the range where experimental data are available [25]. But the activation energy ($E_A \approx 5.3$ eV) extracted from the simulation [5] agrees very well with the experimental result. A similar good agreement was found for the self-diffusion constants, which experimentally are rather difficult to measure [26,27], while the simulations yield them straightforwardly, following the mean square displacement of tagged particles and applying the Einstein relation [5].

Of course, these simulations not just only reproduce and complement experimental data, but they also yield a lot of physical insight. For example, the results for the viscosity and the diffusion constants deviate at very high temperature from Arrhenius laws very strongly, just as they do for the so-called ‘‘fragile’’ glassformers [28]; in fact, the analysis of the intermediate scattering function reveals that mode coupling theory [29] does account for the dynamics of SiO_2 at very high temperatures, with a critical temperature of $T_c \approx 3330$ K. Thus, the distinction between ‘‘strong’’ and ‘‘fragile’’ glassformers [28] presumably is not as strict as originally thought.

3. Mixtures of molten silicondioxide and sodiumoxide

Sodium silicates are paradigms of ionic conductors: at low temperatures the sodium ions are much more mobile than the silicon and oxygen ions. While in pure silica melts the dynamics is controlled by the ‘‘lifetime’’ of the Si–O covalent bond [3–8], the behavior in molten sodium silicates is much more complicated, since the sodium ions in their local environment partially destroy the disordered tetrahedral network that occurs in pure silica, with Si ions in the centres of the tetrahedra and O ions at the corners, such that every O ion is shared by two tetrahedra (‘‘bridging oxygen’’) [30]. Again MD is a very valuable tool to clarify the structure and hence explain how it is possible that the diffusion constants of the Na ions can be orders of magnitude larger than those of Si and O (Fig. 1).

First of all the model potential was again tested by comparing the static structure factor to neutron scattering data [31], and good agreement was found [7]. However, the partial structure factors $S_{\alpha\beta}(q)$ accessible in the simulation (but not accessible in the experiment!) showed a structural feature associated with a characteristic length $l \approx 7$ Å, which shows up as a pronounced ‘‘prepeak’’ at $q \approx 0.9$ Å^{-1} in the NaNa and SiSi correlations (Fig. 2). While there was no evidence whatsoever in the early experiment [31], later careful work [32] compellingly verified this theoretical

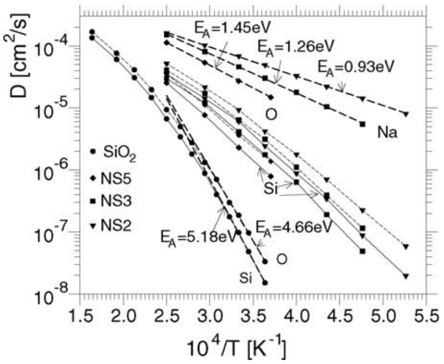

Fig. 1. Arrhenius plot of the self-diffusion coefficients of Si, O, and Na in SiO_2 and $(Na_2O)(x{\cdot}SiO_2)$ [denoted as NS x in the figure] plotted vs. inverse temperature. Straight lines indicate the Arrhenius relations, $D \propto \exp[-E_A/(k_BT)]$, and the various activation energies E_A are quoted.

prediction. A detailed analysis [12–14] revealed that this prepeak is due to the formation of a percolating network of Na-rich channels, in which fast diffusion of the Na ions is possible. There have been suggestions of such mechanisms since a long time [33,34], but only the extensive recent simulations [12–14] and their analysis in conjunction with the new careful experiments [32,35] could settle this controversial issue.

4. Mixtures of molten silicondioxide with aluminiumoxide

While the introduction of Al_2O_3 also weakens the random network structure of the glassforming fluid, as is evident from the behavior of the diffusion constants of $(Al_2O_3)(2{\cdot}SiO_2)$ [denoted as AS2] in comparison with those of pure SiO_2, see Fig. 3, it is clear that the diffusion constants of Al and of Si and O are very similar. Thus, unlike Na the Al ions do not separate out in separate channels but rather they are incorporated into the tetrahedral network. However, the stoichiometry of Al_2O_3 and that of SiO_2 do not fit together: when two SiO_2 units are replaced by an Al_2O_3 unit the chemical rules of the network (each oxygen is neighbor of two silicon ions, each silicon has four oxygen neighbors) cannot be maintained. This problem has led to the hypothesis [36–38] that ‘‘triclusters’’ occur, i.e. structural units where an oxygen atom is surrounded by these cations, whereby at least one of them is an aluminium atom.

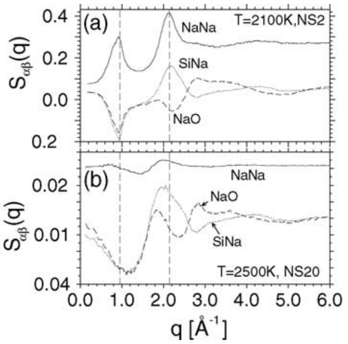

Fig. 2. Partial structure factors $S_{NaNa}(q)$ (solid lines), $S_{SiNa}(q)$ (dotted lines) and S_{NaO} (dashed lines) for (a) NS2 at $T = 2100$ K and for (b) NS20 at $T = 2750$ K. The vertical lines mark the positions of the prepeak (at $q_1 \approx 0.95$ Å^{-1}) and the peak characteristic for the nearest neighbor distance of the cations (at $q_2 \approx 2.1$ Å^{-1}). From Horbach et al. [14].

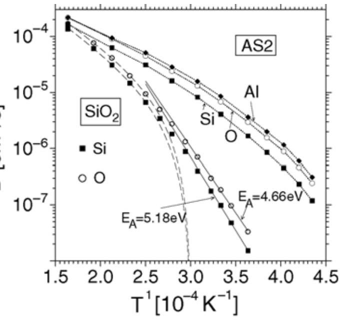

Fig. 3. Arrhenius plot of the diffusion constants of silicon, aluminium, and oxygen: comparison of the systems AS2 and SiO_2. The dashed lines for SiO_2 indicate the power law fits [5] $D(T) = D_0(1 - T_c/T)^\gamma$ with T_c= 3330 K. From Winkler et al. [15].

The occurrence of these triclusters can be inferred rather directly from the MD simulations by sampling the distribution of coordination number $P_{\alpha\beta}(z)$ (Fig. 4). Here $P_{\alpha\beta}(z)$ gives the probability that a particle of type α is surrounded by exactly z neighbors of type β within a distance $r \leq r_{\min}^{\alpha\beta}$, where $r_{\min}$ corresponds to the position of the first minimum in $g_{\alpha\beta}(r)$. It is seen from P_{SiO} and P_{AlO} that at low temperatures most of the Si and Al atoms are four-fold coordinated by O atoms. Thus, also Al is integrated in the tetrahedral network structure, but the ‘‘packing’’ of the tetrahedra is different from pure silica: only 70% of the O atoms are two-fold coordinated but around 30% of the O

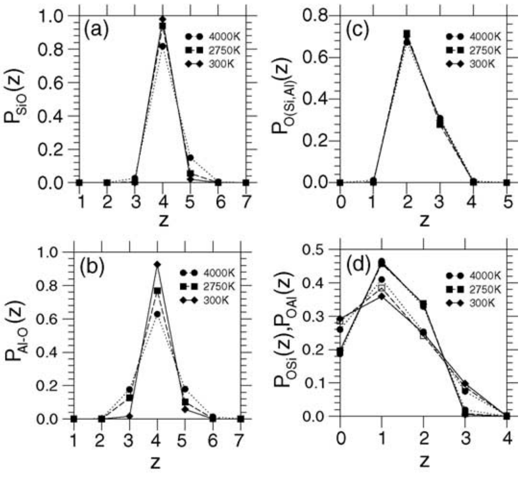

Fig. 4. Distributions of coordination number $P_{\alpha\beta}(z)$ for the temperatures $T = 4000$ K, 2300 K, and 300 K for AS2: (a) $P_{SiO}(z)$, (b) $P_{AlO}(z)$, (c) $P_{O(Si,Al)}(z)$, and (d) $P_{OSi}(z)$ and $P_{OAl}(z)$. The three curves that at $z = 2$ have the largest values correspond to $P_{OSi}(z)$. From Winkler et al. [15].

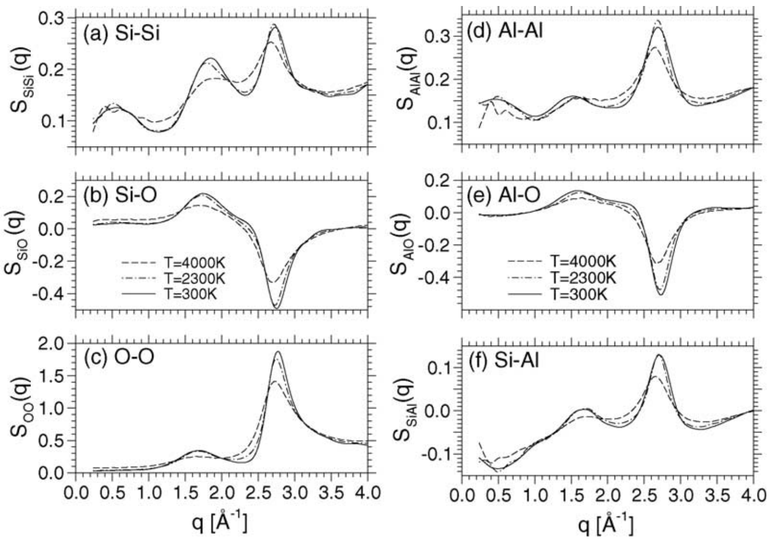

Fig. 5. Partial static structure factors $S_{\alpha\beta}(q)$ for AS2 and the three temperatures $T = 4000$ K, 2300 K, and 300 K: (a) $S_{\rm SiSi}(q)$, (b) $S_{\rm SiO}(q)$, (c) $S_{\rm OO}(q)$, (d) $S_{\rm AlAl}(q)$, (e) $S_{\rm AlO}(q)$, and (f) $S_{\rm SiAl}(q)$. From Winkler et al. [15].

atoms are three-fold coordinated by (Si, Al) atoms, as Fig. 4c shows. This is the signature of the triclusters.

Although Al thus is incorporated into the network, its distribution is nonrandom. This again is seen from a study of the partial structure factors (Fig. 5). Again in both the Si–Si correlations and the Al–Al correlations a prepeak at $q \approx 0.5$ Å^{-1} is seen, while the peaks at 1.6–1.7 Å^{-1} are due to the order from the tetrahedral network structure. The prepeak, however, implies that AlO_4 tetrahedra are preferentially surrounded by other AlO_4 tetrahedra, and thus Al-rich regions form. The O ions, however, are homogeneously distributed (Fig. 5c). The clustering of AlO_4 tetrahedra may be considered as a precursor effect to the unmixing transition, that is known to occur [39] in metastable Al_2O_3–SiO_2 melts for $T < T_c = 1920$ K. However, a direct simulation study of this phase separation on macroscopic scales is a challenging problem that must be left to future work.

5. Conclusions

Examples have been presented to show that MD simulations can give a very useful and detailed information on the structure, dynamics, and thermodynamic properties of molten silica and its mixtures with various other oxides and the glasses that can be formed from cooling these materials to low temperatures. These simulations can complement experiments in several ways, e.g. data can be obtained at high temperatures and pressures that are not accessible in the laboratory. Quantities can be determined which are not easily available in the experiment (e.g. partial structure factors, see Figs. 2 and 5, or the ring statistics [1,15], etc.). While here only work on bulk properties has been mentioned, surface properties are accessible as well [22,40]. A particular strength of these simulations is that from a simple model Hamiltonian a multitude of observables can be obtained simultaneously, atomic configurations are accessible in arbitrary detail, and hence structure–property relations of materials can be comprehensively investigated.

However, the basic limitations of the approach must not be forgotten: there is the need to carefully watch out for finite size effects, and the accessible time span (of the order below 1 μs) restricts also the temperature range that is accessible (or necessitates the use of unrealistically large cooling rates). And clearly the most pressing problem is the lack of transferable effective potentials that could be used for wide classes of materials. For example, good pair potentials exist for SiO_2 [17] and for GeO_2 [41], but the O–O interactions in both potentials are rather different, and hence already the treatment of SiO_2–GeO_2 mixtures is a formidable problem. At the time of writing, a convenient recipe for the construction of effective potentials for this system and related cases has not yet been found.

Acknowledgements

This work was partially supported by SCHOTT GLAS and by the Deutsche Forschungsgemeinschaft (DFG) under grant No. HO 2231/2-1. We thank the HLRS Stuttgart and the NIC Jülich for generous grants of computing time.

References

[1] K. Vollmayr, W. Kob, K. Binder, Phys Rev. B 54 (1996) 15808.
[2] J. Horbach, W. Kob, K. Binder, C.A. Angell, Phys. Rev. E 54 (1996) R5897.
[3] J. Horbach, W. Kob, K. Binder, Phil. Mag. B 77 (1998) 297.
[4] J. Horbach, W. Kob, K. Binder, J. Non-Cryst. Solids 235–237 (1998) 320.
[5] J. Horbach, W. Kob, Phys. Rev. B 60 (1999) 3169.

[6] J. Horbach, W. Kob, K. Binder, J. Phys. Chem. B 103 (1999) 4104.
[7] J. Horbach, W. Kob, Phil. Mag. B 79 (1999) 1981.
[8] J. Horbach, W. Kob, Phys. Rev. E 64 (2001) 041503.
[9] J. Horbach, W. Kob, K. Binder, Eur. Phys. J. B 19 (2001) 531.
[10] P. Scheidler, W. Kob, A. Latz, J. Horbach, K. Binder, Phys. Rev. B 67 (2001) 104204.
[11] J. Horbach, W. Kob, K. Binder, Chem. Geol. 174 (2001) 87.
[12] J. Horbach, W. Kob, K. Binder, Phys. Rev. Lett. 88 (2002) 125502.
[13] J. Horbach, W. Kob, K. Binder, J. Phys.: Condens. Matter 15 (2003) 903.
[14] J. Horbach, A. Winkler, W. Kob, K. Binder, Mat. Res. Soc. Symp. Proc. 754 (2003) 147.
[15] A. Winkler, J. Horbach, W. Kob, K. Binder, J. Chem. Phys. 120 (2004) 384.
[16] M.P. Allen, D.J. Tildesley, Computer Simulations of Liquids, Clarendon Press, Oxford, 1987.
[17] B.H.W. van Beest, G.J. Kramer, R.A. van Santen, Phys. Rev. Lett. 64 (1990) 1955.
[18] G.J. Kramer, A.J.M. de Man, R.A. van Santen, J. Am. Chem. Soc. 64 (1991) 6435.
[19] R. Car, M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471.
[20] M. Benoit, S. Ispas, P. Jund, R. Jullien, Eur. Phys. J. B 13 (2000) 631.
[21] S. Ispas, M. Benoit, P. Jund, R. Jullien, Phys. Rev. B 64 (2001) 214206.
[22] C. Mischler, W. Kob, K. Binder, Comp. Phys. Comm. 147 (2002) 222.
[23] D.L. Price, J.M. Carpenter, J. Non-Cryst. Solids 92 (1987) 153.
[24] A. Polian, D. Vo-Tanh, P. Richet, Europhys. Lett. 57 (2002) 375.
[25] G. Urbain, Geochim. Cosmochim. Acta 46 (1982) 1061.
[26] J.C. Mikkelsen, Appl. Phys. Lett. 45 (1984) 1187.
[27] G. Brebec, R. Seguin, C. Sella, J. Bevenot, J.C. Martin, Acta Metall. 28 (1970) 327.
[28] C.A. Angell, J. Non-Cryst. Solids 131–133 (1991) 13.
[29] W. Götze, R. Sjögren, Rep. Progr. Phys. 55 (1992) 241.
[30] R. Zallen, The Physics of Amorphous Solids, John Wiley & Sons, New York, 1983.
[31] M. Misawa, D.L. Price, K. Suzuki, J. Non-Cryst. Solids 37 (1980) 85.
[32] A. Meyer, H. Schober, D.B. Dingwell, Europhys. Lett. 59 (2002) 708.
[33] G.N. Greaves, J. Non-Cryst. Solids 71 (1985) 203.
[34] M.D. Ingram, Philos. Mag. B 60 (1989) 729.
[35] A. Meyer, J. Horbach, W. Kob, F. Kargl, H. Schober, Phys. Rev. Lett. 93 (2004) 027801.
[36] B.T. Poe, P.F. Mcmillan, C.A. Angell, R.K. Sato, Chem. Geol. 96 (1992) 333.
[37] M. Schmücker, H. Schneider, Ber. Bunsenges. Phys. Chem. 100 (1996) 1550.
[38] J.D. Kubicki, M.J. Toplis, Am. Mineral. 87 (2002) 668.
[39] J.F. Macdowell, G.H. Beall, J. Am. Ceram. Soc. 52 (1969) 17.
[40] A. Roder, W. Kob, K. Binder, J. Chem. Phys. 114 (2001) 7602.
[41] R.D. Oeffner, S.R. Elliott, Phys. Rev. B 58 (1998) 14791.