

Modeling glass materials

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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.

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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

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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 ($\delta t = 1.6$ 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], $\text{SiO}_2\text{--Al}_2\text{O}_3$ mixtures [15] at $T = 2300$ K, and $\text{SiO}_2\text{--Na}_2\text{O}$ 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 silicodioxide 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

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