



THE INTERPLAY BETWEEN STRUCTURE AND IONIC MOTIONS IN GLASSES

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ALTHOUGH HUMANS HAVE TOUCHED OR USED “GLASS” DAILY SINCE ANCIENT EGYPTIAN TIMES, WE HAVE YET TO ACHIEVE A DETAILED UNDERSTANDING OF ITS ATOMISTIC

structure.¹ Glass, like all amorphous material, lacks the periodic long-range order that characterizes crystals (in which the atoms occupy the positions of a regular lattice). However, chemical-bonding constraints enforce the rather high degree of short-range order that is already present in glass during its high-temperature fluid state—the state from which glass is eventually produced via cooling. Although we have some knowledge as to what each atom’s immediate surrounding typically looks like in glass, the degree of order on intermediate length scales (the medium-range order) has been controversial for decades.^{1,2}

This incomplete understanding of glass’s structure has its counterpart in our lack of knowledge about its dynamic properties. How do ions move in a deeply supercooled melt that consists of various oxides or in the glass that is ultimately formed from it? How does this motion depend on temperature and composition? Are there significant local differences of this motion or do all atoms of one species have the same dynamics? You can read about various concepts and plausible models of these issues in the literature, but proof for them by experiment does not exist because such experiments do not give access to the necessary microscopic information.

We present a few research examples here that demonstrate how molecular dynamics (MD) simulations of real materials have reached a high level of sophistication. For simplicity, we focus on examples taken from our own research—although many other groups have done similarly valuable work on other systems and problems.

The Contribution of Computer Simulations

In recent years, computer simulations of refined atomistic models have provided remarkable insight into glass’s atomic

structure.^{3–6} This breakthrough in understanding is possible thanks to progress along three lines.

First, researchers have developed accurate effective potentials (such as the BKS potential for silica⁷) from quantum-chemical methods suitable for efficient MD codes. Detailed comparisons with more accurate (but considerably more time-consuming) methods, such as the *ab initio* MD and the Car–Parrinello methods, have further validated these potentials.^{8,9}

Potentials have limitations in that they do not reproduce certain features of the real material.¹⁰ However, these shortcomings don’t really matter for the questions discussed here because we’re only interested in the qualitative (or semiquantitative) properties of the systems of interest. Past research has shown that the BKS potential can reproduce the medium-range order’s salient features and consequences for the dynamics in glasses, so the BKS potential is sufficiently reliable for our purposes.^{4,6}

Second, powerful supercomputers are now so efficient at number crunching that sufficiently long runs (20 nanoseconds or more) of large systems (of the order of 10^4 atoms) are feasible, despite the fact that an MD simulation’s individual time step is only of the order of a femto second (10^{-15} s).^{4–6,11,12} Most current potentials for oxide glasses include a long-range Coulomb part. In a system made quasi-infinite via periodic boundary conditions, the treatment of these long-range Coulomb forces among ions necessitates using the Ewald summation method. This method copes with each charged atom’s interaction not only with all the other charged atoms in the simulation box but with all their infinitely many periodic images.^{11,12} Obviously, each time step requires heavy computation, which would have been infeasible 10 years ago.

Third, recent experiments, some of which were extremely difficult,¹³ provide crucial data and prove that computer models correctly capture the real material’s crucial properties. Although researchers frequently claim that computational materials science has reached maturity—it’s gone from *ab initio* quantum-mechanical input to the macroscopic properties of matter—we feel that really convincing

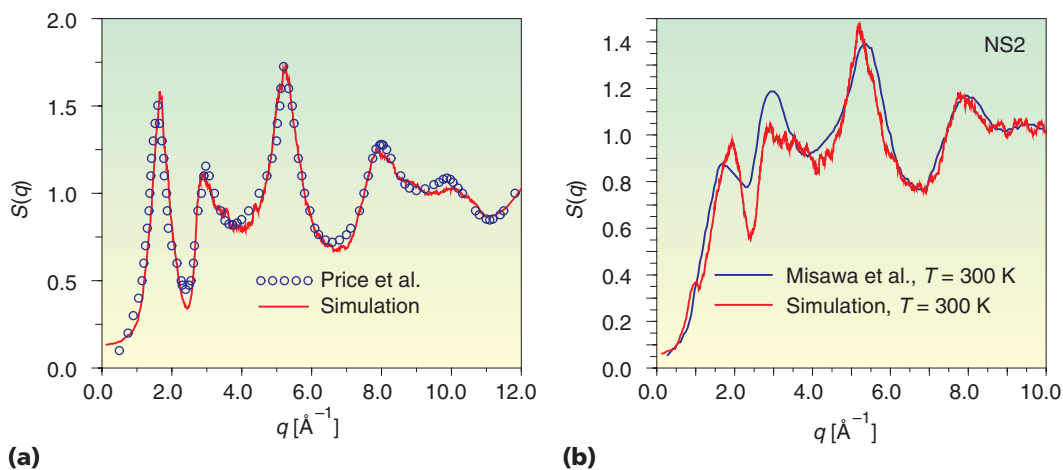


Figure 1. (a) Static structure factor of quartz glass (SiO_2) at room temperature ($T = 300$ K) plotted against wave number q (q is related to the experimental scattering angle Θ via $q = (4\pi/\lambda) \sin \Theta$, λ being the wavelength of the radiation used for the scattering experiment). The full curve is the molecular dynamics simulation, which uses the measured neutron-scattering lengths of Si and O atoms, and the circles are experimental data.² (b) Same structure factor but for sodium disilicate. The full curve is the MD simulation; the broken curve represents experimental data.

demonstrations of this approach still are rather scarce, thus a broad experimental verification still is desirable. Although experiments probably will never give information as complete and detailed as a simulation, the “tiles” that the experiment delivers must appear at exactly the right place in the “mosaic.” This is indeed the case for molten silica and its mixtures with sodium oxide and aluminum oxide, which we discuss in detail here.^{4–6}

Why Are Experimental Studies of Glassy Structures Incomplete?

The standard experimental tool for clarifying the atomistic structure of matter is elastic scattering of x-rays or neutrons. In a crystal, the location of the Bragg peaks in reciprocal space, together with an analysis of the intensities of these peaks, usually describes the crystalline lattice accurately, as well as any thermal disorder due to lattice vibrations.

However, in a fluid or glass, the material’s overall isotropy implies that only a radially averaged structure factor $S(q)$ is available, which exhibits just a few broad peaks (see Figure 1) that by no means suffice to specify the detailed structure.^{4,5,14,15} In fact, for neutrons, the structure factor in Figure 1 is a superposition of various partial structure factors $S_{\alpha\beta}(q)$, where α and β refer to the various types of atoms (Si, O, and Na, in this case), with neutron-scattering lengths b_α , b_β as weighting factors:

$$S(q) = \frac{1}{\sum_{\alpha} N_{\alpha} b_{\alpha}^2} \sum_{\alpha, \beta} b_{\alpha} b_{\beta} S_{\alpha\beta}(q)$$

$$S_{\alpha\beta}(q) = \frac{1}{N} \sum_{k=1}^{N_{\alpha}} \sum_{l=1}^{N_{\beta}} \langle \exp[i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)] \rangle \quad (1)$$

For x-rays, the measured intensity is also a superposition of the form in Equation 1, but now b_{α} depends on the wave vector q . The partial structure factor is a spatial Fourier transform of a partial radial density distribution function $g_{\alpha\beta}(r)$, which is proportional to the probability to find an atom of type β at a distance r from an atom of type α . If only the total structure factor $S(q)$ is accessible, this information cannot uniquely be obtained in a material containing several types of atoms. Of course, in principle, $S_{\alpha\beta}(q)$ is accessible by preparing several samples containing different isotopes of the various atoms—if available—and by measuring several $S(q)$ for the same material with different weight factors b_{α} , b_{β} . However, in practice, this is almost impossible due to the lack of isotopes and experimental resolution. Instead, experimentalists try to combine $S(q)$ with data from other techniques,¹ but such approaches don’t yield a unique characterization of the structure.

A particular puzzle in the dynamics of a glass-forming liquid is that a decrease of temperature T dramatically slows down the melt, whereas in the same temperature region, $S(q)$ changes only slightly. This rapid slowdown has the effect that at a given temperature T_g (the *glass-transition temperature*), the relaxation time becomes macroscopically large and the system falls out of equilibrium: essentially, it becomes a glass. We see this slowdown in various ions’ self-diffusion constants $D(T)$.⁴

Although measuring $D(T)$ experimentally is difficult, we can observe the quantity readily in a computer simulation. We simply follow the trajectories of the different atoms $\{\vec{r}_i(t)\}$ as a function of time and apply the Einstein relation,¹¹

$$D_{\alpha} = \lim_{t \rightarrow \infty} \langle [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle / (6t), \quad (2)$$

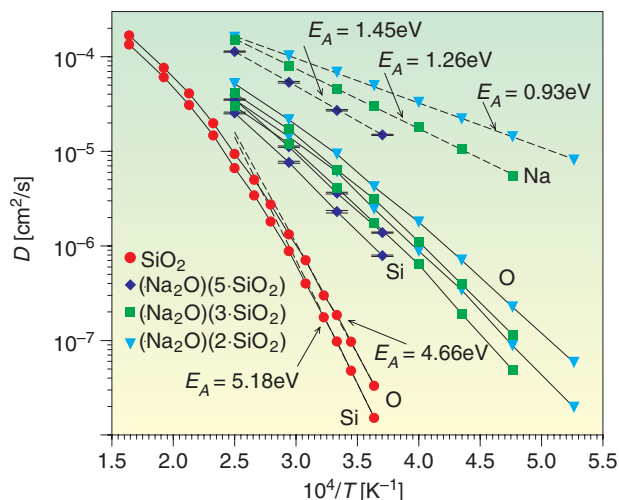


Figure 2. Arrhenius plot of the self-diffusion coefficients of Si, O, and Na in SiO_2 and sodium silicates plotted against inverse temperature. Straight lines indicate the Arrhenius relations, $D_\alpha \propto \exp(-E_A^\alpha / (k_B T))$. The various activation energies E_A^α are quoted in the figure.⁵

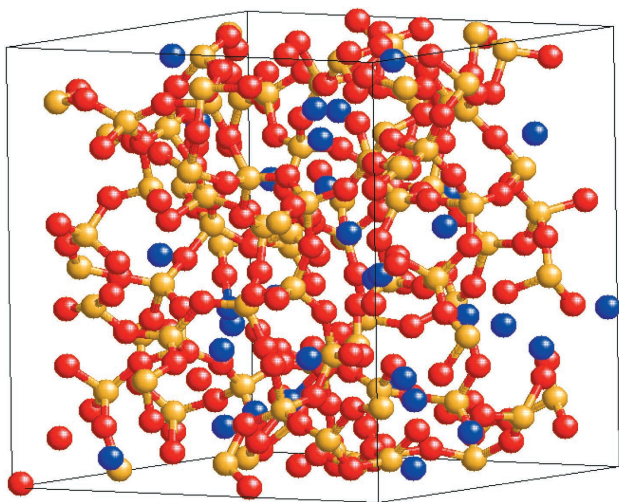


Figure 3. This snapshot of $(\text{Na}_2\text{O})_x(\text{SiO}_2)$ at $T = 2,700$ K shows a cube of linear dimension 16.19 \AA (the linear dimension of the total simulated box is about 48 \AA , containing 8,064 atoms). Silicon atoms are light brown and ideally located in the center of a tetrahedron, with covalent bonds to the oxygen atoms shown in red. Note, however, that bonds that cross one of the cube surfaces are not shown. Sodium ions are in blue.

where $\langle \dots \rangle$ includes an average over all N_α particles of type α .

Figure 2 shows corresponding simulation results⁵ for various sodium silicate melts— $(\text{Na}_2\text{O})_x(\text{SiO}_2)$ with $x = 2, 3, 5$, henceforth abbreviated as NS_x —compared with pure SiO_2 .

For pure SiO_2 , corresponding experimental data (albeit at lower temperatures) are available and yield comparable activation energies for the self-diffusion—namely, $E_A = 4.7 \text{ eV(O)}$ ¹⁶ and $E_A = 6 \text{ eV(Si)}$.¹⁷ Analogous experiments for the NS_x systems in Figure 2 still must be performed.

However, the data that do exist on the dynamics of sodium silicate melts are compatible with Figure 2's findings in that the introduction of Na into the random SiO_2 network leads to a breakup of some of the covalent bonds and thus enhances atomic mobility. In fact, the basic idea about the covalent binding in these network glasses is that Si atoms “sit” in the center of a tetrahedron (with oxygen atoms at its four corners) and that neighboring tetrahedra share one oxygen.¹ If Na were introduced into the network, we would expect¹ that network to be broken up locally, non-bonding oxygens (O-atoms that belong only to a single tetrahedron rather than being shared by two) to be created, and so on.

Although such ideas are indeed plausible, experiments allow only crude and qualitative conclusions about these effects. In contrast, the simulation yields very clear evidence for the network breakup (see Figure 3). So, from the simulation, we can expect a clarification of the anomalous high mobility of cations (such as Na^+) in the molten glass: as Figure 2 shows, already at very high temperatures, $D_{\text{Na}}(T)$ is orders of magnitude larger than $D_{\text{Si}}(T)$ or $D_{\text{O}}(T)$. This effect becomes even more pronounced at much lower temperatures—in particular, near the melt's glass-transition temperature, which is the most relevant region from an experimental viewpoint.

This (experimentally observed) anomalous enhancement of cationic mobility has led to the speculation that in NS_x glasses there exists a percolating network of Na^+ -rich channels.¹⁸ In such channels, the Na^+ ions can move relatively freely, whereas the remaining random SiO_2 network is comparatively rigid.¹⁸ Let's look at what simulations can tell us about this issue.

Atomistic Models for Silicate Glasses

MD simulation means that we can describe the liquid or solid as an assembly of atoms interacting with forces derived from a classical interatomic potential (the *force field*).¹¹ The dynamics of such a system of many interacting point particles is then simply given by Newton's equations of motion, which a suitable algorithm (such as the velocity Verlet algorithm) can solve numerically.¹¹ Discretizing time in steps of size δt , the position and the velocity of the i th particle $\vec{r}_i(t + \delta t)$ and $\vec{v}_i(t + \delta t)$ at time $t + \delta t$ are thus

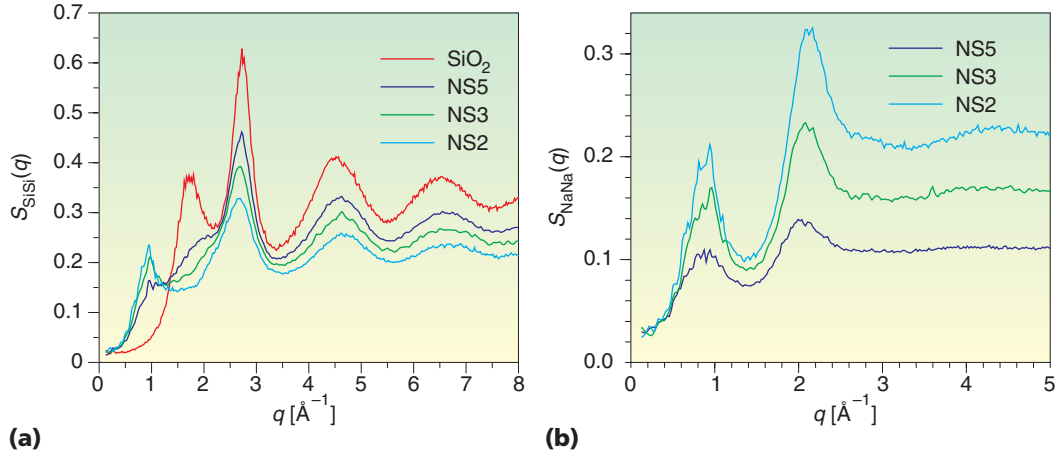


Figure 4. Partial structure factors (a) $S_{\text{SiSi}}(q)$ and (b) $S_{\text{NaNa}}(q)$ of NSx at $T = 3,000$ K plotted against q . We include (a) the result for pure SiO_2 to show that the prepeak is completely absent.⁵

$$\bar{r}_i(t + \delta t) = \bar{r}_i(t) + \bar{v}_i(t)\delta t + \bar{f}_i(t) \frac{(\delta t)^2}{2m_i} \quad (3)$$

$$\bar{v}_i(t + \delta t) = \bar{v}_i(t) + \frac{\delta t}{2m_i} [\bar{f}_i(t) + \bar{f}_i(t + \delta t)], \quad (4)$$

where m_i is the i th particle's mass, and $\bar{f}_i(t)$ is the force acting on it at time t .

For a model with purely pairwise interaction potentials $u(r_{ij})$, $r_{ij} = |\bar{r}_i - \bar{r}_j|$, we have

$$\bar{f}_i = - \sum_{j(\neq i)} \partial u(r_{ij}) / \partial \bar{r}_i, \quad (5)$$

whereas in pure SiO_2 , the choice made in the BKS potential for $u(r_{ij})$ is⁷

$$u_{\alpha\beta}(r) = \frac{q_\alpha q_\beta e^2}{r} + A_{\alpha\beta} \exp(-B_{\alpha\beta} r) - \frac{C_{\alpha\beta}}{r^6}, \quad (6)$$

where $\alpha, \beta \in [\text{Si}, \text{O}]$. Here, e is the elementary charge, $q_{\text{Si}} = 2.4$, $q_{\text{O}} = -1.2$, and $A_{\alpha\beta}$, $B_{\alpha\beta}$, $C_{\alpha\beta}$ are constants. If we include Na or Al, the chosen potentials^{5,6} are similar but slightly more complicated: the effective charge for Na and Al depends on distance $q_{\text{Na}}^{\text{eff}}(r)$, $q_{\text{Al}}^{\text{eff}}(r)$, meaning that they're screened.

For the present discussion, these details are not important. As we've already mentioned, time step δt must be short (say, $\delta t = 1.6$ fs). Recall that the long range of the (pseudo-)Coulomb interactions $q_\alpha q_\beta e^2 / r$ necessitates our use of Ewald techniques the computational load of which scales with the number of particles N like $N^{3/2}$.^{4,11} Newton's equations of

motion conserve energy E . Hence, the system's trajectory through the phase space that follows from the solution of Equations 3 through 6 realizes the "microcanonical" ensemble of statistical thermodynamics. Actually, we can introduce a coupling to an external heat bath in such a way (the so-called Nosé-Hoover thermostat) that the time average along the system trajectory realizes an average according to the canonical ensemble of statistical mechanics.¹¹ There, the temperature T rather than the energy E is the given quantity. In making this assertion, we tacitly have made the "hypothesis of ergodicity" of statistical mechanics, which states the equivalence between time and static averages in the appropriate ensemble.

Since the relaxation times of glass-forming melts near the glass-transition temperature are very large (of the order of hundreds and thus many orders of magnitude beyond the MD simulation's reach), we must consider with great care the configuration's preparation.⁴ We found imposing a constant density of the glass (taken from experiment) useful for the simulation of melts at high temperatures,⁴ which we first carefully equilibrated in long runs. "Long" means 20 ns—roughly 10^7 time steps δt . "High temperature" means 2,750 K for molten SiO_2 ; for NSx, somewhat lower temperatures (about 2,000 K) are accessible because a network that contains sodium ions is less rigid.

If we want to compare with experimental data at room temperature,⁴⁻⁶ as in Figure 1, we cool down from these high temperatures T in the melt region by decreasing the temperature $T(t)$ linearly in time $T(t) = T - \gamma t$ until we reach the desired (low) temperature. Although this is, in principle, the same procedure as the one used in glass factories, there is an important difference with respect to the value of the cooling rate γ . Whereas we have to use a rate $\gamma = 10^{12}$ K/s or even higher here, in a real experiment, we typically would use values of 1 K/s. Due to these very fast quenches, the fact that we reach such good agreement with experiment is nontrivial.

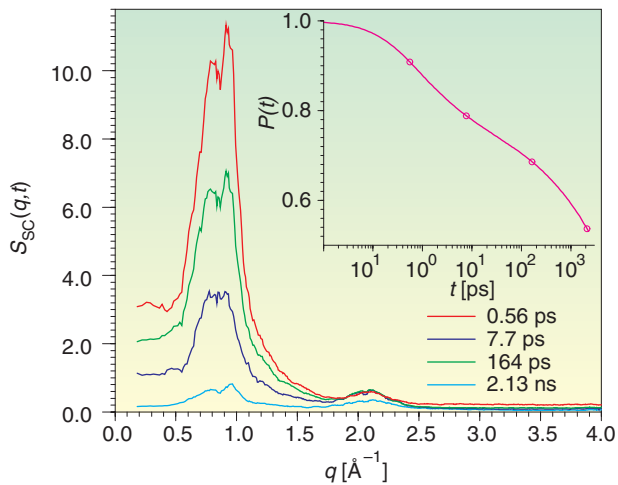


Figure 5. A Swiss cheese-like structure factor for sodium-free regions plotted against q at $T = 2,100$ K for the four indicated times. The insert shows the conditional probability $P(t)$ that a cube free of Na^+ at $t = 0$ has not been visited by a Na^+ ion during time t .⁴

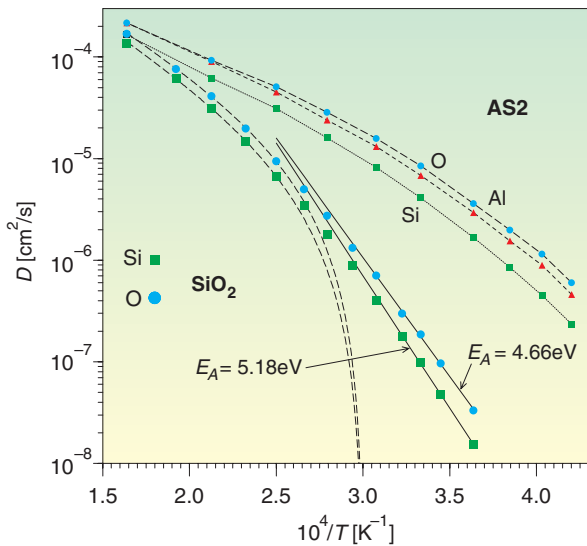


Figure 6. Arrhenius plot of the self-diffusion coefficients of SiO_2 and Al in SiO_2 and aluminum disilicate (AS2) melts. In SiO_2 , curves represent fits according to an Arrhenius law. In AS2, curves are guides for the eye only.⁵

Clearly, there is an element of good luck in the BKS model yielding fluid structures of silica at $T \geq 2,750$ K, which are close to real silica at much lower temperatures.¹⁹ Due to the enormous disparity between experimental cooling rates and those accessible in simulation, we don't win much by working with a more accurate description of interatomic forces than Equa-

tion 6 provides.¹⁹ Moreover, these more accurate methods (such as ab initio MD, which is a factor 10^5 slower) require even larger cooling rates.

Evidence for the Channel Picture in Sodium Silicates

What can simulations tell us about the idea that the anomalously high mobility of Na^+ ions is due to percolating Na-rich channels?¹⁸ A weak hint appears in Figure 1b, in which we see a small prepeak in the simulated $S(q)$ at $q_p \approx 0.9 \text{ \AA}^{-1}$. Because this very weak signal is not resolved in the corresponding experimental data,¹⁵ we might think this little hump is nothing but statistical noise—but this is not the case, as the partial structure factors in Figure 4 show. In both the NaNa and SiSi correlations at $q_p \approx 0.9 \text{ \AA}^{-1}$ in NSx, we see a very pronounced peak.

The reason the prepeak in the total $S(q)$ is so weak is that in mixed-structure factors $S_{\text{NaO}}(q)$ and $S_{\text{NaSi}}(q)$, we find a deep minimum at q_p , thus the prepeak in the total $S(q)$ almost cancels out. Moreover, we can interpret the characteristic linear dimension $l \approx 2\pi/q_p \approx 7 \text{ \AA}$ as the typical distance between the Na-rich channels. Such an interpretation is motivated by the following analysis.^{6,20}

Let's conduct a “Gedankenexperiment” in which we divide our simulation box into small cells of linear dimensions—say, 1 \AA . If a cell contains a Na^+ ion at time $t = 0$ in an equilibrated NSx melt, we color the cell blue; otherwise, the cell is left white. The centers of the white cells are labeled $\{\vec{r}_k\}$. As time passes, an Na^+ ion visits some of the cells that did not contain such an ion at $t = 0$. Therefore, the probability $P(t)$ that a cube free of Na^+ at $t = 0$ still has not been visited up to time t decreases, and, correspondingly, the number $N_{\text{sc}}(t)$ of white cells decreases. It is thus of interest to define a structure factor $S_{\text{sc}}(t)$ that characterizes the geometry of sodium-free regions:

$$S_{\text{sc}}(q, t) = N_{\text{sc}}^{-1}(t) \sum_{k=1}^{N_{\text{sc}}(t)} \sum_{l=1}^{N_{\text{sc}}(t)} \left\langle \exp[i\vec{q} \cdot (\vec{r}_k - \vec{r}_l)] \right\rangle. \quad (7)$$

The index “sc” stands for Swiss cheese, because the picture proposes that NSx contain a Swiss cheese-like SiO_2 network in which the Na^+ ions occur in the “cheese's” holes. These holes are not isolated spheres, of course. Rather, a thin percolating network connects them (otherwise, there could not be fast Na^+ diffusion).

Figure 5 shows that $S_{sc}(t)$ does indeed have a peak at q_p that is most pronounced on the nanosecond timescale—the Swiss cheese structure’s lifetime at the shown temperature. On this timescale, we see from D_{Na} (in Figure 2) that the sodium ions have diffused almost fully through the full simulation box. This analysis is corroborated by a study of the coherent intermediate dynamic structure factor of the sodium ions,⁶

$$F_{NaNa}^{coh}(q,t) = [S_{NaNa}(q)]^{-1} \sum_{k=1}^{N_{Na}} \sum_{l=1}^{N_{Na}} \langle \exp[i\vec{q} \cdot (\vec{r}_k(t) - \vec{r}_l(0))] \rangle, \quad (8)$$

which decays on the same (large) timescale of 2 ns at $T = 2,100$ K, which is characteristic for the sodium-free SiO_2 network’s lifetime. In contrast, this quantity’s incoherent counterpart (in which we follow the motion of the same particle i from position $\vec{r}_i(0)$ to position $\vec{r}_i(t)$) already shows a strong decay on the 10-ps timescale, which we would expect from the fast Na^+ diffusion along the channels.⁶

Of course, this study’s relevance is not just that a quite plausible picture is confirmed qualitatively: for the first time, the quantitative aspects (such as linear dimensions between channels and their lifetimes) are characterized. This example also shows how to use atomistic MD or Monte Carlo simulations profitably to test concepts by measuring quantities that even in principle are inaccessible experimentally—such as $S_{sc}(q,t)$. Recently, difficult measurements of $S(q)$ for NSx at high temperatures could confirm at least a shoulder in $S(q)$ at q_p , further corroborating this simulation’s findings.¹³

Molten Aluminum Disilicate

In the example of sodium silicates, we saw that the Na^+ ions act as network modifiers by breaking up some of the connected SiO_4 tetrahedra and leaving oxygens in nonbridging positions. However, not all ions mixed with silica behave like this: the added ions might be included in the network, thus changing locally the oxygen coordination. As an example, for aluminum, a hypothesis exists that says *triclusters* form—oxygen atoms that have three covalent bonds, to one Al and two Si neighbors.²¹

Again, MD modeling can shed light on this issue. For $(Al_2O_3)_2(SiO_2)$ —which we henceforth will call AS2—we find this peak at $q_p \approx 0.5 \text{ \AA}^{-1}$. Despite this prepeak’s presence, the diffusion constants of aluminum and oxygen are almost

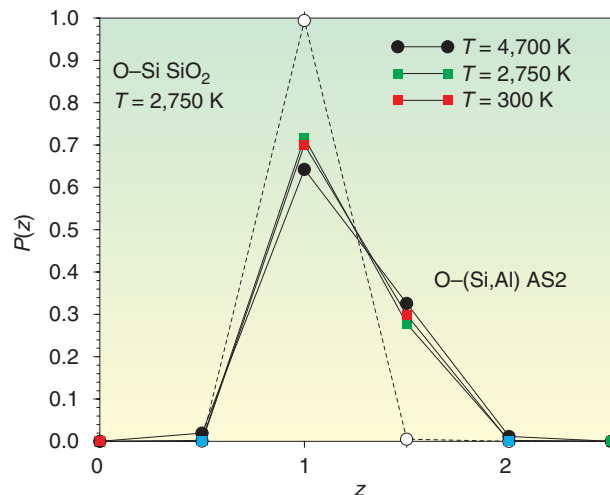


Figure 7. Distribution $P(z)$ of the coordination number z of oxygen atoms in AS2 at three temperatures. Here, it is not distinguished whether an oxygen has an Si or Al neighbor. Oxygen in pure SiO_2 at $T = 2,750$ K is included for comparison.⁵

always the same (see Figure 6). This fact indicates that the lifetime of oxygen bonds in the Si-O-Al network controls mobility, although there is *some* local phase separation between Si and Al in the network—as reflected in the prepeak. Examination of the experimental phase diagram shows that in supercooled SiO_2 - Al_2O_3 mixtures, even a liquid–liquid miscibility gap occurs at low temperatures, hence the prepeak found in the simulations is probably a precursor of this macroscopic phase separation.

However, the simulation can prove directly the existence of triclusters, because we can directly analyze the local neighborhoods of all the atoms in the system’s simulated configurations with little ambiguity, count how many bonds there are, and estimate the distribution $P(z)$, where z is the number of bonds each O-ion has (see Figure 7). Although in pure SiO_2 this count yields $P(z = 2) \approx 1$, $P(z = 1) \approx P(z = 3) \approx 0$, in AS2, $P(z = 3) \approx 0.3$ due to the triclusters present.

Simulation of materials properties is now a broad international effort, which has experienced quite a few spectacular successes already and promises more for the future. For amorphous materials (sometimes called *ill-condensed*) where experiments¹³ are notoriously hard to interpret uniquely, such simulations are particularly valuable, as we have emphasized here. Future work along the lines of this study can address some of the many other longstanding puzzles concerning the interplay of structure and dynamics in glasses—for example the “mixed alkali effect” (a dramatic decrease of diffusion constants in glasses containing several types of alkali ions).

Acknowledgments

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