

First-Principles Study of Enhancement of Transport Properties of Silica Melt by Water

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(Received 4 January 2010; published 25 May 2010)

First-principles molecular dynamics simulations show that water (8.25 wt%) dramatically affects the transport properties of SiO₂ liquid increasing the diffusivity and decreasing the viscosity by an order of magnitude. At 3000 K, the diffusivity of Si, O, and H, and the viscosity vary anomalously with pressure. Highly mobile protons make the hydrous liquid a potential superionic conductor. The predicted dynamical changes are associated with structural depolymerization and water speciation, which changes from being dominated by hydroxyls at low pressure to extended structures at high pressure.

DOI: 10.1103/PhysRevLett.104.215901

PACS numbers: 61.20.Ja, 62.50.-p, 66.10.-x, 66.20.-d

Silica liquid, a prototype of network-forming liquids, is of substantial interest in physics and geosciences [1–3]. It is a major component of silicate melts (magmas), believed to exist over a range of depths up to the core-mantle boundary (2890 km depth, 136 GPa, and 4000 K) [4]. Melts might have played an even more important role in the past when Earth's mantle was largely molten (a magma ocean) [5]. Along the MgO-SiO₂ join, this end member has the smallest diffusivity and the largest viscosity. Moreover, pair potential calculations [1,6] predicted that the diffusivity and viscosity vary anomalously with pressure as also confirmed by first-principles study of diffusion [7]. The slow, anomalous dynamics of liquid silica (and silicates) is usually attributed to highly polymerized structures [8,9].

Magmas are commonly hydrous containing up to several weight percent water, and water solubility increases with pressure [10]. Water substantially influences physical properties of liquids [11]. Interesting questions arise: How much is the dynamics of silica liquid enhanced by water? And are the dynamical anomalies predicted in the pure phase preserved in the hydrous phase? It has also been speculated that the enhanced dynamics (higher diffusivity and lower viscosity) occurs because water depolymerizes the melt structure. However, the exact microscopic origin is still unknown. Another important issue is related to proton conduction experimentally detected in some silicate glasses [12]. Can hydrous silica liquid be a potential proton conductor? A first-principles approach [13–15] correctly describing hydrogen bond, which is an issue in widely used (dominantly) ionic models [16], can answer these questions.

Here, we use the first-principles molecular dynamics method [17] to investigate the structure and dynamics of hydrous (with 8.25 wt% water) and anhydrous silica liquids as a function of pressure (P) and temperature (T) and evaluate or isolate the effects of water unlike in the case of other silicates (e.g., MgSiO₃) that are already

depolymerized due to other cations. The local density approximation [18] and projector augmented wave method [19] (with a cutoff of 450 eV and gamma point) were used. The canonical (NVT) simulations were performed with time steps of 0.5 (1.0) fs for hydrous (anhydrous) liquid at several volumes: $V/V_X = 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.45,$ and 0.4 , where the reference volume V_X is 1099.1 \AA^3 for both hydrous ($20\text{SiO}_2 + 6\text{H}_2\text{O}$) and anhydrous (24SiO_2) systems. The initial structure was first melted at 6000 K, and then cooled down isochorically to 4000 K and then to 3000 K [20]. The finite size effects [1,7] are relatively small compared to the effects of P , T and water (S1 [21]).

The self-diffusion coefficients (D_α) and the shear viscosity (η) were calculated using the well-known Einstein and Green-Kubo relations (S2, S3 [21]). We find that water dramatically enhances the dynamics increasing the self-diffusivity (of both Si and O) and decreasing the viscosity (Fig. 1). At V_X and 3000 K, the diffusivity (viscosity) increases (decreases) by more than an order of magnitude in the presence of water, and the water effects are suppressed on heating and compression. The activation energies ($E_{D_{\text{Si}}}^* = 2.6$, $E_{D_{\text{O}}}^* = 2.2$, $E_\eta^* = 2.9$ in eV) for diffusion and viscous flow of the hydrous liquid are smaller than those (3.8, 3.7, 3.8 eV) of the anhydrous liquid (S4 [21]). The H activation energy of 1.7 eV falls within the broad experimental range [22]. Our results show that all three self-diffusion coefficients strongly vary with pressure: At 3000 K, not only Si and O atoms but also H atoms show anomalous diffusion—their diffusivities increase with pressure initially, reach a maximum, and then decrease on further compression (Fig. 1). Consistently, the viscosity decreases initially with pressure, reaches a minimum, and then increases at higher pressures. In Arrhenian formalism, this means that the activation volumes [$V_{D_\alpha}^* = (d \ln D_\alpha / dP)_T$, $V_\eta^* = (d \ln \eta / dP)_T$] change from negative to positive as pressure increases. The dynamical anomalies are weak or absent at higher temperatures, and are sup-

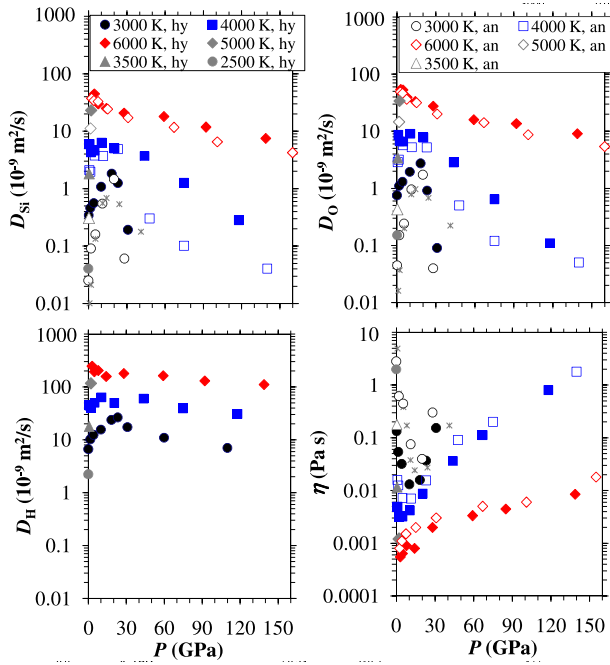


FIG. 1 (color online). Pressure variations of diffusivity (D_a) of Si, O, and H, and viscosity (η) of hydrous (solid symbols) and anhydrous (open symbols) silica liquids at 3000 K (circles), 4000 K (squares), and 6000 K (diamonds). Also shown are 2500 K (hydrous), 3500 K, and 5000 K for the reference volume, and previous 3000 K MD results [6] (asterisks). The 3000 K results are at $V/V_X = 1.0, 0.9, 0.8, 0.7, 0.6, 0.58$ (anhydrous), and 0.55 and 0.50 (hydrous).

pressed by water (Fig. 1). Our predicted diffusion and viscosity anomalies from first principles have been observed experimentally in silicate liquids [8,9].

Our results show that protons are highly mobile (Fig. 1). The diffusivity of H is an order of magnitude higher than that of Si and O at low pressure, and the differences remain large at all conditions ($D_H/D_{Si} \sim 100$; $D_H/D_O \sim 200$ at $0.5V_X$ and 3000 K). We estimate the electrical conductivity arising from the migration of protons considered as the primary charge carriers using the Nernst-Einstein equation [23]. The conductivity is 46 S m^{-1} at V_X and 3000 K and increases rapidly with pressure exceeding 300 S m^{-1} around 25 GPa. On further compression, it gradually decreases but remains large (118 S m^{-1} at 110 GPa) in high-pressure regime where the Si and O diffusion rates are too slow to calculate and liquid behaves as glass. Temperature systematically increases the proton conductivity. Thus, hydrous silica liquid is an ionic conductor and becomes even more conductive on both compression and heating. This has geophysical implication that a neutrally buoyant (partial) hydrous melt layer can produce a detectable conductance [14]. Proton conduction measured in hydrous silicate glasses [12] is yet to be detected experimentally in hydrous silica glass [24]. The absent or weak proton conduction in glasses means that water diffuses primarily

as molecular water because the structural relaxation is too slow to form other hydrous species, which can facilitate proton migration as in the liquid (discussed later).

Now we relate the water-induced changes in the transport properties to the structural changes. The major effect of water is to systematically depolymerize the melt. The mean O-Si coordination of the hydrous liquid varies from 1.7 to 2.6 on compression compared to the anhydrous values of 2 to 3 (S5 [21]). It contains large contribution (25% at V_X , 3000 K) from nonbridging oxygen, NBO ($_1C_{OSi}$ species), almost absent in the pure liquid, formed at the cost of bridging oxygen, BO ($_2C_{OSi}$ species), see Table I and S6 [21]. The depolymerization is also reflected by the reduced Si-Si coordination (see, S6, S7 [21]). We find a gradual increase in the mean Si-O coordination from 4 to 6 on compression as in the anhydrous phase [7] occurring through the preponderance of $_5C_{SiO}$ species at mid compressions (Table I).

Since three-coordinated silicon ($_3C_{SiO}$) is rare (Table I), its dynamical relevance can be ignored. Tetrahedra ($_4C_{SiO}$), pentahedra ($_5C_{SiO}$), NBO ($_1C_{OSi}$), BO ($_2C_{OSi}$), and O3 ($_3C_{OSi}$) are present in significant amounts at low pressures (Table I). Not all pentahedra are associated with O3 (oxygen tricluster) because $n(_3C_{OSi}/_5C_{SiO})$, where n is O/Si ratio of 2.3 (2) for hydrous (anhydrous) liquid, decreases from 0.51 at V_X to 0.36 at $0.8V_X$ along 3000 K. Its value is 1.0 for the anhydrous liquid in which every pentahedron is formed via $BO \rightarrow O3$ transformation. This suggests a mechanism in which an NBO and a four-coordinated silicon together form one pentahedron and one BO. The pentahedron eventually loses one of its original BO's as NBO and becomes a tetrahedron. In effect, one oxygen (O_1) enters into and another oxygen (O_2) exits from the silicon coordination shell under consideration (Fig. 2, upper).

TABLE I. Abundances of various Si-O and O-Si coordination species of hydrous (first row) and anhydrous (second row) silica liquids at each condition. Z represents the coordination number.

V, T condition	$_zC_{SiO}$ species $Z = 3, 4, 5, 6$	$_zC_{OSi}$ species $Z = 0, 1, 2, 3$
$V_X,$	1.1, 96, 2.5, 0.04	0.54, 25, 74, 0.55
3000 K	0.41, 98, 2.0, 0.03	0.02, 0.2, 99, 1.0
$V_X,$	8.4, 79, 12, 0.33	1.5, 25, 70, 3.4
4000 K	4.6, 87, 8.2, 0.2	0.04, 2.1, 94, 4.0
$0.8V_X,$	0.57, 92, 7.1, 0.17	0.62, 23, 76, 1.1
3000 K	0.32, 97, 3.2, 0.04	0.05, 0.14, 98, 1.6
$0.6V_X,$	0.21, 44, 45, 11	0.40, 13, 70, 16
3000 K	0.03, 43, 46, 11	0.02, 0.08, 58, 39
$0.4V_X,$	0.00, 0.16, 7.7, 85	0.12, 5.4, 31, 60
3000 K	0.00, 0.10, 4.0, 74	0.02, 0.08, 5.5, 79
$0.4V_X,$	0.00, 0.29, 9.1, 75	0.14, 3.5, 35, 54
4000 K	0.00, 0.12, 5.2, 65	0.03, 0.11, 4.5, 77

Previous studies of anhydrous liquids associated the dynamic anomalies to five-coordinated Si species, i.e., pentahedra [7,25]. In particular, the pressure at which ${}_5C_{SiO}$ species is most abundant coincides with the pressures of the diffusivity maxima and viscosity minimum. We show that pentahedra facilitate self-diffusion in hydrous silica liquid via two mechanisms of which only one is relevant in pure silica liquid. The first is the single pentahedron mechanism (described earlier) mainly operative at initial compression. On further compression, both the pentahedra and O3's become highly abundant (Table I) and $n({}_3C_{OSi}/{}_5C_{SiO})$ increases to 0.82 at $0.6V_X$ (i.e., more pentahedra are associated with O3). A second mechanism operates involving pentahedron and oxygen tricluster. In Fig. 2 (lower), a pentahedron (about Si_1) is formed when one BO atom (O_1) turns into O3. Subsequently, the pentahedron loses another BO atom (O_2). The O3 continues to exist and a second pentahedron (Si_2) is formed with bonding to the NBO atom (O_3). Finally, the Si_2 - O_1 bond breaks, and the O3 turns into BO and the pentahedron (Si_2) turns into tetrahedron. Two pentahedra (about Si_1 and Si_2), one NBO (O_3), and one O3 (O_1) are thus involved in this mechanism. Both mechanisms enhance the diffusivity in the hydrous liquid, as compared with the anhydrous liquid, and their contributions increase on compression. Because of the absence of NBO in the anhydrous liquid, the transition state must involve two pentahedra and only oxygen triclusters, such as sharing two O3's so that oxygen exchange occurs between two silicon atoms.

The dynamical relevance of pentahedra changes on compression. In the low-pressure regime (mostly tetrahedral environment), the over-coordination state (pentahedron) is energetically unstable and tends to lose oxygen thereby serving as a source. The atoms (in particular, NBO) have higher angular mobility in the open space available so D_O is larger than D_{Si} . However, at high pressures where the liquid tends to adopt octahedral coordination (Table I and S6 [21]), the pentahedron acts as a sink and acquires oxy-

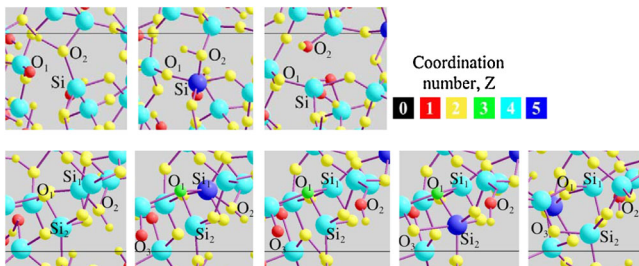


FIG. 2 (color online). Oxygen atom transfer mechanisms involving single pentahedron (upper panel) and two pentahedra (lower panel). The colors of large spheres (Si) and medium spheres (O) represent ${}_zC_{SiO}$ and ${}_zC_{OSi}$ species, respectively. Si atoms are mostly four-coordinated (tetrahedra) and five-coordinated (pentahedra) displayed as cyan and blue large spheres. O atoms are NBO, BO, and O3 (red, yellow, and green medium spheres). Small (yellow) spheres are H atoms.

gen turning into an octahedron via $BO \rightarrow O3$ or $O3 \rightarrow O4$ transformation. Also NBO (present in small amounts) effectively bridges two silicon atoms via hydrogen. The decreased role of pentahedra and NBO results in the asymmetric diffusion peaks and viscosity valley with a steeper slope on the high-pressure side (Fig. 1). Also, D_O is similar to or smaller than D_{Si} , a trend previously predicted in B_2O_3 liquid [26].

How water dissolves in the liquid impacts the degree of polymerization and hence the transport properties. Water speciation occurs through oxygen-hydrogen bonding in various forms whose abundances are shown in Fig. 3 (S8 [21]). The most abundant speciation is hydroxyls ($\sim 90\%$ at V_X , 3000 K) all attached to the silicon matrix. The strong polyhedral association is also reflected by the first peak of the Si-H radial distribution function lying at a distance smaller than the sum of the Si-O and H-O peak distances (S7 [21]). The NBO sites are more abundant than the BO sites, consistent with the reaction [27]: $Si-O-Si + H_2O = 2Si-OH$. The number of hydroxyls decreases rapidly initially on compression. Water molecules are present in small amounts (6% at V_X , 3000 K), a shallow peak in the H-H radial distribution function occurs at a distance similar to the H-H separation in the free water molecule (S7 [21]). The other important speciation is polyhedral bridging in which an H atom is bonded with two O atoms from different polyhedra. The number of bridges gradually increases on compression and starts to decrease at high compression ($<0.5V_X$). A similar nonmonotonic trend is

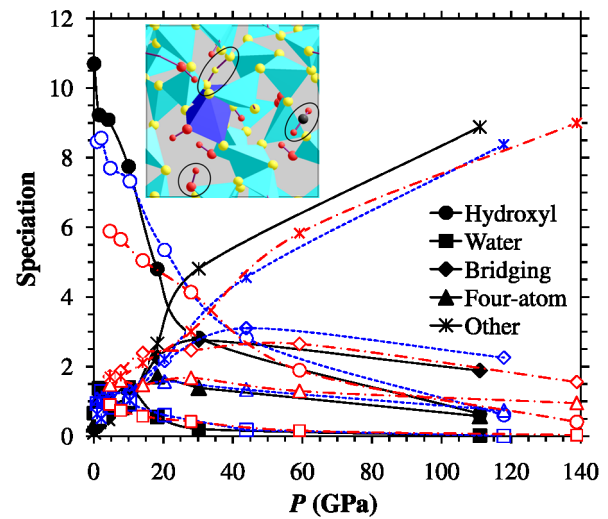


FIG. 3 (color online). Abundances (in terms of the number of H atoms, 12 in total) of different forms of water speciation at 3000 K (black solid lines), 4000 K (blue dashed lines), and 6000 K (red dashed-dotted lines). Species grouped under "Other" mostly represent long chains. Visualization snapshot (inset) at 4.2 GPa and 3000 K [29] shows hydroxyls, free water molecule, and H bridging (marked). Polyhedra, large (O), and small (H) spheres encode Si-O, O-Si, and H-O coordination, respectively, using the color scheme of Fig. 2.

shown by the abundance of four-atom structures (O-H-O-H). As the liquid is compressed, the extended structures involving a total of five or more H and O atoms appear in increasing abundances. The mean H-O coordination becomes two or higher as in the high-pressure form of water and ice (see, S9 [21]). The greater O participation in hydrogen bonding suggests that the solubility of water in the silica melt is unlimited and the silica-water system becomes increasingly ideal on compression [14,16].

We now explore the microscopic mechanisms responsible for fast and anomalous diffusion of hydrogen. The transfer of H occurs via the momentary formation of an H bridge between two polyhedral oxygens (PO, which can be NBO or BO): PO-H...PO \rightarrow PO-H-PO \rightarrow PO...H-PO. Alternatively, when both the source and destination are polyhedral hydroxyls, the intermediate state is a four-atom sequence: PO-H...PO-H \rightarrow PO-H-PO-H \rightarrow PO...H-PO-H. The abundance of both intermediate states (O-H-O and O-H-O-H) increase on compression accounting for the rapid increase in H diffusivity with increasing pressure at 3000 K (Fig. 1). At higher pressures, still longer chains increase in abundance and the number of ...O-H-O... groups saturates as the H-O coordination number approaches 2. This leads to a normal high-pressure regime in which H diffusivity decreases with increasing pressure and which is separated from the low-pressure anomalous regime by a local maximum (Fig. 1). These bridges are the major contributors to diffusion as neither the motion of hydroxyls, water molecules, nor free protons play a significant role. Free hydroxyls are absent (<0.5% at 3000 K) and the movement of hydroxyls does not occur because it requires the rupture or formation of highly stable Si-O bonds (S10 [21]). Free water molecule (once formed via Si-O bond breaking) (Fig. 3, inset) moves stably for long durations (S10 [21]) implying fast diffusion, consistent with previous suggestion [28]. However, this contribution is small since molecular water tends to remain polyhedral and eventually forms part of extended structures. Thus, proton transfer occurs between polyhedral groups through the rupture or formation of O-H bonds.

The authors thank the Center of Computation and Technology at LSU for computing resources. The National Science Foundation (EAR-0809489) and the UK National Environmental Research Council (NE/F01787/1) supported this work.

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