Pressure-Induced Structural Changes in Liquid SiO_2 from Ab Initio Simulations

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First-principles molecular dynamics simulations at constant pressure have been used to investigate the mechanisms of compression of liquid SiO_2. Liquid SiO_2 is found to become denser than quartz at a pressure of about 6 GPa, in agreement with extrapolations of lower pressure experimental data. The high compressibility of the liquid is traced to medium-range changes in the topology of the atomic network. These changes consist in an increase of network connectivity caused by the pressure-induced appearance of coordination defects.

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Understanding the properties of liquid SiO_2, and, in particular, its response to compression, has important implications in geophysics and in materials science [1]. Liquid SiO_2 is in fact the main constituent of all geologically relevant melts (magmas), and when rapidly quenched produces vitreous silica (glass), a material of enormous technological relevance. Liquid SiO_2 is also of interest for more fundamental reasons, as it is a prototype of network-forming liquid. As such it is believed to share with liquid water a number of thermodynamical and dynamical anomalies [2], the origin of which is still widely debated. Contrary to water, however, experiments on liquid SiO_2 are challenging because of its high freezing point (2000 K). Volumetric experiments [3] suggest that the compressibility of liquid SiO_2 between 0 and 10 GPa is substantially higher than that of quartz, the dominant solid phase at those pressures (β-quartz at high temperature). Extrapolation of the solid and liquid equations of state at pressures higher than the stability limit of quartz indicates that the liquid eventually becomes denser than (then metastable) quartz [4,5]. A density inversion may have important consequences. First, it implies, by virtue of the Clausius-Clapeyron relation, that the metastable extension of the quartz/liquid melting line displays a reentrance, i.e., a change in slope from positive to negative (decreasing melting temperature for increasing pressures), that could be related, if extrapolated to room temperature, to the observed amorphization of quartz [6]. Second, if density inversion were to be a general property of silicates, the possibilty of sinking deep magmas would have important geochemical consequences [7].

Because the local microscopic structure of liquid SiO_2 is believed to consist, like quartz, of rather incompressible corner-sharing SiO_4 tetrahedra, the large difference in the compressibility of liquid and solid SiO_2 has been tentatively explained by substantial pressure-induced changes in the structure and spatial arrangement of tetrahedra in the liquid. Various microscopic mechanisms can be invoked to explain such rearrangements, including reduction of the intertetrahedral distance, as observed in SiO_2 glass [8], partial collapse of the network [9], and topological effects related to changes in the statistics of closed loops (rings) in the network [10]. Partial rupture of the tetrahedral units due to a continuous increase in the Si coordination has also been proposed [7].

Given the obvious experimental difficulties in achieving the high temperatures required for liquid SiO_2, simulations based on standard empirical force fields have been instrumental in understanding the microscopic mechanisms of compression [10–13]. However, we show here that empirical force fields are not sufficiently accurate to reproduce pressure-induced phenomena such as changes in coordination and increasingly strained geometries. Here we report the results of first-principles simulations of liquid SiO_2 at pressures $P < 30$ GPa, indicating that the key for the large compressibility of liquid SiO_2 is the increased connectivity of the network induced by coordination defects.

First-principles simulations [14] were performed in the NPT ensemble using a variable cell method [15]. The time step for the integration of the equations of motion using the Verlet algorithm was set to 0.36 fs. Temperature was kept to 3500 K, and electrons were kept close to the ground state by means of thermostats [16]. Small corrections to temperature and pressure, intrinsic to the Car-Parrinello approximation, were applied as described in Ref. [17]. The electron-ion interaction was modeled with ultrasoft pseudopotentials [18], and electron wave functions were expanded in plane waves with a kinetic energy cutoff of 26 Ry. The simulation cell contained 24 SiO_2 units (72 atoms), and electronic states were assumed to have the periodicity of the cell. The local density approximation to density functional theory was supplemented with gradient corrections [19]. Such

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approximations provide a very accurate description of the low-temperature equations of state of quartz and stishovite [20] as well as of liquid SiO_2 at ambient pressure [21]. Convergence of the runs with respect to cell size was checked by means of a recently developed polarizable force field parametrized on *ab initio* configurations [22]. No significant structural differences (density, pair correlations, and Si coordinations) were observed in classical runs containing 72 and 512 atoms, at all reported pressures. This justifies the choice of a 72-atom simulation cell for the *ab initio* simulations. However, classical runs with 72 atoms and <2 ps duration showed that convergence of the thermodynamical observables with simulation time is poor at low pressure ($P < 5$ GPa), where the viscosity of liquid SiO_2 is large. Therefore, two independent sets of *ab initio* molecular dynamics (MD) runs were conducted. In the first set (run # 1) the 0 GPa configuration was taken from a well equilibrated liquid run generated with the polarizable force field described above. Because of incomplete equilibration, we expect this run to provide, between 1 and 5 GPa, an upper bound to the correct volume of liquid SiO_2. In the second set (run #2) the 0 GPa configuration was generated by melting a quartz crystal at 10 000 K and then quenching the liquid down to 3500 K. Because of the higher density of the initial quartz structure, we expect this run to provide a lower bound to the correct volume. In both cases pressure was then increased at intervals of a few (2 to 5) GPa. Each run at a new pressure started from the final atomic configuration of the previous run, and consisted of an initial thermalization (~ 0.2 ps) followed by at least 1.2 ps of MD where data were collected. As a reference, we also performed simulations of quartz at the same P-T conditions. Although quartz is thermodynamically unstable towards the liquid at 3500 K, we took advantage of the limited time/size scales of our simulations and of the periodic boundary conditions to keep the solid in superheated conditions for the full duration of the MD runs. In Fig. 1 we show the volume versus pressure curves for quartz and liquid SiO_2, at 3500 K. As expected, the two liquid simulations yield very similar results above 5 GPa, while below 5 GPa they bracket the experimental curve, which was, however, measured at lower temperature (2000 K) [3]. Despite the scatter of our results below 5 GPa, density inversion can be clearly identified at a pressure of 6 ± 3 GPa. If we assume that the density inversion is independent of temperature, the Clausius-Clapeyron relation $dT_m/dP = \Delta V/\Delta S$, where $T_m(P)$ is the melting temperature at pressure P, and ΔV and ΔS are the volume and entropy jumps upon melting, respectively, implies that the quartz/liquid melting line must change slope at about 6 GPa, and start to decrease afterwards. This is in good agreement with extrapolations based on lower pressure experimental data [4,5]. It is consistent with the hypothesis that the observed room temperature amorphization of quartz might be related to the low-temperature

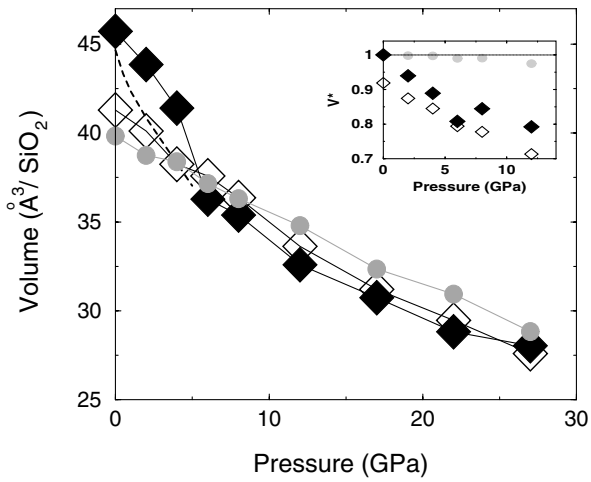

FIG. 1. Equations of state of quartz and liquid SiO_2 at 3500 K. Diamonds: liquid (solid diamonds: run #1; open diamonds: run #2); gray circles: quartz. Dashed line: equation of state of the liquid at 2000 K, from experiments [3]. Inset: Volumes scaled with the average value of $R^3_{\mathrm{Si-Si}}$.

reentrant "tail" of the quartz melting line [6], although other mechanisms may concur to cause pressure amorphization [23].

We now analyze in more detail the microscopic mechanisms responsible for the density inversion. We start by considering the simplest mechanism, which consists in attributing the large compressibility of the liquid to an average increase in the coordination number of Si, from ^{IV}Si to ^{V}Si and eventually ^{VI}Si. This mechanism, in principle supported by the low-temperature thermodynamical stability of the all-^{VI}Si stishovite phase above 8 GPa, has been ruled out, however, for liquid SiO_2 on the basis of NMR experiments, where no ^{V}Si or ^{VI}Si defects have been found up to 6 GPa [24]. Experiments were, however, performed on glasses quenched from high temperature and high pressure, and so inferences on the actual high pressure behavior had to rely on the assumption that the local microscopic structure of the liquid was preserved by the quenching process. In Fig. 2(a) we report the percentage of Si atoms coordinated four to six, as a function of pressure, in our simulated liquids. We remark that Si-coordination changes obtained with one of the most commonly used nonpolarizable force fields for SiO_2 (BKS) [25] are much larger (Fig. 2(b)), predicting a 45% of ^{V}Si at 10 GPa [13], to be compared with a first-principle value of only $18 \pm 4\%$. Although much smaller than the values extracted from the BKS force field, first-principle MD still predicts a non-negligible amount of coordination changes, contrary to what observed experimentally in quenched samples. We believe that the discrepancy is most likely due to the "slow" (on atomic time scales) quenching rate in experiments, which allows coordination defects to disappear as in ordinary glass. The calculated coordination changes are, however, not sufficient, alone, to explain the density inversion and, in

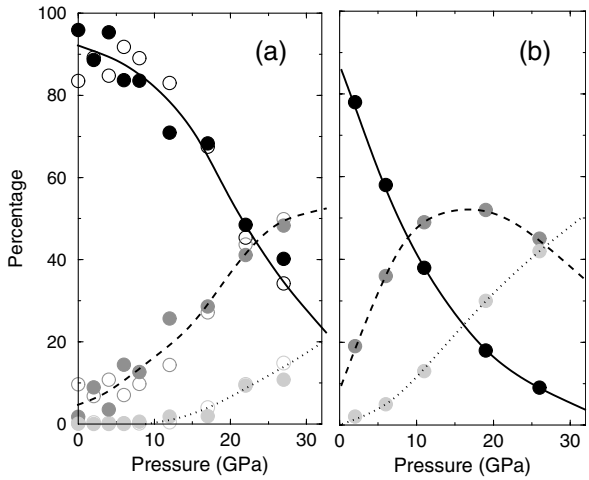

FIG. 2. Percentage of Si atoms coordinated to 4, 5, and 6 oxygen atoms (black, gray, light gray, respectively). (a) *ab initio* simulations (solid symbols: run # 1, open symbols: run # 2); (b) simulations with the BKS force field [13,25]. Lines are a guide to the eye.

particular, the substantial decrease of the ratio V_l/V_q between liquid (V_l) and quartz (V_q) volumes between 0 to 12 GPa (29% in run #1 and 19% in run #2). In fact, assuming that each ^{VI}Si contributes with a 30% volume reduction with respect to ^{IV}Si, by analogy with the quartz/stishovite density ratio at 12 GPa (and ^{V}Si contributes with a ~15% reduction), then the reduction in V_l/V_q expected for the coordination percentages shown in Fig. 2 would be of only 4% (run #1) and 1% (run #2) between 0 and 12 GPa. It is interesting to note that the large coordination changes obtained with the BKS force field would give a reduction as large as 12% in V_l/V_q, which erroneously assigns to coordination changes an important role in explaining the density inversion.

Having ruled out coordination changes alone as a possible mechanism for compression in liquid SiO_2, we now analyze mechanisms based on the reduction of the interatomic distances in an otherwise fourfold-coordinated Si network. The Si-O bond is only minimally affected by pressure, as in quartz. At variance with quartz, however, where compression is dominated by a decrease of the intertetrahedral distance $R_{\mathrm{Si-Si}}$ or, equivalently, by a reduction of the SiÔSi angle α [$R_{\mathrm{Si-Si}} = 2R_{\mathrm{Si-O}}\sin(\alpha/2)$], in liquid SiO_2 α is already considerably smaller at low pressure (127° at 0 GPa), than in quartz (140° at 0 GPa), in spite of the larger volume of the liquid. Moreover, α decreases much more slowly with pressure in the liquid than in quartz, reaching, at 12 GPa, a value of 125° in the liquid and 133° in quartz. This is in very good agreement with the findings of Ref. [26], where a decrease of α of less than 2° has been measured in silicate liquids between 0 and 8 GPa. The dominance of the SiÔSi angle closing as a mechanism for compression in quartz is highlighted by the pressure independence of the ratio $V^\star = (V/V^\circ)/(R_{\mathrm{Si-Si}}/R^\circ_{\mathrm{Si-Si}})^3$, where the apex ° refers to $P = 0$ GPa values (inset of Fig. 1). This is not the case of the liquid, where the volume seems to be little correlated with $R_{\mathrm{Si-Si}}$, suggesting that other mechanisms are to be sought to explain its larger compressibility.

Failure to ascribe the liquid compressibility to any of the above simple mechanisms leads us to consider more complex, medium-range rearrangements of the network. To this aim, we determined the topological connectivity of the network by focusing on the network of the Si atoms and defining connections between Si pairs as the presence of a bridging oxygen between them (-Si-O-Si-). We then define the nth-topological "cluster" surrounding a specific Si atom as the set of all Si atoms that can be reached from the central atom in at most n connections. A compression mechanism leading to the pressure-induced increase of the population of topological clusters has been proposed earlier in Ref. [10]. It is based on a perfectly fourfold coordinated network and manifests itself with an increase in the average length of the closed loops (rings) in the network, or equivalently with a gradual disappearance of three-membered rings with increasing pressure which causes an increase of the $n = 2$ cluster population (see Fig. 3(b)). Unfortunately, this is not consistent with the observed increase in the number of small (three and four)-membered rings in compressed SiO_2 glass [8]. We calculated the average number of three-membered rings in our simulated liquid and we also find that it increases with pressure. In spite of this, the population of the nth topological cluster increases in our simulations, indicating that topological mechanisms are relevant, even though they differ from the ones proposed in Ref. [10]. In run #1, the second, third, and fourth topological clusters increase their population by 17%, 21%, and 23%, respectively, between 0 and 12 GPa. The fourth topological cluster accounts almost completely for the 27% increase of the liquid density between the same pressures. Very similar results were obtained for run #2. This shows that

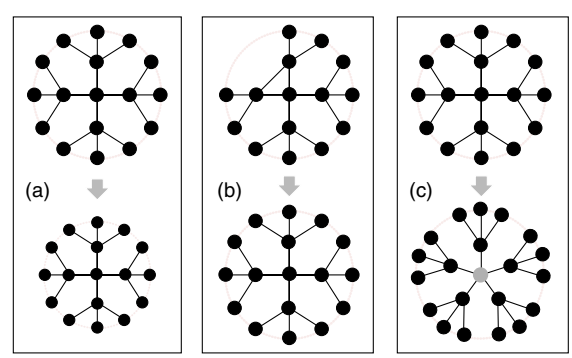

FIG. 3 (color online). Schematic diagrams of three different mechanisms of densification in liquid SiO_2. Only Si atoms are shown. Pressure increases from up to down. (a) Reduction of the Si-Si distance, as in quartz; (b) elimination of three-membered rings [10]; (c) increase in connectivity caused by coordination defects.

the anomalous compressibility of the liquid can indeed be largely accounted for by a topological rearrangement of the network.

At variance with the theory of Ref. [10], which was based on a defect-free network, we find that the topological changes are connected to the small increase in the Si-coordination number, which brings about a substantial increase of the overall network connectivity as shown schematically in Fig. 3(c) and detailed below. In particular, we find that the average local connectivity (defined as the average number of Si atoms connected to a central one) reaches the value of 4.4 ± 0.1 at 12 GPa, considerably higher than the low pressure value of 4.0 ± 0.1. Local changes in the atomic structure of the network, and, in particular, the appearance of coordination defects, provide a microscopic explanation of the increased connectivity. Three types of defects are most frequently observed in our simulations: (a) oxygen atoms in threefold coordination; (b) ^{V}Si; and (c) ^{III}Si. Defect (a) causes an increase of the local Si connectivity from 4 to 5, for the three Si atoms surrounding the threefold oxygen. Defect (b) causes the same increase for the ^{V}Si atom only, and finally defect (c) decreases the local connectivity of the ^{III}Si atom to 3. We find that for increasing pressure the concentration of defects (a) and (b) increases while that of defect (c) decreases, which leads to the observed large increase of the average local connectivity. It is interesting to remark that type-(a) defects have also been advocated as transition states for atomic diffusion, and their increased stability upon compression is thus likely to contribute to the known pressure-induced enhancement of mobilities in liquid silica [11].

Usually in pressure-induced phase transitions, coordination increments are largely counterbalanced by an increase of the interatomic distances, resulting in a reduced density increase. In SiO_2, this is known to happen in the glass compressed above $\sim$10 GPa [27], and of course also at the coesite to stishovite phase transition. This is not the case of liquid SiO_2 however, because the average value of $R_{\mathrm{Si-Si}}$ actually decreases, by about 2%, from 0 to 12 GPa, as a consequence of the small reduction of the $\mathrm{Si\hat{O}Si}$ angle described above. We therefore conclude that liquid SiO_2 densifies by means of an increased connectivity of the network and of a concomitant reluctance of interatomic distances to elongate. The same densification mechanism is found in simulations using larger supercells (up to 512 atoms) and the polarizable force field, further supporting the convergence of the first-principles results with cell size.

In summary, we find that none of the compression mechanisms previously proposed is compatible with the results of our simulations. Rather, efficient compression (far more efficient than in quartz) is due to a topological rearrangement of the network caused by an increase in connectivity. Our findings support the view that, even at moderate pressures, small changes in coordination can have profound consequence on the mechanisms of compression of a network-forming liquid. They also imply that any topological model of SiO_2 network, in particular, those meant to describe compressed vitreous SiO_2, should include the effect of such changes.

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