

COMPRESSION OF TETRAHEDRALLY BONDED SiO₂ LIQUID AND SILICATE LIQUID-CRYSTAL DENSITY INVERSION

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Abstract. We have investigated the response to pressure of liquid SiO₂ by performing a quantitatively realistic Monte Carlo simulation. The model liquid was restricted to at most four-fold Si-O coordination by the effective imposition of an infinite potential barrier to a fifth bond. We thus obtained an unambiguous comparison of the compression mechanisms of solid and liquid tetrahedral networks. In spite of this restriction, the density of the simulated liquid exceeds that of the corresponding models of quartz, coesite and cristobalite at high pressure. The efficient compression of the liquid results from a continuous restructuring of the network that leaves the mean Si-Si distance virtually unchanged and does not require an increase in the coordination number. The restructuring is effected by local breaking and reconnecting of bonds, a mechanism that is not available to a perfect crystal.

Introduction

The evolution of the terrestrial planets depends to a large extent on the thermodynamic properties of silicate liquids, which mediate chemical differentiation processes. In particular, the recent suggestion that the density of silicate liquids may surpass that of coexisting crystals at pressures of 5–20 GPa has important consequences for terrestrial chemical evolution (Rigden et al., 1984). For instance, magma formed below a few hundred km in the Earth would never reach the surface, and chemical differentiation would proceed by the sinking of magma to greater depths.

It is a common assumption that the mechanism responsible for the density inversions is a pressure-induced increase in the Al-O and Si-O coordination (e.g., Rigden et al., 1984). There is now good evidence that such coordination changes do occur (Xue et al., 1989). However, the flexibility of liquids' structures suggests that liquids containing tetrahedral networks can respond to pressure far more effectively than crystals by simply rearranging the connectivity of the networks, even when no coordination changes occur. The role of this network restructuring in liquid-crystal density inversions has not yet been examined.

We report here the results of a Monte Carlo simulation of liquid silica based on an accurate covalent potential model of tetrahedrally coordinated SiO₂ phases (Stixrude and Bukowinski, 1988). We find that the liquid's density overtakes that of all the crystals by 50 GPa. Although the comparison is not with thermodynamically coexisting crystals, it nevertheless

demonstrates that, at high pressures, liquids can adopt inherently denser network structures than crystals of the same Si-O coordination.

The Model

Monte Carlo (and molecular dynamics) simulations of condensed matter are generally based on a model of interatomic forces. How faithfully the model describes real interatomic forces determines how faithfully the simulations reproduce known properties of the real material. Previous simulations of silicate liquids have mostly used simple ionic models (Kubicki and Lasaga, 1988; Erikson and Hostetler, 1987, and references therein). Despite the demonstrated utility of these simulations, the potentials used are not suitable for our purposes since they have not been shown to reproduce available data on the corresponding crystals. The bulk moduli of SiO₂ crystals predicted by ionic models are too large by as much as an order of magnitude (Erikson and Hostetler, 1987).

We based the simulations on a recently developed covalent model of tetrahedral Si-O bonding (Stixrude and Bukowinski, 1988). The model incorporates essential physics, including the short range and directional dependence of the covalent Si-O bond, the dichotomy between strong intra- and weak inter-tetrahedral forces, and a form of the inter-tetrahedral force suggested by molecular orbital calculations. Furthermore, the model is quantitatively accurate: these are the first simulations of a liquid silicate to use a potential model which reproduces the equation of state, structure, compression mechanisms and phase stability of the corresponding tetrahedral crystalline phases (Stixrude and Bukowinski, 1988).

The model potential energy is given by:

$$\begin{aligned}
 U = & \sum_{i=1}^{N_{Si}} \sum_{j=1}^4 f_c(r_{ij}) D \left\{ \exp[2\beta(r_{ij} - r_0)] - 2 \exp[\beta(r_{ij} - r_0)] \right\} \\
 & + \sum_{i=1}^{N_{Si}} \sum_{j=1}^4 \sum_{k>j}^4 f_c \left[\max(r_{ij}, r_{ik}) \right] \frac{1}{2} r_e^2 k_\alpha (\alpha_{ijk} - \alpha_0)^2 \\
 & + \sum_{i=1}^{N_0} \sum_{j=1}^2 \sum_{k>j}^2 f_c \left[\max(r_{ij}, r_{ik}) \right] \frac{1}{2} k_L (r_{jk} - L_0)^2 \\
 & + \sum_{i=1}^{N_0} \sum_{j>i}^{N_0} A \exp(-r_{ij}/b) \tag{1}
 \end{aligned}$$

and

$$f_c = \left\{ 1 + \exp[\gamma(r_{ij} - r_c)] \right\}^{-1} \tag{2}$$

where N_{Si} and N_0 are the number of silicon and oxygen atoms respectively, r_{ij} is the distance between atoms i and j , α_{ijk} is the intra-tetrahedral O-Si-O angle, and the multiple summations of the first three terms indicate that at most the four nearest oxygens about a silicon and the two nearest silicons about

an oxygen are included. The model is identical to the ORM model of Stixrude and Bukowinski (1988) except for the function $f_c(r_{ij})$, which introduces a smooth cutoff of the three covalent forces as a function of Si-O distance. The values of r_c and γ (2.5 Å and 20 Å⁻¹, respectively) are chosen so that $f_c(r)$ does not affect the properties of crystalline phases. The other parameters in the model were constrained by molecular orbital calculations on silicate molecules and the equation of state of α -quartz. For a complete discussion of the model's construction see Stixrude and Bukowinski (1988).

The model is intentionally restricted to describe only tetrahedral Si-O bonding. This restriction manifests itself not only in the requirement that at most four oxygens be bonded to a silicon but also in the functional form and parameters of the potential: the O-Si-O angle bending term, for instance, favors the ideal tetrahedral angle ($\alpha_0 = 109.47^\circ$). X-ray diffraction (Spackman et al., 1987) and molecular orbital studies (Newton and Gibbs, 1980) show that tetrahedral bonding (controlled by highly directional sp³ hybrids) is substantially different from octahedral bonding (controlled by more spherically symmetric sp³d² hybrids) which occurs in high pressure silicate polymorphs such as stishovite. While a complete description of Si-O bonding must also include octahedral bonding, we concentrate here on our simpler model, which is a qualitatively and quantitatively realistic description of tetrahedral bonding. Although we cannot realistically simulate octahedrally coordinated phases or four- to six-fold coordination changes, our model allows us to examine compression mechanisms in a simplified silicate liquid which retains four-fold bonded coordination at all pressures and to address the central question of this paper: whether mechanisms other than coordination changes contribute significantly to liquid-crystal density inversions.

Computations

Monte Carlo simulations were performed in the constant pressure, temperature and particle number (NPT) ensemble (Adams and McDonald, 1974). The simulated liquid consisted of 192 atoms repeated with periodic boundary conditions to minimize finite size effects. Although larger systems were not tested, the primary cell was large enough (15 Å on a side at zero pressure) so that the radial distribution function fluctuated less than 2% about its long range limiting value (unity) at half the cell size. Although Si-O bonds were allowed to break and new bonds to form, Si-O coordinations greater than four were prohibited. The maximum allowable volume fluctuation and particle displacement were chosen so that approximately 50% of the configurations were accepted. The volume was allowed to change with every configuration. Typical run lengths were from 8 to 12 million configurations.

The simulations were started by melting ideal β -cristobalite at 10,000 K and 10 GPa. The liquid was then cooled to different pressures on the 6,000 K isotherm (0-50 GPa). Each 6,000 K point was then isobarically cooled to 4,000 K. At 2,000 K, liquids cooled isobarically from 4,000 K differed somewhat from those cooled directly from 6,000 K (volumes differed by 7% at 0 GPa, but less than 2% at all other pressures). Since the simulations were initialized with higher temperature (larger volume) configurations, and since the volumes decreased steadily towards their final stable values during the

simulations, we expect any effects of metastability to produce volumes that exceed those of the equilibrium liquid. Therefore, we took the results of the simulation which produced the smaller 2,000 K volume as the best estimate of the equilibrium liquid volume. We assume the uncertainty in the 2,000 K volumes if half the difference between the two cooling histories. Statistical uncertainties (Adams and McDonald, 1974) in the calculated volumes were much smaller, not exceeding 0.2%.

Crystal computations are described fully in Stixrude and Bukowinski (1988). Briefly, WMIN (Busing, 1981) is used to calculate static crystal properties. Debye model thermal corrections are added to account for the effects of temperature.

Results and Discussions

The calculated 2,000 K equation of state of liquid SiO₂ agrees well with available experimental data, including the zero pressure volume: 27.81 ± 0.6 cc/mol vs 26.9–28.2 cc/mol experimental (Lange and Carmichael, 1987) and zero pressure bulk modulus: 11.2 ± 3 GPa vs. 13 GPa experimental (Krol et al., 1986). Figure 1 shows that the simulated structure of the liquid at 2,000 K, as measured by the radial distribution function, is in good agreement with experiment. The calculated room temperature equations of state of α -quartz, coesite and α -cristobalite agree well with experiment as shown in Figure 2. Our model also accurately predicts the structure and compression mechanisms of α -quartz and coesite and the α -quartz to coesite phase transition (Stixrude and Bukowinski, 1988).

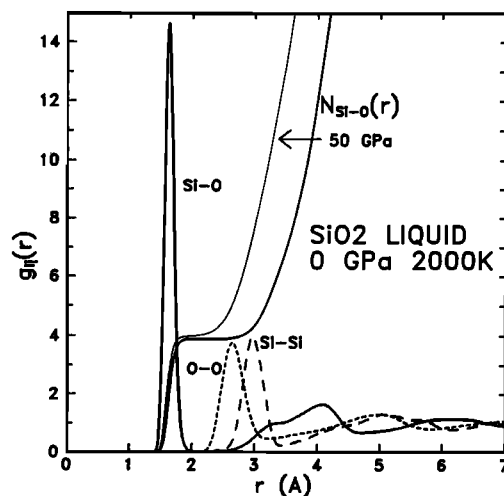


Fig. 1. The radial distribution functions $g_{ij}(r)$ (Si-O, O-O, Si-Si) computed from Monte Carlo simulations of our tetrahedrally bonded SiO₂ liquid at 0 GPa and 2,000 K. Also plotted is the cumulative Si-O coordination number ($N_{Si-O}(r)$, proportional to the area under $g_{Si-O}(r)$) as a function of Si-O distance at 0 GPa (bold line) and 50 GPa (thin line). The positions of the first six peaks (Si-O, O-O, Si-Si, 2nd Si-O, 2nd O-O, 2nd Si-Si) are consistent with experiment (Waseda and Toguri, 1977) except the first Si-Si peak which occurs at a distance 0.15 Å smaller than the observed value. The Si-O, O-O and Si-Si coordination numbers and also consistent with experiment (Waseda and Toguri, 1977). The plateaus in $N_{Si-O}(r)$ at around 2 Å show that the Si-O coordination number is well defined and does not exceed four up to 50 GPa.

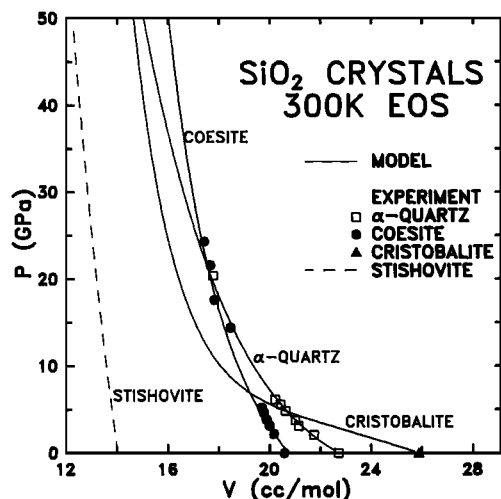


Fig. 2. Room temperature experimental data (symbols) for α -quartz (Levien et al., 1980; Hemley et al., 1988), coesite (Levien and Prewitt, 1981; Hemley et al., 1988) and α -cristobalite (Peacor, 1973) compared with theoretical equations of state (solid lines) based on the same potential model that was used in the liquid simulations. The size of the symbols is comparable to uncertainties in the high pressure data. The experimental stishovite curve (dashed line) (Bass et al., 1982) is shown for comparison.

The density of the model liquid surpasses that of the tetrahedral crystalline phases by 50 GPa (Figure 3). These liquid-crystal density inversions occur without an increase in Si-O coordination number in the liquid: the model guarantees that the bonded coordination of the liquid remains four-fold, and Figure 1 shows that the effective coordination of the liquid also remains four-fold, at least up to 50 GPa. Even the room temperature densities of the tetrahedral crystals (Figure 2) are surpassed by the 2,000 K liquid at 24, 30 and 60 GPa for coesite, α -quartz and α -cristobalite, respectively. Further, the reported liquid densities, if they differ from true equilibrium values, are likely to err towards lower density, as discussed above, thus leading us to overestimate the pressures of liquid-crystal density inversion. Thus, uncertainties in the calculations due to thermal corrections of the crystalline equations of state (due to inadequacies of the Debye model at high temperature) and possible metastability in the liquid simulations, do not affect our conclusion that, for our model, the liquid is the densest four coordinated phase at high pressure.

Although these density inversions do not involve coexisting liquids and crystals (experimentally, octahedral stishovite is the thermodynamically stable crystal phase above 12 GPa), they do illustrate the efficient densification of the tetrahedral liquid and suggest liquid compression mechanisms very different from those in the crystals. The structures of liquid and crystalline phases consist of a continuous network of nearly rigid, corner-sharing SiO₄ tetrahedra. While compression of a crystal is accomplished without breaking bonds by simply reducing the distance between tetrahedra, we find that the model liquid compresses by breaking and reforming bonds, thus rearranging the connectivity of the tetrahedral network without substantial changes in the inter-tetrahedral distance (*L*) (Stixrude and Bukowinski, to be published). The contrast

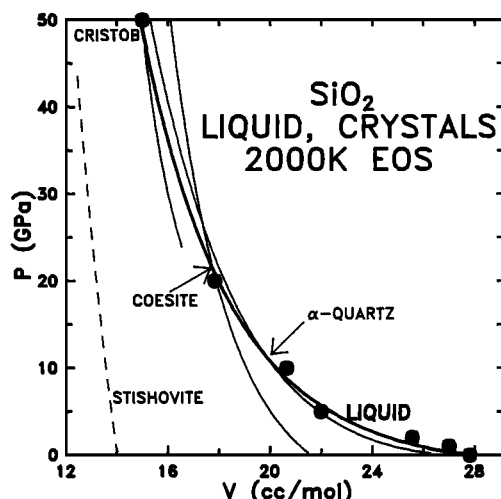


Fig. 3. Results of 2,000 K Monte Carlo simulations of liquid SiO₂ (circles and bold lines) compared with 2,000 K equations of state of crystals (thin lines). The bold line is a Birch-Murnaghan fit to the simulated liquid volumes, denoted by the circles; the size of the circles is comparable to volume uncertainties (see text). The crystal equations of state are labelled at the pressure where the liquid surpasses their density. For clarity, only the high pressure portion of the cristobalite equation of state is shown. Because of the unusual shape of the cristobalite equation of state (negative curvature at low pressures, see Figure 2) it crosses the liquid equation of state twice: at 12 and 50 GPa. The experimental stishovite curve (the same as in Figure 2) is shown for comparison.

between liquid and crystal compression mechanisms is illustrated in Figure 4. The large differences between volume (*V*) and scaled volume (*V**) for the crystals at high pressure reflect large pressure-induced decreases in *L*. In contrast, the near identity of the scaled and standard equations of state of the liquid reflect small changes in *L* (*V* and *V** for the liquid differ by only 9% at 50 GPa compared with 40% for α -quartz).

The compression of the model liquid is analogous to pressure-induced phase transitions in crystals. For instance, the transition from α -quartz to coesite at 2 GPa, like compression in the liquid, changes the way the tetrahedra are connected rather than the distance between them: both model and data (Levien et al., 1980; Levien and Prewitt, 1981) show that the transition causes only a 1% change in *L* (coesite actually has a slightly larger *L* than α -quartz) but an 8% increase in density. The liquid is ultimately the densest phase because, unlike the crystals, it is not limited to structural change at phase transitions but is free to continuously adopt inherently denser arrangements of its tetrahedral network with increasing pressure.

Summary

We have compared densities of crystals and liquid at pressure in a simple silicate system based on a realistic model of tetrahedral Si-O bonding. Even though the model liquid remains four-fold coordinated, it becomes denser than tetrahedral crystals at high pressure. We attribute the more efficient compaction of the liquid to its ability, unlike a crystal, to easily rearrange its structure in response to pressure.

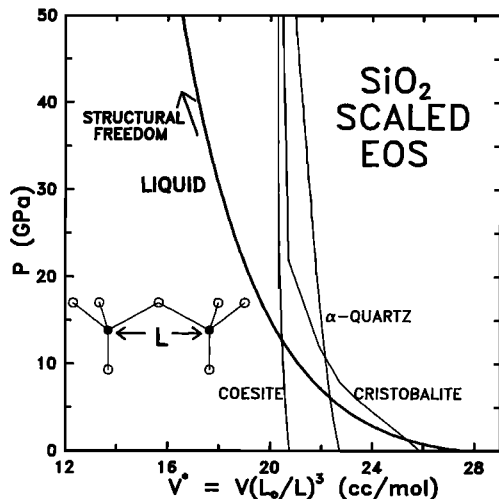


Fig. 4. 300 K crystal equations of state and 2,000 K liquid equation of state scaled to the zero-pressure inter-tetrahedral distance (L_0). The plot exhibits two interesting end-members: the first, approximating the crystals, is homogeneous compression (V scales with L^3) which would appear as a vertical line; the second, approximating the liquid, is inherent compression (involving no change in L) which would appear identical to the standard equation of state (P vs. V). Values of L are structural averages. For the liquid, L was taken as the position of the Si-Si peak in $g(r)$ (see Figure 1). Also shown is a schematic drawing of the Si_2O_7 bitetrahedron (filled circles = Si atoms, open circles = O atoms), the largest unit that all the tetrahedral structures share, indicating the inter-tetrahedral distance, L .

It is likely that silicate liquids undergo pressure-induced coordination increases (Xue et al., 1989), and that these will tend to increase the density of liquids relative to coexisting solids. However, although our simplified model does not allow us to draw firm conclusions about complex natural magmatic systems, we suggest that the efficient, purely tetrahedral liquid compression mechanism illustrated here may be equally important in determining liquid-crystal density inversions in the Earth.

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