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## Molecular Simulation

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Jean-Louis Barrat<sup>a</sup>; James Badro<sup>b</sup>; Philippe Gillet<sup>c</sup>

<sup>a</sup> Département de Physique des Matériaux (UMR CNRS 5586), Université Claude Bernard, Villeurbanne Cedex, France <sup>b</sup> Laboratoire de Sciences de la Terre (URA 726), Lyon Cedex 07, France <sup>c</sup> Laboratoire de Sciences de la Terre (URA 726), Institut Universitaire de France, Lyon Cedex 07, France

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## A STRONG TO FRAGILE TRANSITION IN A MODEL OF LIQUID SILICA

JEAN-LOUIS BARRAT<sup>a</sup>, JAMES BADRO<sup>b</sup>  
and PHILIPPE GILLET<sup>c</sup>

<sup>a</sup>*Département de Physique des Matériaux (UMR CNRS 5586),  
Université Claude Bernard, 43 bd. du 11 novembre 1918, F-69622  
Villeurbanne Cedex, France;* <sup>b</sup>*Laboratoire de Sciences de la Terre  
(URA 726), Ecole Normale Supérieure de Lyon, 46 Allée d'Italie F-69364  
Lyon Cedex 07, France;* <sup>c</sup>*Laboratoire de Sciences de la Terre (URA 726),  
Institut Universitaire de France, Ecole Normale Supérieure de Lyon,  
46 Allée d'Italie, F-69364 Lyon Cedex 07, France*

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The transport properties of an ionic model for liquid silica [1] at high temperatures and pressure are investigated using molecular dynamics simulations. With increasing pressure, a clear change from “strong” to “fragile” behaviour (according to Angell’s classification of glass-forming liquids) is observed, albeit only on the small viscosity range that can be explored in MD simulations. This change is related to structural changes, from an almost perfect four-fold coordination to an imperfect five or six-fold coordination.

**Keywords:** Liquid silica; strong to fragile transition

### INTRODUCTION

More than 10 years ago, Angell [2] proposed a classification of glass forming liquids according to their “fragility”, a concept that has since then proved extremely useful for our understanding of these systems. Broadly speaking, “strong” glass formers are characterized by weak discontinuities of their thermodynamic properties at the glass transition, and an almost Arrhenius behaviour of their transport properties (viscosity) as a function of temperature. The corresponding activation energy  $E_a$  can be assigned to a typical microscopic “event” that controls transport properties, such as breaking of a “bond”. The archetype of “strong liquids” is  $\text{SiO}_2$ , with a

perfectly Arrhenius behaviour of the viscosity in the range  $1500 < T < 2500$ . The activation energy is in that case about 70000 K, and is supposed to correspond to the energy for breaking an Si—O bond.

Fragile liquids, on the other hand, display a strongly non Arrhenius behaviour of their transport properties. The flow in these systems can not be traced back to a single microscopic event, but is of a much more collective nature. Typical fragile liquids are organic or ionic systems with a much weaker local organization than in “strong” liquids. It is now widely accepted that at least for relatively low viscosities, the transport properties in these systems are well described by the so called “mode-coupling” theories [3].

It has long been suspected, and also shown in some pioneering MD simulations [4], that the transport properties of  $\text{SiO}_2$  could exhibit an unusual behaviour as a function of pressure. In particular, a nonmonotonous, “water-like” behaviour of the diffusion coefficient is expected due to the tetrahedral network structure of molten  $\text{SiO}_2$ . It is also expected [5, 2] that the disruption of this network by an applied pressure will cause a change in behaviour from “strong” to “fragile”.

In this work, we present a systematic Molecular Dynamics (MD) study of the transport properties in a *purely ionic* model of  $\text{SiO}_2$  [1], which is an improvement of an earlier model by Tsuneyuki and coworkers [6]. Both models have now been studied in much detail for their static properties [7, 8, 10, 11, 9]. Transport properties at zero pressure have also been briefly investigated in [14], and their pressure dependence was considered in [15].

## METHOD

The system we consider is made up of 216  $\text{SiO}_2$  units (in some cases this number was increased to 512 in order to check the size dependance of the results). The equations of motion are integrated using the Verlet algorithm with temperature control [12]. Four series of runs at four different densities (2.2, 3.1, 3.3 and 4.2 g/cc) were carried out. For each density, the sample is equilibrated at high temperature (5000 K), then cooled stepwise at an average cooling rate of about  $10^{12} \text{ K.s}^{-1}$ . At each new temperature, the system is equilibrated during 0.25 to 0.5 nanosecond. As usual [5], this equilibration time limits the temperature range for which the system can be considered to be at thermodynamic equilibrium. By analogy with the situation in real systems, the lowest temperature at which the system is equilibrated for an equilibration time of 0.5 nanosecond defines the “computer glass transition temperature” for our simulation. In terms of viscosities, this corresponds to viscosities close to 1. Pa.s.

The self diffusion coefficients of Si and O,  $D_{\text{Si}}$  and  $D_{\text{O}}$ , were computed from the mean squared displacement of the corresponding ions. The shear viscosity  $\eta$  was computed from the stress-stress autocorrelation function using the usual Kubo Formula [5].

## RESULTS

The results for  $\eta$  and  $1/D_{\text{Si}}$  are shown in Figures 1 and 2, in the form of an Arrhenius plot. As usual, the error bars on  $\eta$  (estimated from the contributions of the 3 components of the stress tensor) are large, typically 100% for the larger viscosities. The results, however, are unambiguous. At the lowest density (2.2 g/cc), the Arrhenius plot is almost a perfect straight line, with an activation energy about 40000 Kelvins. As previously noted by Della Valle and Andersen [7], this activation energy is smaller than the experimentally observed one. Most likely, this constitutes an inadequacy of the purely ionic model. Another

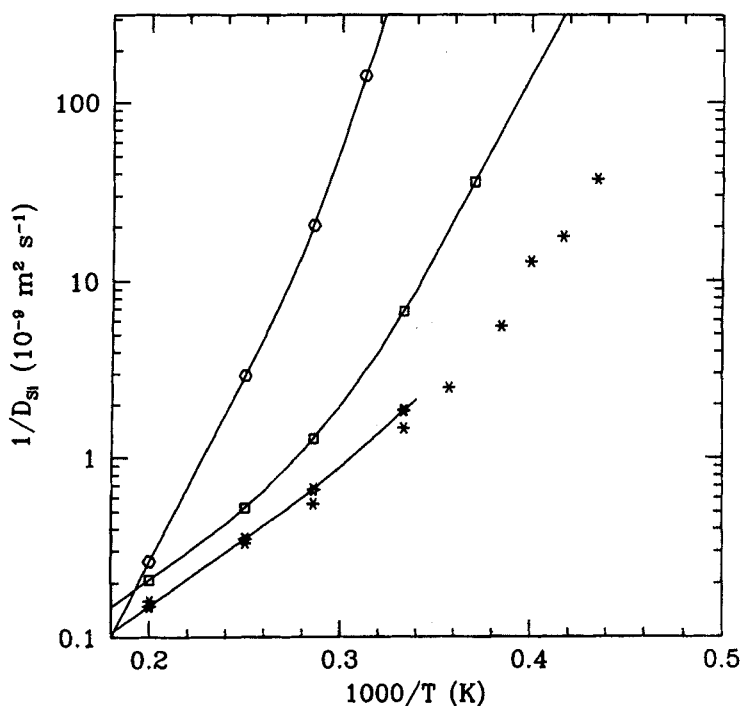


FIGURE 1 Arrhenius plot of  $1/D_{\text{Si}}$  at four different densities. Open dots:  $\rho = 2.2$  g/cc. Open stars:  $\rho = 3.3$  g/cc. Stars:  $\rho = 3.7$  g/cc. Squares:  $\rho = 4.2$  g/cc. The lines are a guide to the eye.

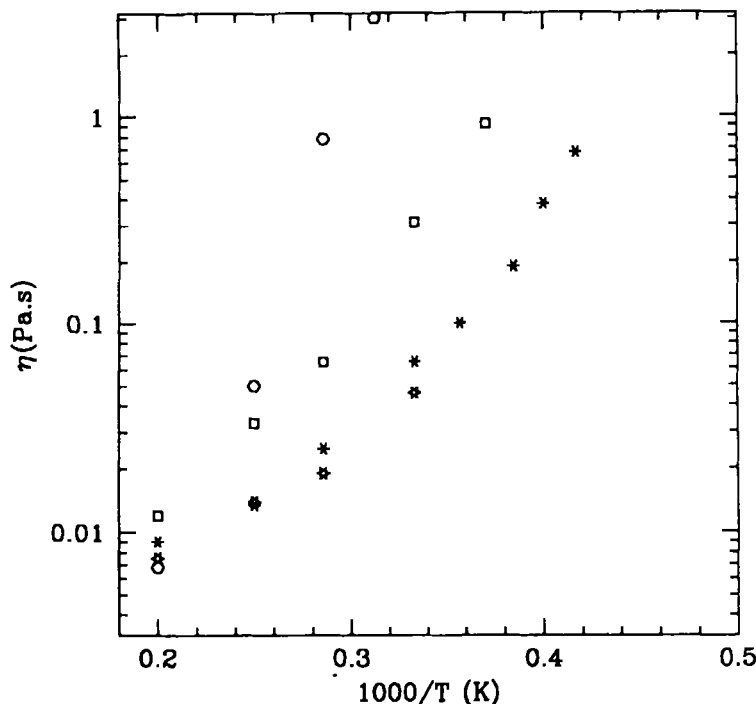


FIGURE 2 Same as Figure 1, for the viscosity. The symbols are as in Figure 1.

interesting possibility, however, is that the difference is due to the different temperature range investigated. Experiments are done at low temperatures, while simulation investigates high temperatures. In fact, a slight curvature of the Arrhenius plot is perceptible if the last point, corresponding to a temperature of 3200 K, is included. This would mean that the activation “energy” changes with temperature. Unfortunately, the error bar on this point is large, due to the very small diffusivity. High temperature experiments on  $\text{SiO}_2$  would be useful to clarify this issue. As the density is increased, a decrease in  $\eta$  and  $1/D_{\text{Si}}$  is observed, while the Arrhenius plot displays a noticeable curvature. At the higher density, the viscosity has increased close to its low density value, but the Arrhenius plot is clearly bent, in a way characteristic of fragile liquids. The nonmonotonous variation of  $D_{\text{Si}}$  with pressure is illustrated in Figure 3 for a fixed temperature ( $T=4000$  K). As pressure is increased,  $D_{\text{Si}}$  increases by almost an order of magnitude, with a maximum in the 10–15 GPa range. This effect was already observed in [13] (with a different model) and [15]. The size effect reported in the latter paper is not observable in our results, as seen from the two points in Figure 3 obtained with a 1536 particles system.

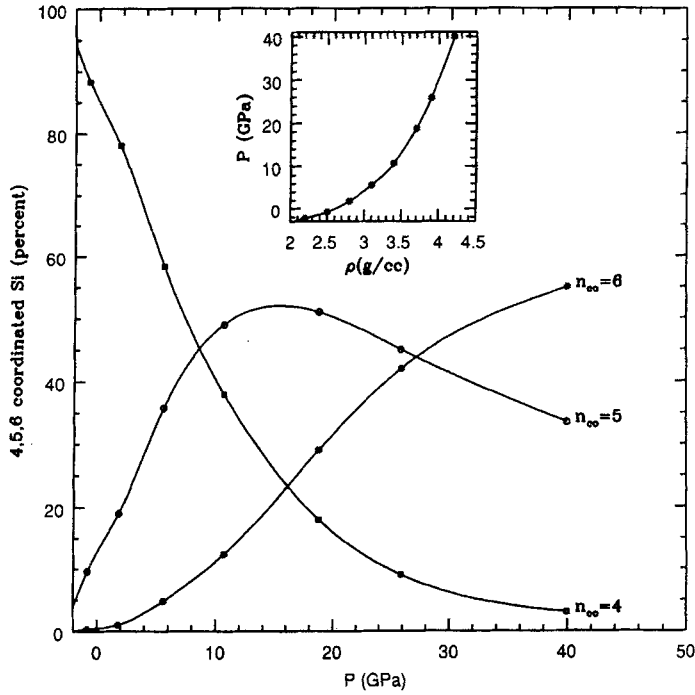


FIGURE 3 Pressure dependence of the silicon diffusion constant at  $T=4000$  K. The points corresponds to densities  $\rho = 2.2, 2.5, 2.8, 3.1, 3.4, 3.7, 3.9, 4.2$  g/cc. For  $\rho = 2.5$  g/cc and  $\rho = 3.4$  g/cc two different system sizes ( $N = 256$  and  $N = 512$   $\text{SiO}_2$  units) were considered.

Diffusion and viscosity are often related by introducing a “Stokes Einstein diameter”  $d_{SE}$  of the atoms, defined as  $d_{SE} = k_B T / 3\pi\eta D$ . This quantity, shown (for the Si ions) in Figure 4 for the four densities investigated, is seen to be fairly independent of temperature. The scatter observed at low temperature for the lower density is probably due to the large error bars on the corresponding viscosities. At the lowest density,  $d_{SE}$  is large (3 to 4 Å), but becomes much smaller, and almost independent of density (1 to 1.5 Å), for the higher densities. This illustrates the very peculiar character of low density  $\text{SiO}_2$ , with a perfectly tetrahedral coordination. The evolution of the local structure with pressure is illustrated in Figure 5, which shows the proportion of four, five and six fold coordinated Si as a function of pressures at  $T=4000$  K. In the standard picture of diffusion in  $\text{SiO}_2$  [4], five-fold coordinated Si are often described as “defects” of the tetrahedral network that favour diffusion. Figure 5 shows that the proportion of these “defects” increases very rapidly with pressure, and that in the vicinity of the diffusion maximum a large majority of Si ions are indeed five-fold coordinated. Hence it seems unlikely

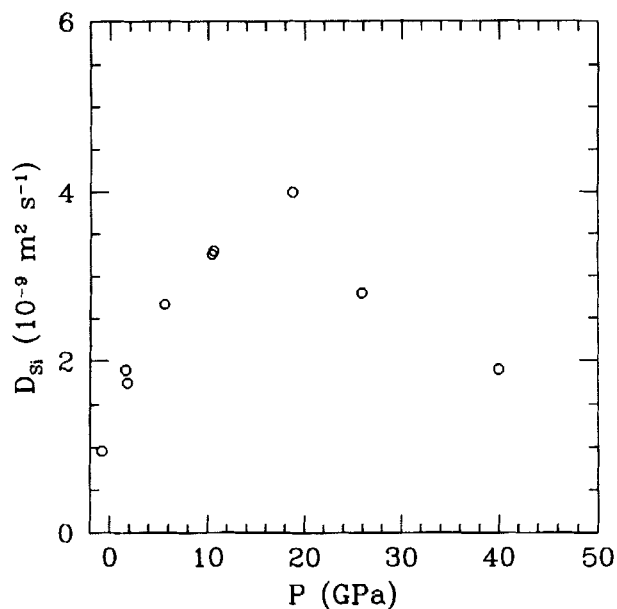


FIGURE 4 Stokes-Einstein diameter of the silicon ions as a function of temperature, for the same four densities, as in Figures 1 and 2. Symbols as in Figures 1 and 2.

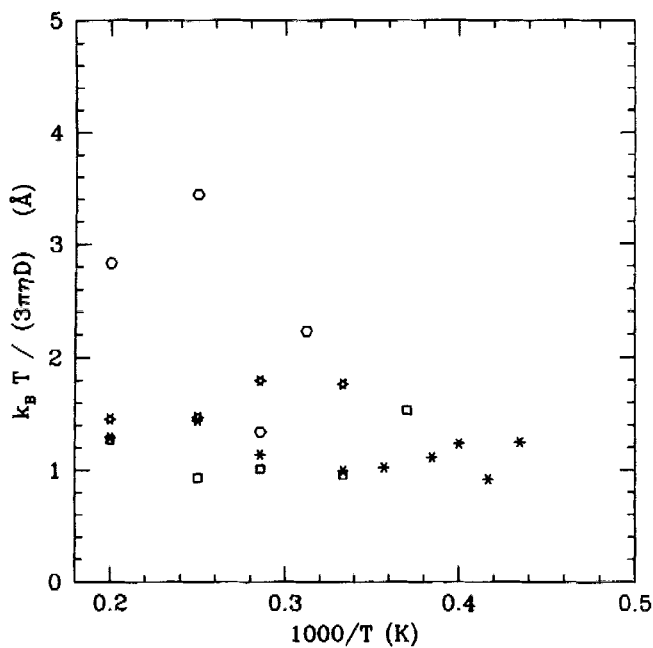


FIGURE 5 Fraction of 4, 5, and 6 coordinate silicon ions as a function of pressure, for  $T = 4000 \text{ K}$ . The densities are the same as in Figure 3. Inset: the equation of state of the simulated system at  $T = 4000 \text{ K}$ .

that a “defect based” picture of  $\text{SiO}_2$  can be useful in describing the pressure dependance of its properties, except perhaps at very low pressures. Figure 5 also shows the evolution of coordination with pressure, from fourfold at  $P=0$  to fivefold in the 10–15 GPa range and sixfold above 20 GPa. The low pressure four fold coordination, however, is very special in the sense that it is almost perfect, with more than 99% of the ions. At higher pressures, the coordination is much less well defined.

Finally, the influence of the local structure on self diffusion is illustrated in Figure 6. The mean squared displacement of Si ions with different initial coordinations (3, 4, or 5) is plotted as a function of time. For long times, these quantities become parallel straight lines. However at short times, the difference between the different curves is a measure of the influence of coordination on the diffusion. This role is very clear in low density  $\text{SiO}_2$ , where three or five fold coordinated Si (defects) diffuse initially much faster than the four-coordinated Si. At a density of 2.8 g/cc, (corresponding to about 6 GPa in Figs. 3 and 5), the role of initial coordination has become almost negligible. The overshoot in

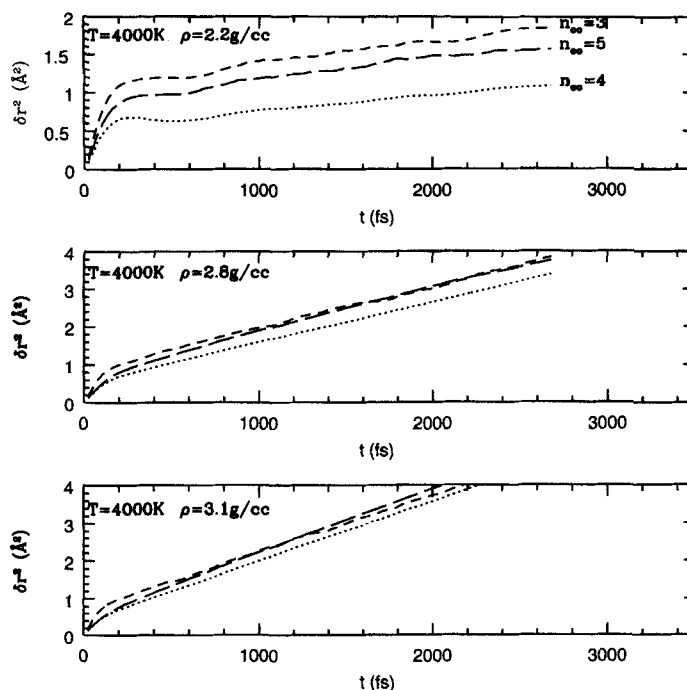


FIGURE 6 Mean squared displacement of silicon ions that are initially 3, 4, and 5 fold coordinated. Dots: fourfold coordinance. Long dashes: fivefold coordination. Short dashes: threefold coordination. From top to bottom:  $\rho = 2.2$  g/cc,  $\rho = 2.8$  g/cc,  $\rho = 3.1$  g/cc.  $T = 4000$  K.



the mean squared displacement that exists at low densities and disappears at higher densities was noticed in [16] and associated to the existence of a “boson peak”. This overshoot, however, might be associated to a finite size effect [17].

## CONCLUSION

In summary, our results indicate that the disruption of the tetrahedral network of low density  $\text{SiO}_2$  by the application of pressure very rapidly induces a change from strong to fragile behaviour. It must be remembered, however, that the change observed here corresponds to a viscosity variation of less than three decades. Experimentally, the same kind of change could be expected to take place in a much larger viscosity domain, covering more than ten decades. In the vicinity of the diffusivity maximum, the behaviour is already that of a fragile liquid. The role of five or three fold coordinated “defects” in the diffusion becomes negligible before the diffusivity maximum is reached.

These findings corroborate those obtained with other ionic models of  $\text{SiO}_2$  [16]. They confirm the richness of these simple models. Beyond the fact that they provide a relatively accurate description of silica, a great interest of these models lies in the fact that they involve simple pair potential, for which accurate theoretical methods have been devised. They could therefore provide a useful benchmark for theoretical studies of strong/fragile transitions. Finally, the connection between these results and experiment could be made in the high temperature-high pressure range (typically  $T \sim 2500$  K,  $P \sim 20$  GPa. This range can be explored experimentally, and corresponds (according to the model) to diffusion constants and viscosities measurable on the simulation time scale. A comparison with experimental data would allow a better evaluation of the usefulness of such models in the prediction of dynamical properties.

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