

Poroelastic Theory Applied to the Adsorption-Induced Deformation of Amorphous Silica

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Abstract

Under a high pressure of helium, the volume change of amorphous silica is much smaller than expected from its elastic properties. This is due to helium insertion in the free volume of the glass network. Here, we report spectroscopic experiments using either helium or neon as penetrating pressurizing media and molecular simulation that indicate a relationship between the amount of gas adsorbed and the strain of the network. A generalized poromechanical approach, describing the elastic properties of microporous materials upon adsorption, is shown to successfully describe the physics of deformation of such silica glasses in which the free volume exists only at the sub-nanometer scale.

INTRODUCTION

Recent high pressure studies provide new important results to the field of mechanical properties of amorphous silica (Sato et al. 2011, Shen et al. 2011, Weigel et al. 2012, Coasne et al. 2014). Below 10 GPa, hydrostatic pressures P are obtained in diamond-anvil cells using a liquid pressure transmitting medium such as a methanol-ethanol mixture (ME4:1) (Klotz et al. 2009). When such experiments are performed in the GPa pressure range for amorphous silica, the volume change of the sample is close to that expected from its bulk modulus $K \sim 35\text{-}40$ GPa (Kondo et al. 1981, Schroeder et al. 1990, Zhang et al. 1994, Meade et al. 1987, Tsiok et al. 1998, Weigel et al. 2012). The latter can be obtained by measuring the velocity of both longitudinal, v_L , and transverse, v_T , acoustic waves, $K = \rho (v_L^2 - 4/3 v_T^2)$, where ρ is the mass density of the sample. On the other hand, the compressibility of vitreous silica inferred from the volumetric strain is strongly reduced when He is used as pressurizing medium (Sato et al. 2011,

Shen et al. 2011), leading to an apparent bulk modulus $K_{app} \sim 110\text{-}120$ GPa. Using Brillouin light scattering, it was shown that K is weakly affected by the presence of He, $K \sim 35\text{-}50$ GPa, demonstrating that the much smaller apparent compressibility is not due to a stiffening of the network (Weigel et al. 2012). The large difference between K_{app} and K indicates that silica pressurized under He behaves as an open system. In this case, the static measurement underestimates the compressibility of the network by a term due to the gas loading of the sample.

Though glasses are not characterized by an open porosity it is expected that thermal motion opens the interstitial voids to gas atom diffusion. Hence, an adapted poromechanical description of adsorption-induced deformation of glasses makes sense. Such general poroelastic constitutive equations, which were revisited only recently (Brochard et al. 2012), offer a very appealing theoretical framework. The present work reports on a joint experimental and theoretical study providing a unifying and comprehensive picture of adsorption-induced deformation of bulk amorphous silica (Figure 1). We show that generalized poromechanics, a theory that was initially developed to describe the properties of porous elastic materials upon adsorption, can be extended to dense glass networks exhibiting only interstitial voids (Coasne et al. 2014).

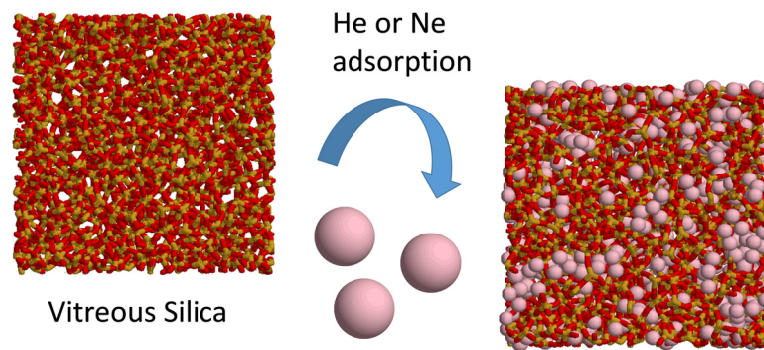


Figure 1. Typical molecular configuration showing helium and neon adsorption into vitreous silica in high pressure experiments. The pink spheres are the rare gas atoms (He or Ne) while the red and orange sticks show the chemical bonds between O and Si atoms in vitreous silica. The size of the configuration shown here is typically a few nm.

RESULTS

The measured volumetric strains of vitreous SiO_2 immersed in Ne fluid at pressures below 9 GPa are shown in Figure 2. The results are compared with those obtained previously under He atmosphere at room temperature (Sato et al. 2011). The equilibrium values of the volumetric strain in Ne atmosphere are only slightly smaller than those found with He, indicating that the penetration of Ne produces almost the same effect as that of He. In both cases the change in volume is much smaller than the deformation obtained when vitreous silica is pressurized using

the non-penetrating fluid ME4:1 (more details can be found in Weigel et al. 2012 and Coasne et al. 2014).

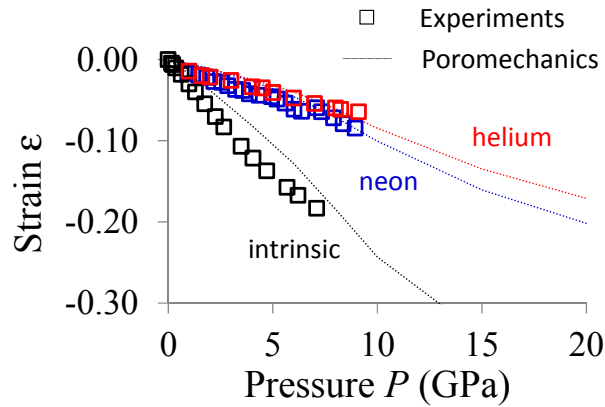


Figure 2. Volumetric strain ϵ of vitreous SiO_2 as a function of the pressure P exerted by an adsorbing fluid, Ne (red squares), He (blue squares) (Sato et al. 2011), and by the non-penetrating fluid ME4:1 (black squares) (Weigel et al. 2012). The dotted lines show the theoretical predictions as discussed in the text for He and Ne, respectively, and in the absence of adsorption.

Grand Canonical Monte Carlo simulations in the framework of the generalized poromechanics developed by Brochard et al. (Brochard et al. 2012) were performed to probe at the microscopic scale the deformation of vitreous silica upon adsorption. One first determines the number $n(\epsilon, P)$ of Ne or He atoms per unit volume of solid penetrating a realistic model of silica as a function of the volumetric strain and bulk fluid pressure, ϵ and P being taken as independent external variables (Coasne et al. 2011, Coasne et al. 2014). For both fluids, the adsorbed amount increases monotonically with increasing volumetric strain and bulk fluid pressure. Given that the molecular density of the model silica is $\sim 21.8 \text{ mol/nm}^3$, the simulated adsorption isotherms show that relatively high He and Ne solubilities can be reached. At given ϵ and P , the number of He atoms adsorbed in the silica network is about 1.5 times that of Ne atoms, consistent with the larger size of Ne.

We now turn to the predictions of the generalized poromechanical theory for $\epsilon''(P)$ and $n''(P)$ (the superscript u denotes that the system is considered uponunjacketed conditions as the fluid is allowed to exchange with the external phase). Using the simulated adsorption isotherms $n(\epsilon, P)$, the unique solution for $\epsilon''(P)$ is found by solving iteratively the following equation:

$$\epsilon''(P) = -\frac{P}{K_0} + \frac{1}{K_0} \int_0^P \frac{\partial n(\epsilon, p)}{\partial \epsilon} \bigg|_{\epsilon=\epsilon''} V_b(p) dp \quad (1)$$

where K_0 is the intrinsic bulk modulus of vitreous silica and $V_b(p)$ is the molar volume of He or Ne at a pressure p . The pressure dependence of $\epsilon''(P)$ predicted by the poroelastic model is shown in Figure 2 for Ne and He. The calculated values are in good agreement with the experimental volumetric strains ϵ . The fact that the theoretical deformation $\epsilon''(P)$ slightly overestimates the experimental data at low P is thought to be due to the larger bulk modulus of the simulated silica. The volumetric strain of the model silica in the absence of adsorption indeed overestimates the experimental values as shown in Figure 2. The above results show that the poromechanical approach provides a framework for a quantitative description of the adsorption-induced deformation in vitreous silica. In particular, in agreement with the experimental data, our calculations show that the silica network expansion induced by He adsorption is larger than that induced by Ne adsorption.

The corresponding adsorbed amount $n''(\epsilon'', P)$ is shown in Figure 3 as a function of P . A typical atomic configuration for He adsorbed in silica glass at $P = 6$ GPa and $\epsilon = -0.03$ is also shown in Figure 3, illustrating the large amount of adsorbed gas-atoms. In this case, the He concentration is about 11 at/nm^3 , *i.e.* 0.53 mole of He per mole of SiO_2 . The amount of He adsorbed in silica is almost twice that of Ne at the same P . In both cases, the predicted $n''(P)$ varies non-monotonically with P . It first increases rapidly to a maximum around 4 and 6 GPa for Ne and He, respectively, and then decreases as the mechanical stress exerted by the fluid outside the sample induces significant volume contraction. We note that a similar pressure dependence has been obtained for the solubility of argon in liquid silica using very long molecular dynamics simulations of the complete system equilibrated at fixed T and P (Guillot et al. 2012).

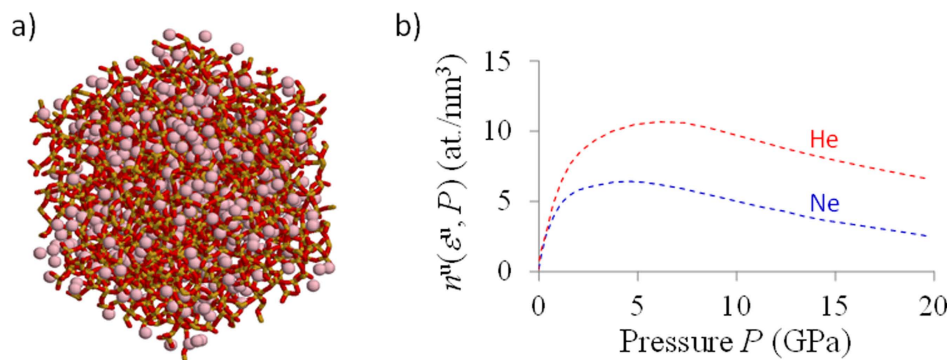


Figure 3. (a) Typical atomic configuration for He adsorbed at room temperature in silica glass at a bulk fluid pressure $P = 6$ GPa and a fixed volumetric strain $\epsilon = -0.03$. To emphasize the large amount of adsorbed fluid atoms, about 11 at/nm^3 , only He atoms are shown (pink spheres). The silica network is shown by sticks that are orange on the Si end and red on the O end. The simulation cube is projected along its [x,y,z] diagonal. (b) Pressure dependence of the amount of Ne and He atoms adsorbed in vitreous SiO_2 predicted by the poroelastic model in *unjacketed* conditions.

CONCLUSION

The present study shows that the small apparent compressibility of silica under high He or Ne pressure is due to an adsorption-induced expansion. It further demonstrates that the elasticity of vitreous silica subjected to noble gas adsorption can be described by generalized poromechanics. This theory for the mechanical properties of microporous solids upon adsorption, is applied here to an amorphous solid exhibiting only interstitial voids, opening the way to a broad range of applications. We anticipate that similar conclusions will be reached for other glasses exhibiting a significant amount of interstitial free volume as in the case of GeO_2 or B_2O_3 . The combined use of Monte Carlo simulations and poromechanics provides an efficient alternative to other theoretical approaches (Coudert et al. 2008, Gor et al. 2010, Guillot et al. 2012, Sarda et al. 2005) describing the complete system equilibrated in isothermal-isobaric or osmotic ensembles but inherently limited to short time scales and by possible equilibration issues. Poromechanics associated with Monte Carlo simulations thus might give the opportunity to extend this study to dense materials, where the equilibration time is long, such as glasses and melts of geological interest, actinide oxide fuels or irradiated metallic alloys.

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