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Deformation of silica glass studied by molecular dynamics: Structural origin of the anisotropy and non-Newtonian behavior

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ABSTRACT

A novel aspect of the medium-range structure of silica drawn into fibers is studied. The network of silica glass structure is composed of corner-shared SiO_4 tetrahedra, and it can be seen as a structure of interconnected rings $(Si–O)_n$ of various size, denoted nMR (n-membered ring). Molecular dynamics simulations show that small-sized silica rings get a preferential orientation during the drawing, either during the high-temperature stage for 3MR, or during the cooling for 4MR and 5MR, and they persist in this state in the fiber at ambient temperature. This leads to a structural anisotropy, more specifically a "transverse isotropy", because of different longitudinal and transversal physical properties. This anisotropic structural rearrangement during the drawing process induces a non-Newtonian behavior of the modeled glass melt, with strain-rate dependent properties.

1. Introduction

Glass is a ubiquitous material with many applications in daily life as well as in high technology, for instance in photonics or photovoltaic areas. To allow such versatility, the knowledge of glass structure is of prime importance. This glass structure has been subjected to many studies and many of them have been referenced by Jiang et al. [1]. Silica glass structure is described as a network of interconnected and randomly distributed SiO_4 tetrahedra forming an isotropic material. However, Brückner [2] has evidenced quite a long time ago that anisotropies and orientations could be introduced into isotropic glass melts through non-Newtonian viscous deformations. A non-Newtonian behavior is described by strain-rate dependant properties. This behavior in silica-based glasses has been studied by Dingwell [3] & Webb [4,5], to understand the rheology of magmas, and by Simmons et al. [6] and Li et al. [7] to address fiber manufacturing issues. It is associated by Simmons et al. [6] to structural rearrangements occurring in the material. In this way, a structural origin of these anisotropies is supposed to explain macroscopic property changes, such as the birefringence of E-glass (silica-based) fiber [8] or, much more recently, the different axial and radial elastic responses to an elastic mechanical stress in silica fiber [9].

Thus, the existence of anisotropy in silica fiber is a known fact, but despite many efforts, the topological nature of the involved structural rearrangement is still unknown. Many numerical simulations have been developed to study silica glass deformation, mostly at ambient temperature. So far, a bulk silica glass under tensile load has been modeled by Pedone et al. at low temperature to study the stress–strain behavior [10]. Yuan et al. have studied parameters such as system size, cooling rate, strain rate and working temperature up to 1500 K, to reproduce the experimental brittle fracture of amorphous silica nanowires [11]. Rountree et al. have simulated bulk silica glass under a simple shear at 300 K and have predicted a permanent plasticity-induced structural anisotropy [12], due to Si–O–Si directions remaining aligned with the strain/stress direction. An experimental radial X-ray diffraction study performed by Sato et al. [13] on silica glass after decompression has evidenced a persistent differential strain equivalent to a remaining differential stress. It has been explained by anisotropic reconstruction of inter-tetrahedra Si–O–Si bonds, therefore validating the above prediction.

In this article, we focus our attention on the drawing of a silica fiber at high temperature. Typically performed around 2300 K, it is the common stage for most of the manufacturing processes to obtain an optical fiber. This crucial part has an important impact on its final properties such as refractive index profile or residual stress. The effects of various experimental conditions (drawing speed, tension, temperature, cooling profile) have been reported by Lancry et al. [14]. Resulting fibers have various profiles of fictive temperature, which is known to describe the glass nanoscale structure. The structural modifications induced by this stage are investigated by means of molecular dynamics (MD)

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simulations. To our knowledge, this is the first MD simulation of the complete drawing process to obtain a fiber, in order to study the effects on silica glass. It appears that small silica rings get a persistent orientation in the fiber, leading to a structural anisotropy, which is called "transverse isotropy" because of different longitudinal and transversal physical properties. Moreover, the experimental link between this anisotropy and the non-Newtonian behavior is verified in the simulations, since this anisotropic rearrangement leads to a non-Newtonian behavior of the MD glass melt, with strain-rate dependant properties.

2. Molecular dynamics simulations

2.1. Silica glass modeling

Classical molecular dynamics simulations are carried out by LAMMPS (large-scale atomic/molecular massively parallel simulator) [15] with periodic boundary conditions (PBC) and using the interatomic potential developed by Pedone et al. [16], designed to reproduce structural and mechanical properties of a wide range of silicates. This potential is composed of three terms: a long-range Coulomb interaction, a short-range Morse function and an additional $1/r^{12}$ repulsive contribution. The long-range Coulomb term is evaluated using the Wolf method [17], consisting in a spherically-truncated, charge-neutralized, shifted, pairwise $1/r$ summation. This method, initially developed for ionic crystals and melts, gives good results for amorphous materials like silica [18,19], and silica-based [20] glasses. It also well reproduces the energetics and the dynamics of various typical systems [21]. The main advantages of the Wolf method are: (a) the computational cost increases linearly with the system size N, instead of, at best, $N^{3/2}$ for Ewald method (N is the number of atoms involved in the simulation); and (b) the inherent periodicity of the Ewald sum is no more imposed to the system. The parameters of the Wolf method are chosen among the tested ones giving the best match between Wolf and Ewald summations, by comparing the total energy and the short- and medium-range structures obtained after melt/quench sequences of a pure SiO_2 system. Hence, the long-range cutoff is set at 7.5 Å and the damping parameter is set at 0.30 $Å^{-1}$. For this study, the short-range cutoff of the Morse function is set at 5.5 Å.

The usual melt/quench technique is used to model a glass from an initial crystalline structure. Unless otherwise indicated, the simulations are made at constant atmospheric pressure (P = 1 bar), using the Nosé–Hoover NPT algorithm (constant number of atoms, controlled pressure and temperature) and a time step of 1 fs. The starting configuration, melted at 4000 K, is continuously cooled down at 5 K/ps, and finally equilibrated at 300 K. Despite a cooling rate many orders faster than in a laboratory, a common choice around 5 K/ps yields the expected structure when compared to experimental data. More specifically, the structure of a silica glass modeled with Pedone potential and the structure derived from experimental neutron diffraction are both in very good agreement [22]. This model of silica glass has a density of 2.28 g/cm^3 and a glass transition temperature T_g of 2620 ± 40 K. This density, 3.6% higher than experimental value of 2.20 g/cm^3, is in agreement with the anomalous behavior of silica glass observed by Brückner [23] and Shelby [24]. Indeed, the slower the quench rate is, the lower the experimental density of silica glass is. MD quench rate being many orders higher than laboratory ones, it seems consistent for the model to have a higher density than experimental one. This anomalous behavior of silica glass also appears in the MD simulations made by Vollmayr et al. [25], using the BKS potential, and it has also been verified for the potential used in this paper for various quench rates. Experimental T_g is estimated to be 1446 K [26] (defined as the temperature when the viscosity is 10^{12} Pa·s) or 1473 K [27] (determined by differential scanning calorimetry at 0.33 K/s). Whatever the type of potential used in MD simulations, the overestimation of T_g is a known problem [25,28], which however does not impact the structural properties of the glass. Therefore, as indicated hereafter, the drawing simulation is performed using this modeled glass as the preform.

2.2. High-temperature drawing process

Experimentally, a silica preform placed on the top of a draw tower is heated between 2200 K and 2600 K, which is over its softening temperature of 1900 K, which is higher than experimental T_g of approximately 1450 K. According to Urbain et al. [29], this temperature range corresponds to working viscosities between 10^3 and 10^5 Pa·s. Fused silica flows down with gravity, forming a fiber which is drawn down to maintain the process. The MD simulation, schematized in Fig. 1, consists in modeling the high-temperature uniaxial deformation and the cooling until complete relaxation of a small volume of silica localized at the center of the preform, along its axis. The starting simulation box, of approximately 300 × 50 × 300 Å^3, contains 314,928 atoms of our modeled silica glass. This box is heated at 2700 K and 1 bar, and equilibrated. This temperature choice is guided by the real process, where the deformation temperature is higher than the T_g. The uniaxial drawing is made by an anisotropic NPT algorithm reproducing a natural deformation along y-axis with a "constant true strain rate": the height evolves as $L_y(t) = L_{y0}e^{\nu t}$ with a "true strain rate" (TSR), also denoted ν, of 10^9 s^{-1}, while no stress is imposed to lateral sides (only interactions due to atoms in periodic–boundary–condition replicas of the box). After 3500 ps, the box volume is approximately 50 × 1800 × 50 Å^3. It is now considered to be outside the furnace and it must be cooled down. Experimental cooling procedures can be either passive in a tall draw tower, or forced when high draw speeds are needed [30], or even controlled with specific temperature profiles leading to industrial patents. In this simulation, the box undergoes simultaneously and progressively for 300 ps a release of the uniaxial stress σ_y and a decrease of the temperature to reach 1 bar and 300 K, respectively, and it is finally equilibrated at 300 K. The resulting fiber density is 2.22 g/cm^3. No fracture is observed. Annealing is out of the scope of this paper.

At a larger scale, assuming an axisymmetric 2D laminar flow in a cylindrical system, the use of a fluid dynamic model with volume discretization leads to a deformation of the whole preform more complex [31] than a simple elongation. But the size of the used elements, at least 4 μm in the radial direction, is far bigger than the size of our simulation box. Hence, a simple elongation remains a very good approximation at the nanoscale level.

The choice of 50 Å as initial and final smallest dimension is a minimum length to proceed with ring statistics up to 14-membered silica rings. Other initial and final dimensions are imposed by the strain rate

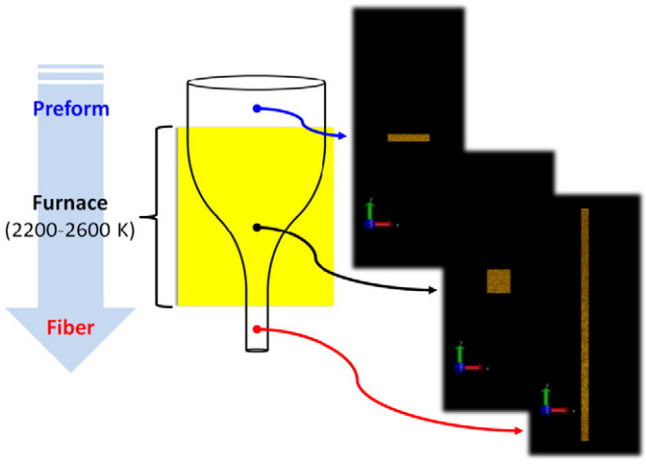

Fig. 1. Laboratory drawing protocol. Rendering of three steps of the MD simulation: initial (preform), during the high-temperature drawing, and final (fiber).