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Elasticity and strength of silica aerogels: A molecular dynamics study on large volumes

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ABSTRACT

The nanoporous structure and the mechanical properties of silica aerogels are studied by molecular dynamics simulations on large samples. For the first time, atomistic simulations are able to reproduce a pore size distribution, centered on 10 nm, comparable to experimental values. Using an unprecedented combination for silica aerogels of large volumes, large strains, and relatively small strain-rates, direct evidence of their peculiar mechanical behavior at the nanoscale is provided, from elasticity to fracture. The surface stress that silica ligaments experience produces a significant tension-compression asymmetry and an unusual discontinuity in the Poisson effect. The ductility of highly porous silica aerogels arises from an interplay between surface stress and a significant amount of reorganization in ligaments. Taking advantage of the large volumes accessible here, the very heterogeneous nature of low-density silica aerogels is reproduced, with an impact both on their elasticity and on their strength. In particular, a clear dependence between tensile strength and sample volume is uncovered, which opens perspectives for the elaboration of multi-scale models.

1. Introduction

Silica aerogels are of great interest from both scientific and industrial perspectives. Their exceptionally low thermal conductivities, acoustical insulation properties and low densities offer unparalleled application opportunities for building insulation, electronics, aerospace, chemistry, pharmacy and many other sectors [1]. The key to this outstanding performance is in their highly porous three-dimensional solid nanosized network [2], which is also responsible for their poor mechanical properties [3]. The understanding and optimization of the mechanical behavior of silica aerogels is challenging. Their complex structure exhibits different sizes of porosity ranging from the nano to the mesoscale [4,5]. An analysis that encompasses these different scales is necessary for such hierarchical fractal materials [6,7].

Molecular Dynamics (MD) simulations are an appropriate tool for the study of mechanical properties at the nanoscale. Atomistic simulations have successfully reproduced the fractal characteristics of the nanoporous structure of silica aerogels [8,9]. MD simulations have correctly predicted the power law that relates thermal conductivity and density, with a good correlation with experimental data [10,11]. Recent efforts in MD have also tackled mechanical properties with a focus on elasticity. The power law characterizing the relationship between elastic modulus and density has been reproduced by Campbell et al. [12] for nanoporous silica and more recently by Murillo et al. [13], Lei et al. [7] and Patil et al. [14] for silica aerogels. Coarse-grained models also offer a route to mechanical properties [15]. Although the power law obtained by these authors is in good agreement with experimental data, there is still a lack of sound knowledge on deformation mechanisms and the links between mechanical properties and porosity size and size distribution. Besides, mechanical properties are not limited to elasticity. Albeit seldom studied [14,16], plastic deformation and failure are paramount for these inherently weak materials. These limitations in the literature are mainly the results of the restricted volume of material that MD simulations can handle. Most of the above-cited MD studies are confined to volumes smaller than 20^3 nm^3, leading to smaller pore size distributions than those of experimental aerogels centered on 10 nm [17–19]. Although some recent studies

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tackle volumes of the order of 30^3 nm^3 [14], simulated silica aerogels in MD studies are still not representative enough for a detailed mechanical investigation. For nanoporous gold, a MD combination of large volume ($21 \times 21 \times 107$ nm^3), large strains (~30%), and relatively small strain-rates ($3 \times 10^8 s^{-1}$) was already attained by Farkas et al. [20].

Additionally, the extremely high surface to volume ratio of those materials involves long computation times for relaxation. Therefore, one of the main prerequisite that MD must confront to realistically investigate the mechanical behavior of nanostructured silica aerogels is a dramatic increase in the capability to simulate large enough volumes together with sufficiently large strains or durations. Computation time in MD simulations is mostly dependent on the interatomic potential. In order to study the mechanical behavior of materials with high surface area, an interatomic potential able to reproduce both bulk and surface properties of amorphous silica with a significantly reduced computation time is needed. A previous study [21] has shown that a simple pair potential optimized in computation time (without long-range interactions) reproduces surface and bulk properties of the BKS potential very satisfactorily [22], while leading to a 3000 gain factor on the CPU time per atom per step.

Using this optimized pair potential, we simulate volumes that are representative of the secondary particles of silica aerogels. The volume of our smallest sample (20^3 nm^3) is representative of the volume used previously in the literature for mechanical studies [7,13]. Our largest sample, depicted in Fig. 1, is 100^3 nm^3 in volume, and contains more than 7 million atoms. More importantly, our simulated samples are large enough to contain an adequate number of pores with a size that matches experiments. Here, these nanoporous structures are investigated in detail for their mechanical behavior from elasticity down to fracture.

2. Methods

2.1. Interatomic potential and aerogel preparation

Interactions between all atoms of the simulation box are defined by the Wolf BKS potential (van Beest, Kramer and van Santen), proposed by Carré et al. [23]. It mainly differs from the original version of the BKS potential [22] by the introduction of a cut-off on Coulombic long-range interactions. Details on the potential and on its validity for satisfactorily reproducing structural and energetic properties of amorphous silica with high surface area may be found in Refs. [21,23] and in section S1 of the Supporting Information.

Simulations are performed with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [24] with a velocity-Verlet algorithm and a 1.0 fs timestep. Periodic boundary conditions are used in all three directions. The fractal structure of aerogel is generated with Kieffer's method [8]. Using the Wolf BKS potential, the strategy is to extend the volume of the dense amorphous silica in order to reach the desired aerogel density. Silicon and Oxygen atoms are located at crystalline sites of β-cristobalite and the structure is melted at 5000 K. The liquid silica is quenched to 300 K at $4.7.10^{12}$ $K.s^{-1}$ to obtain an amorphous solid silica. In MD simulations, this quench-rate is typically of the order of $10^{10} - 10^{12}$ $K.s^{-1}$ [25]. However, during this preparation stage, it is not necessary to look for a finely equilibrated configuration since in the next stage, the structure is isostatically and instantaneously stretched in all directions by approximately 10%. A relaxation stage in the NPT ensemble with Berendsen barostat [26] and Langevin thermostat [27] is applied during 50 ps to equilibrate the structure at 300 K. Stress concentrations appear locally and voids develop during the relaxation stage by the gradual breaking of Si-O bonds. The stretching/relaxation stages are repeated until a predefined aerogel density is reached. A final relaxation stage of 200 ps is performed, which is meant to bring the aerogel structure in a stable state with constant pressure and volume (see section S2 of the Supporting Information). Using Kieffer's method [8], nine samples of silica aerogel are generated with the same final density of 250 kg m^{-3}. The nine aerogel samples differ in the volumes of simulated material (20^3, 30^3, 40^3, 50^3, 60^3, 70^3, 80^3, 90^3 and 100^3 nm^3).

2.2. Structural characterization

All structural characteristics are computed from the 80^3 nm^3 sample, which should be sufficiently large to ensure statistical meaningful results. Here, the fractal dimension, d_f, is computed using the method introduced by Kieffer et al. [8], based on the long-range decay of the total radial distribution function, $g(r)$:

$$d_f = 3 + \frac{d\ln g(r)}{d\ln r}, \tag{1}$$

where r is the distance separating a pair of atoms (see section S3 of the Supporting Information).

The pore size distribution is another structural characteristic of

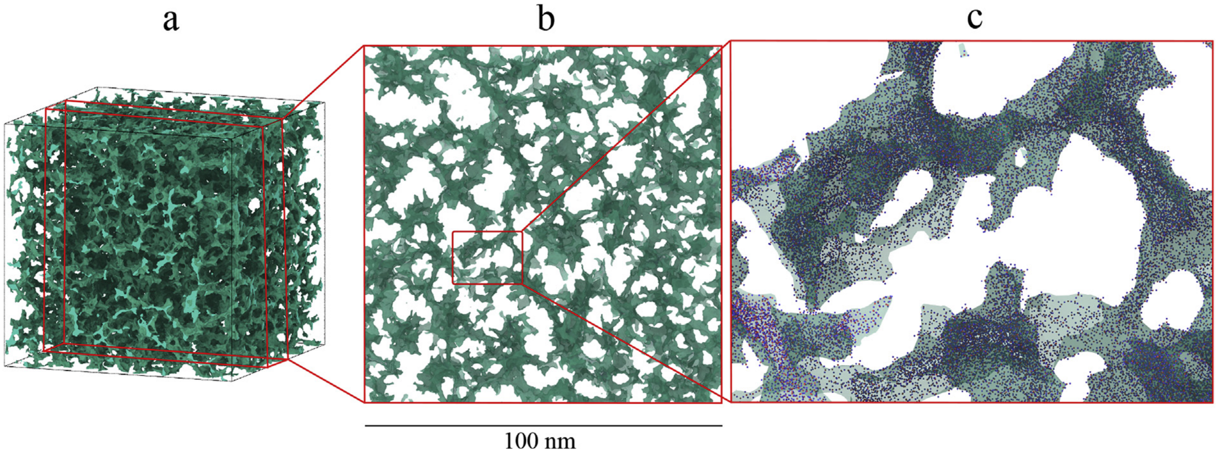

Fig. 1. The largest silica aerogel sample simulated. Sample density is 250 kg m^{-3} in a 100^3 nm^3 volume (more than 7 million atoms). a) 3D view of the simulation box. b) A 20 nm thick slice in the sample. c) Zoom-in image showing oxygen and silicon atoms in blue and red, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)