Silica glass under compression: Insight from computer simulations

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OUTLINE

✓Introduction: motivation, computer simulations

✓Plasticity of silica glass: a view from classical numerical simulations
ANR Plastiglass 2006/08

✓Conclusions

Motivation

- KNOWN:
    - Structure of silica glass at *normal* pressure is relatively well understood (disordered network of tetrahedra; ...)

- QUESTIONS:
    - What happens to the structure if the pressure is increased? Network of tetrahedra is partially destroyed and silicon atoms will have coordination number higher than 4. How does the change of structure happen on the *microscopic* level?
    - Up to what range is the deformation elastic?
    - What about repeated loading?

    - ....
- WHY:
    - Relevant for geology and mechanical contact of glass surface with external load

Computer simulations on atomistic level

GOAL
➢ investigate systems properties at atomistic scales (structure and dynamics)

ALL PHYSICAL PROPERTIES CAN BE COMPUTED (in principle!):

➢ atomic positions $\{\mathbf{R}_i (t)\}$
➢ velocities $\{\mathbf{v}_i (t)\}$
➢ forces $\{\mathbf{F}_i \}$

METHOD: Solve classical equation of motion of atoms

$$m_i \frac{\mathrm{d}^2 \mathbf{R}_i}{\mathrm{d}\, t^2} = \mathbf{F}_i = -\boldsymbol{\nabla}_i E(\{\, \mathbf{R}_j(t)\})$$

How can one obtain **E** or equivalently the **forces F_i** ?

Two possibilities: classical and *ab initio* simulations

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Classical approach

Assumptions:

- atoms considered as interacting point particles
- one postulates a rather simple ansatz for effective interatomic forces

↪ Balance between a simple and realistic description of the system under consideration

↪ Be aware of the influence of nature of the interatomic forces on the results

↪ Simulations are computationally relatively cheap - $O(10^6)$ particles can be simulated

Ab initio approach – a priori parameter free

•Interatomic forces are calculated from the instantaneous positions of the ions   and taking into account the **first principles of quantum mechanics** (Kohn-Sham, DFT approach)

• Universality (i.e. no ansatz for forces)
• It can handle relatively complex systems

•**BUT** it is computationally **very expensive** due the necessity to deal with the many (valence) electrons

•Typical system sizes are 200-1000 atoms

Model and details of the present numerical study

- **Classical approach** - effective interaction potential proposed by van Beest, Kramer, and van Santen (BKS) [PRL (1990)] and cutoff using Wolf procedure

$$\phi_{\alpha\beta}(r) = \frac{q_\alpha q_\beta e^2}{r} + A_{\alpha\beta} \exp\left(-B_{\alpha\beta}r\right) - \frac{C_{\alpha\beta}}{r^6} \quad \alpha, \beta \in [\text{Si}, \text{O}]$$
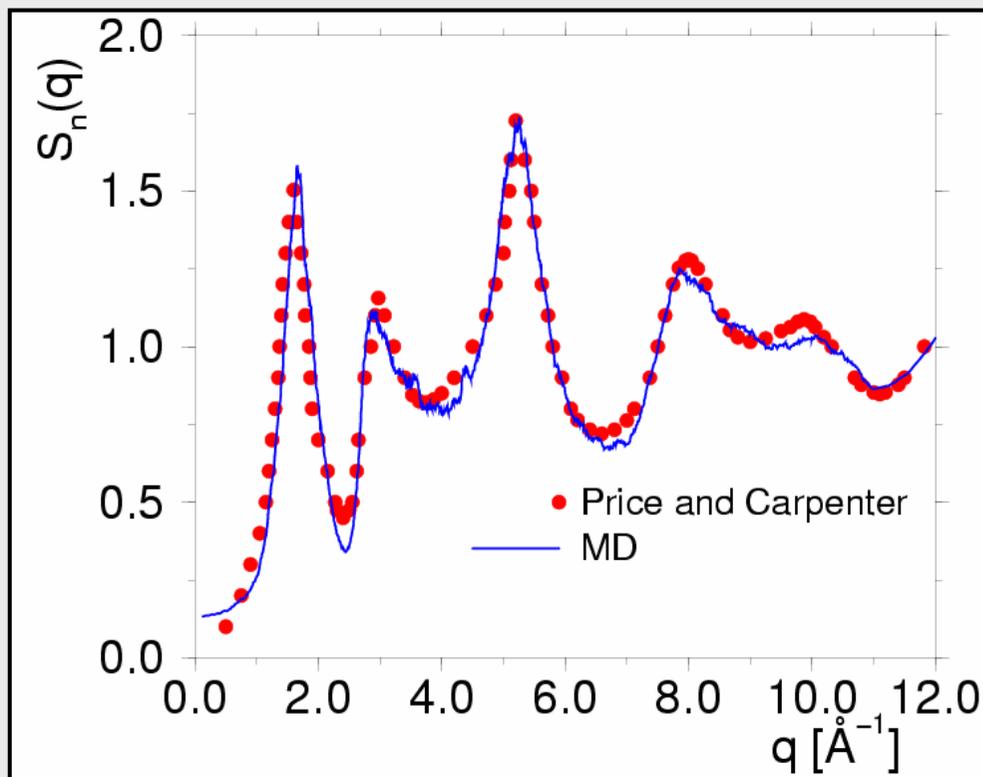
- Structure factor as seen in a neutron scattering experiment at normal pressure

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- 1008 particles in box of 24 Å $\Rightarrow$ density ρ=2.357 g/cm^3

- Cool the system from its liquid phase at T=3100K down to a glass at 0K with cooling rate of 14.3K/ps

- Volume of simulation cell is reduced isotropically by steps of 0.001 g/cm^3 to 4.3 g/cm^3 ; after each compression step, the potential energy is minimized

- 10 different runs to improve statistics

Density dependence of the pressure

- Consider SiO_2 glass at low T (here T=0K)
- Calculate the pressure P from the virial $\Rightarrow$ equation of state
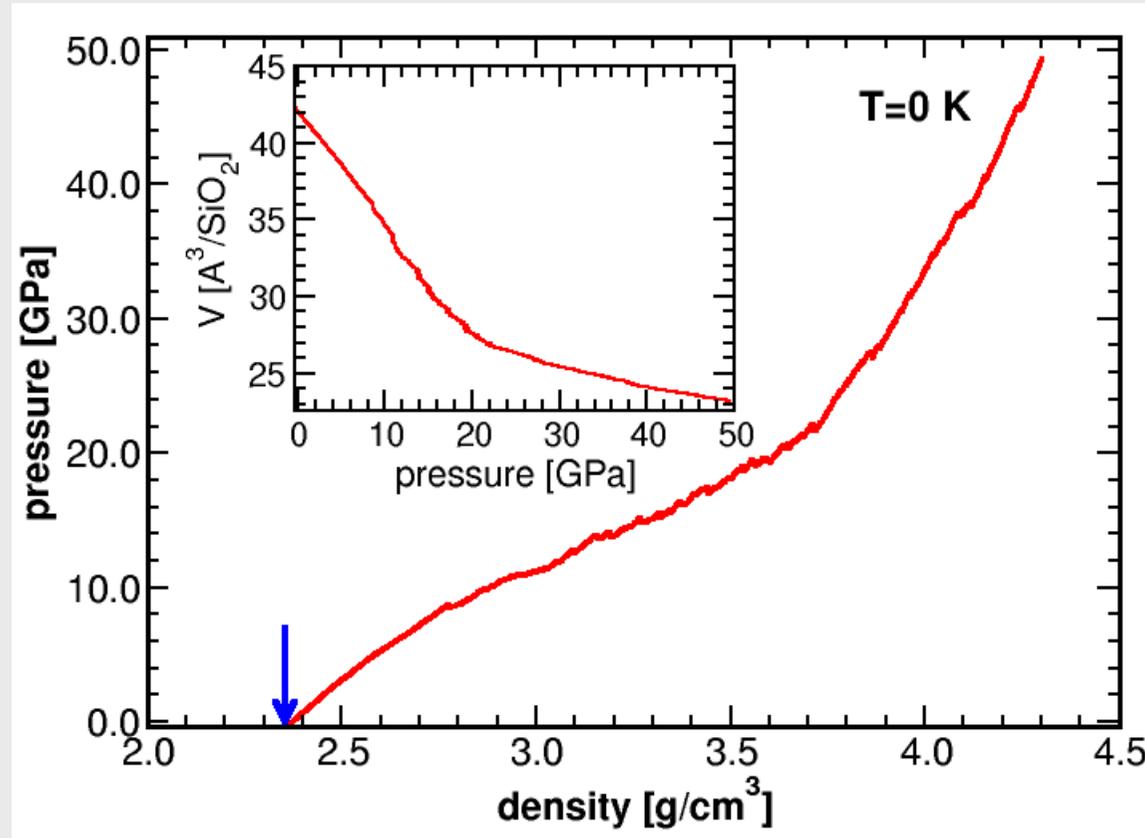
- Present study: isothermal compressibility $\beta = -1/V\, \partial V/\partial P$ drops at around 20 GPa $\Rightarrow$ evidence for a significant change in structure
- Available **exp. data**: elastic regime (P<8 -10 GPa) and plastic regime (P> 10 GPa)

Density dependence of the radial distribution functions

- Calculate the partial radial distribution functions $g_{SiO}(r)$, $g_{OO}(r)$, and $g_{SiSi}(r)$
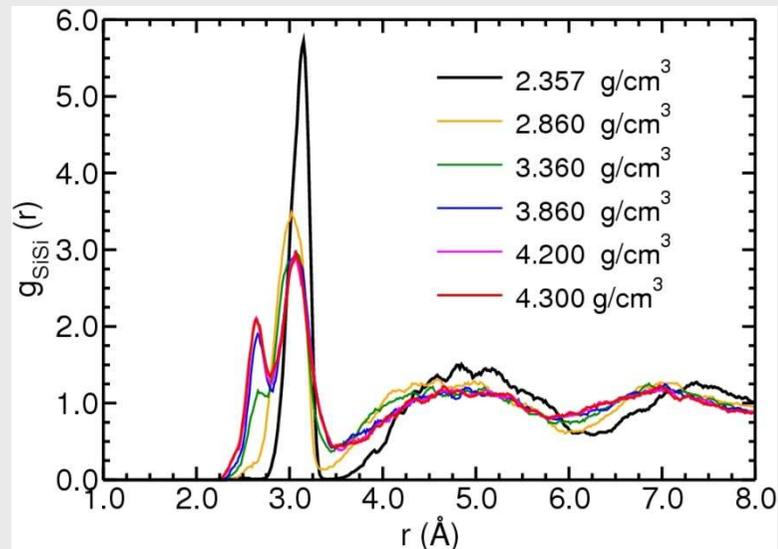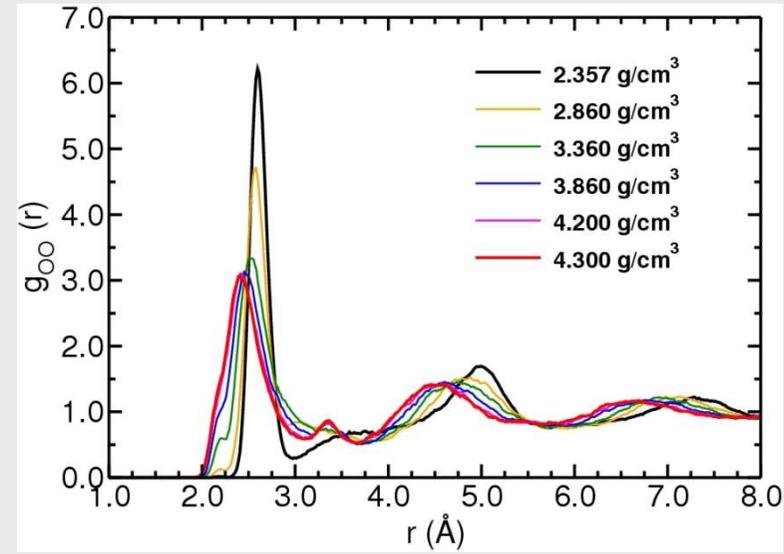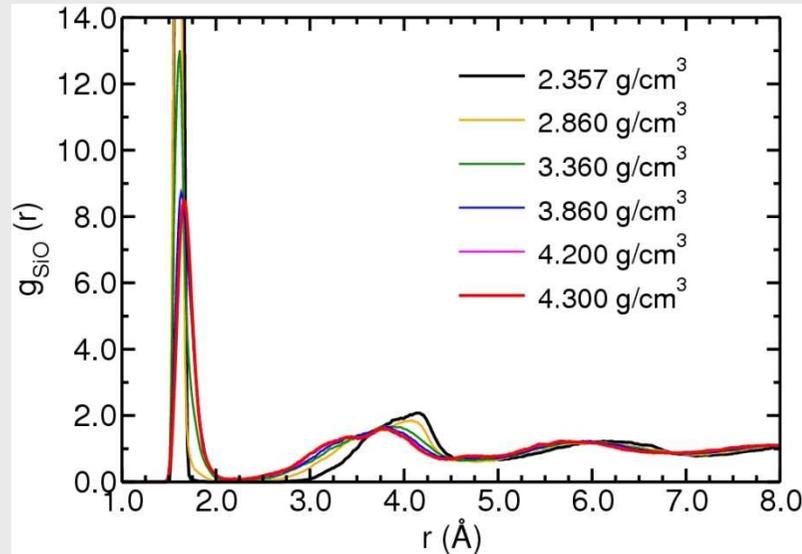
- Relatively mild dependence of $g_{SiO}(r)$ on ρ
- Strong decrease of first peak in $g_{OO}(r)$
- Decrease of first peak and formation of second peak in $g_{SiSi}(r)$

$\Rightarrow$ Evidence for a significant change in structure at around $\rho = 3.7$ g/cm^3

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Density dependence of coordination number of Si

• Calculate partial Si-O coordination number from area under the first peak in $g_{SiO}(r)$
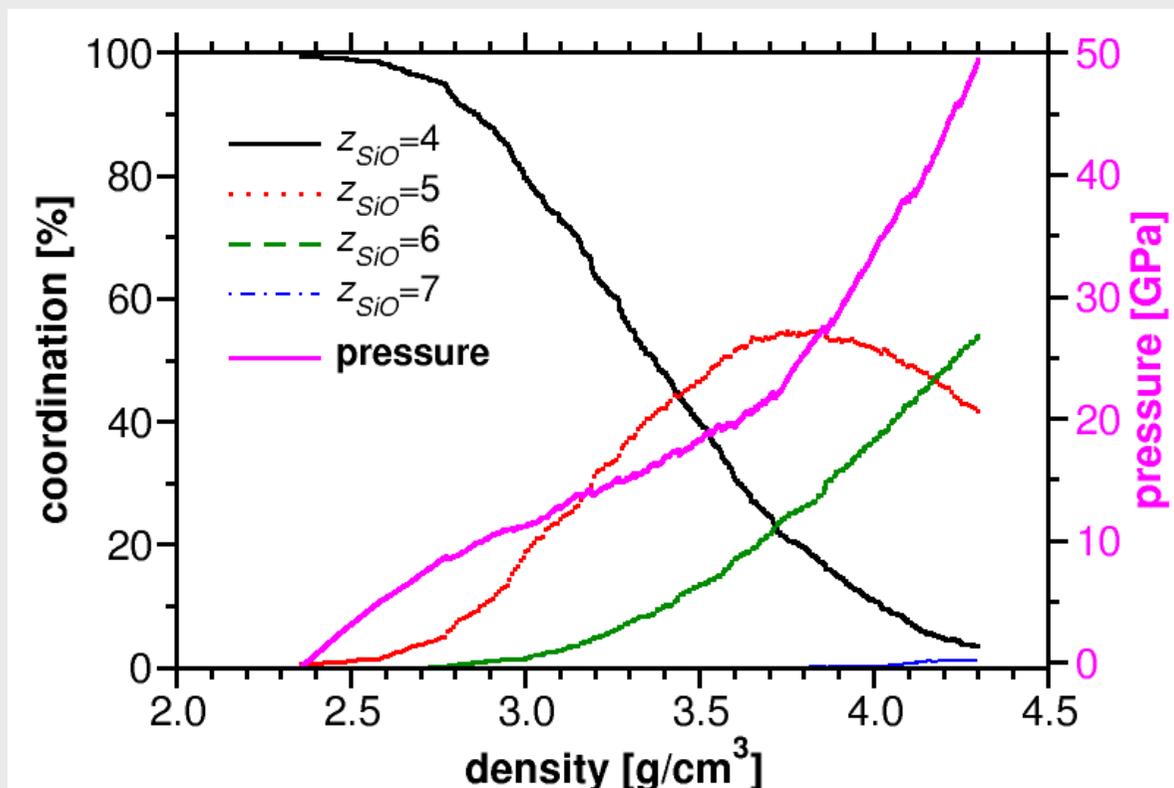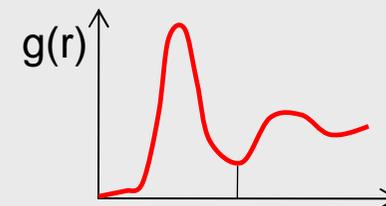
• Small pressures: All Si atoms are 4-fold coordinated.

• Starting around P=4GPa one finds 5-fold coordinated atoms

• At around 20 GPa the number of 5-fold coordinated atoms starts to decrease again and 6-fold coordinated atoms start to increase strongly

• Coordination changes agree with previous calculations and conclusions of various experimental works (at least qualitatively)

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Density dependence of ring size

- Define a ring as the *shortest* chain of Si-O links that makes a *closed* loop that starts/ends on the same Si atom

$\Rightarrow$ define "ring size" as number of Si atoms in a given chain

$\Rightarrow$ distribution of ring size

$\Rightarrow$ information on structure on intermediate length scales
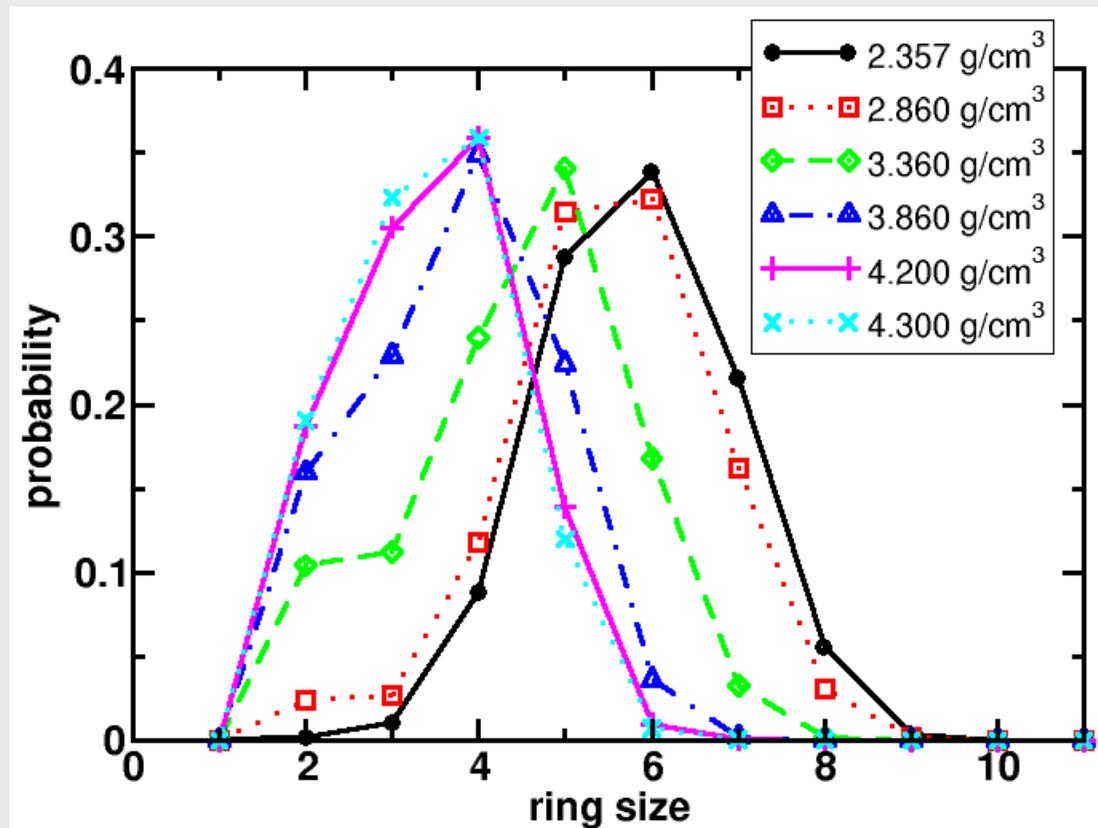
Upon compression the distribution shifts to rings with <u>smaller</u> sizes

$\Rightarrow$ Evidence for a <u>significant</u> change in structure at around $\rho=3.4$ g/cm^3

Behavior supported by exp. data, Benmore et al. PRB 81 (2010)

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Loading/unloading: Pressure

1) Start at ambient pressure ρ_0 and compress up to ρ_{max}
2) Decompress to ρ_0
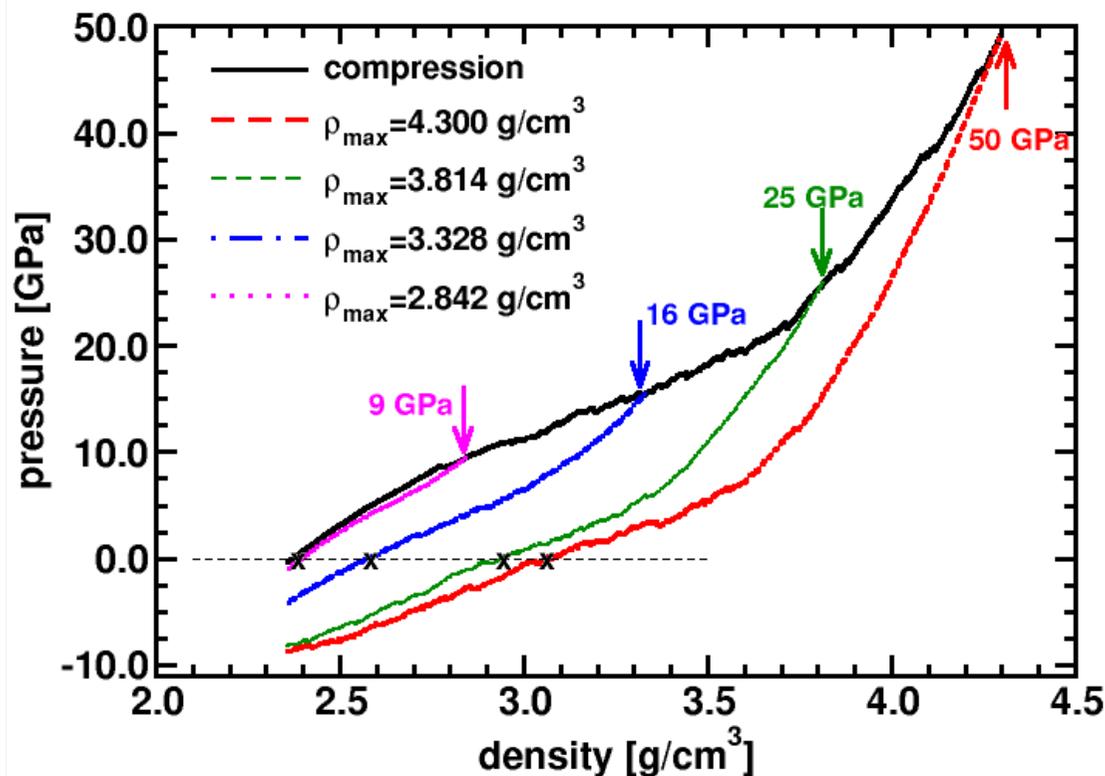
- ρ_{max} is less than 2.8 g/cm^3 : no permanent densification and compression is (basically) elastic

- For higher ρ_{max} the model remains densified permanently and compression is strongly inelastic

- No additional densification at P=0 if the model is compressed and decompressed beyond 3.8 g/cm^3 $\Rightarrow$ similar behaviour reported from Raman exp. Vandembroucq et al. (2008), Rouxel et al. (2008)

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Loading/unloading: Structure

- Look at coordination number of Si-atom
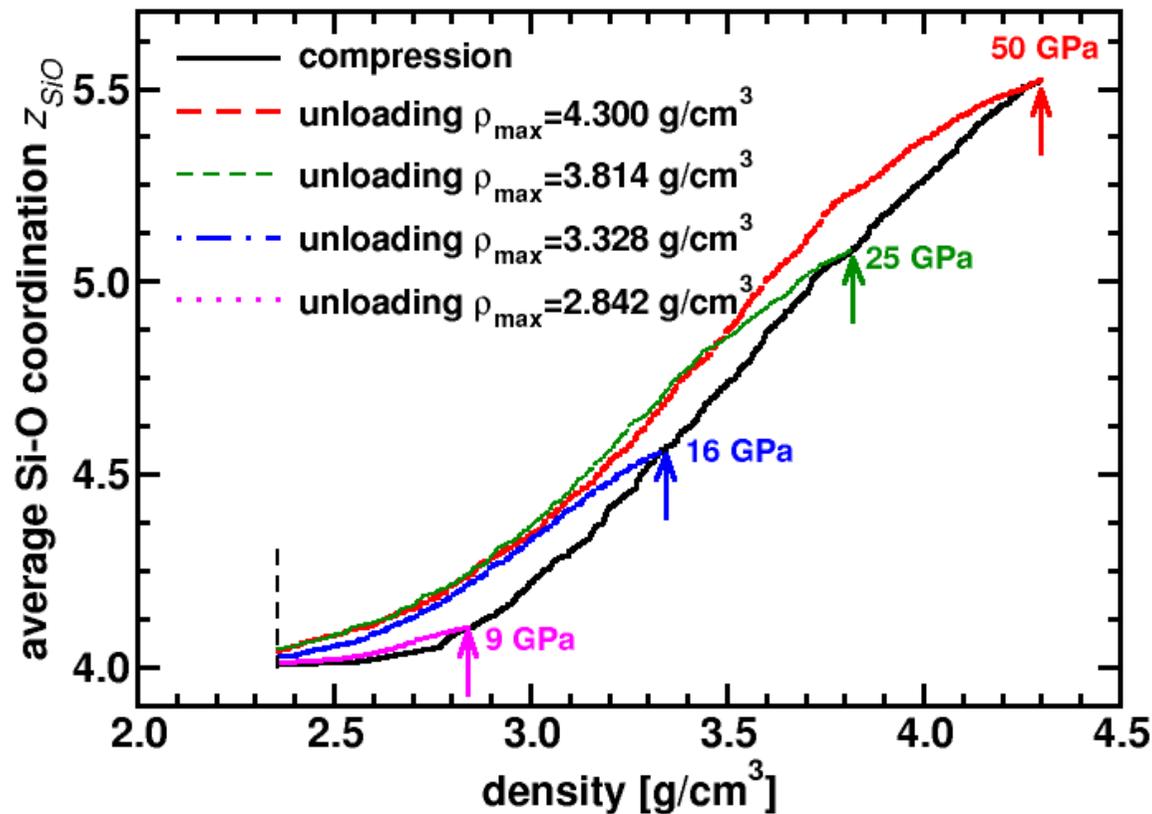
- O-O, and O-Si show similar behavior

- Whatever the value of ρ_{max}, the coordination number at ρ_0 is close to 4.0

- BUT: for P=0 the coordination number is higher than 4.0 (~4.4 for decompression from 4.3g/cm^3, i.e P=50 GPa)

Multiple loading/unloading: Pressure

1) Start at ambient pressure ρ_0 and compress/load up to ρ_{max}=3.328g/cm^3 (i.e. beyond elastic regime)
2) 1st unloading to ρ_0 (ie. initial density!)
3) 2nd loading to ρ_{max}
4) 2nd unloading to ρ_0

ρ_{max}=3.328 g/cm^3

16 GPa

1st loading/compression
1st unloading/decompression
2nd loading
2nd unloading
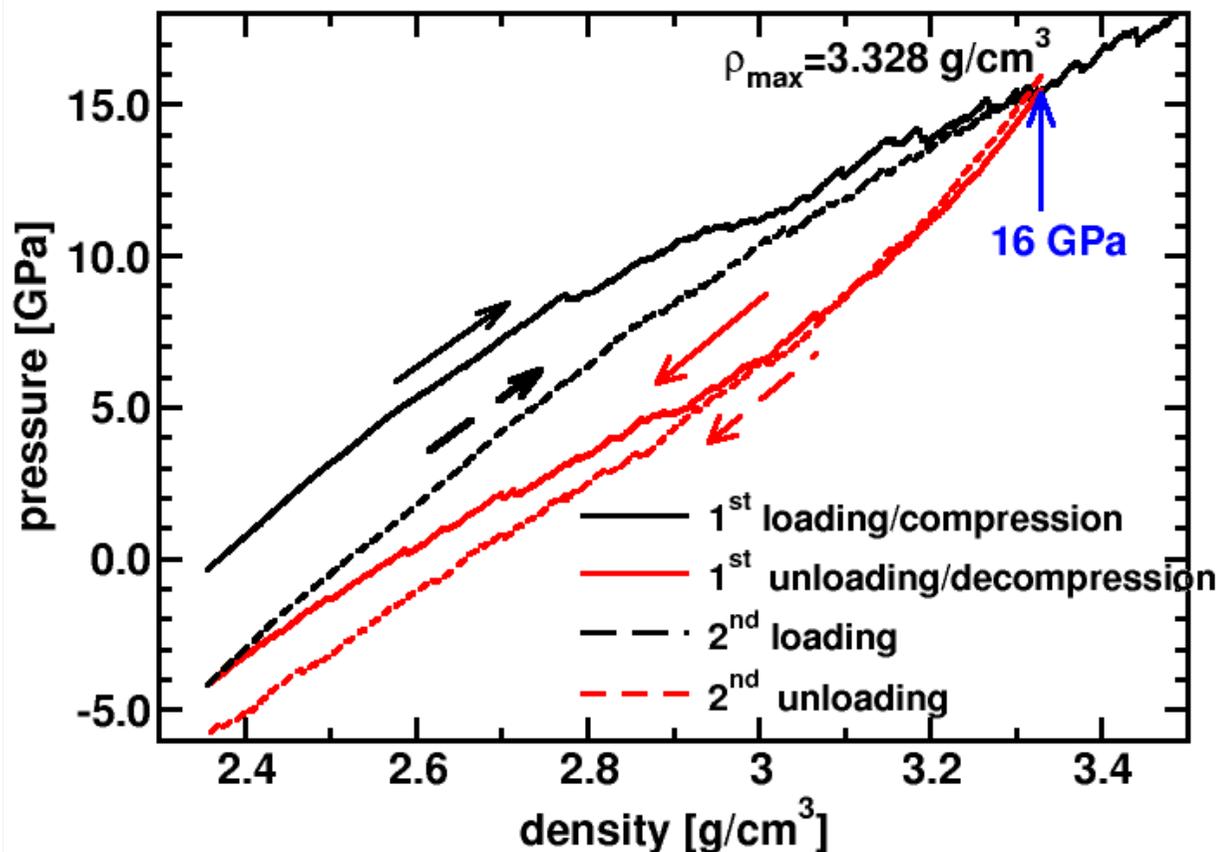
- Pressure for 2nd loading is different from the 1st one

- Pressure for 2nd unloading is similar to 1st unloading, if pressure is not small $\Rightarrow$ weak history dependence at intermediate and high pressures (for this ρ_{max}!)

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Multiple loading/unloading:Structure

1) Start at ambient pressure ρ_0 and compress/load up to $\rho_{max}=3.328 g/cm^3$ (i.e. beyond elastic regime)
2) 1st unloading to ρ_0 (ie. initial density!)
3) 2nd loading to ρ_{max}
4) 2nd unloading to ρ_0
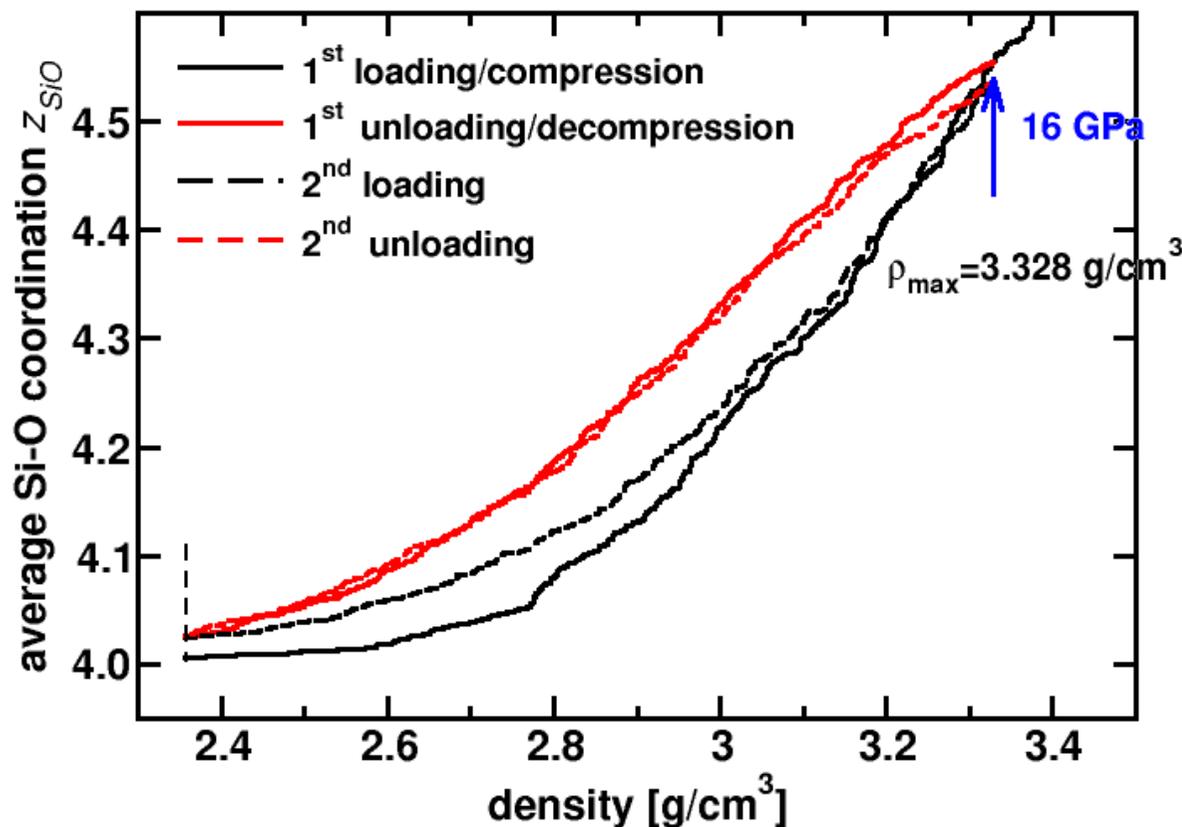
- At ρ_0 the coordination number is always close to 4.0
$\Rightarrow$ no memory effect

- For higher $\rho > \rho_0$, we see strong history dependence upon compression but no history dependence for the 2nd decompression

Summary

- Simulations of a simple but reasonably realistic model for a amorphous silica

- Evidence for a gradual transition from tetrahedral-like structure to a strongly disordered structure with Si-atoms that are 6-fold coordinated

- Relaxation events due to compression are localized at low P and delocalized at high P

- System seems to be elastic if $\rho \leq 2.8$ g/cm^3 (but topology of structure changes!)

- Multiple loading/unloading: Structure (as characterized by Si-O coordination number) seems to be affected less than the density/pressure

Acknowledgments

- ANR funding
- Your attention