

ELASTIC PROPERTIES OF SODA-LIME SILICA GLASS FROM FIRST PRINCIPLES

JAN MACHACEK, ONDREJ GEDEON, MAREK LISKA*

Department of Glass and Ceramics, Institute of Chemical Technology, Technická 5, Prague 166 28, Czech Republic
*Vitrum Laugaricio – Joint Glass Center of Institute of Inorganic Chemistry SAS, Alexander Dubcek University of Trencin and RONA Lednicke Rovne, Studentska 2, Trencin 911 50, Slovak Republic

Email: Jan.Machacek@vscht.cz

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This work describes preparation of soda-lime-silica (NCS) window glass by the first principles molecular dynamics and calculation of elastic properties from the Hellman-Feynman stresses. Small atomic glassy systems reveal deviations from isotropic solid. Such deviations can be quantified using differences among some stress tensor components. The first principles model applied in this work (DFT: PBE/PAW) underestimates elastic constants by 10-20 %. Size effects were studied with help of the classical molecular dynamics of binary glass $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$, which is close to NCS glass stoichiometry. It was found that elastic properties of small atomic systems are essentially size-independent even if silicate ring statistics reveals strong dependence on the number of atoms.

INTRODUCTION

Nowadays, ab initio molecular simulations of bulk materials and surfaces are considered as standard tools of materials research covering electronic band-structure investigations, thermodynamic calculations of phase stability, molecular transport through the bulk and over the surface. The vast majority of applications involve well defined crystalline or slightly perturbed crystalline systems. Conversely, the amorphous systems, including glasses, are very badly defined and their modeling by a molecular simulation of any kind is rather troublesome. The electronic structure methods can handle only small systems comprising not more than several hundreds of atoms. On the other hand, the simulations with empirical force-fields contain usually much larger sets of atoms, but precision and generality of such simulations are incomparably lower. Small systems suffer from several illnesses: they are not isotropic but quasi-periodic; the medium (and long) range order is essentially lost; some physical quantities and parameters are not size invariant; and, last but not least, the calculated physical quantities are significantly noisy.

In spite of the limitations enumerated above, the ab initio molecular dynamics (MD) of glasses is becoming recognized by the scientific community as a valid analytical tool. Recently, this method was used to study structure and properties of many oxide glasses including silica [1], silicate [2-4] phosphosilicate [5], oxynitride [6, 7], and aluminate glasses [8-10]. Vast majority of papers focus on atomic and electronic structure, some of them

also provide vibrational properties. To the best of the authors' knowledge, elastic properties of alkali silicate glasses have been already calculated only by classical MD with empirical potentials, where analytical second derivatives of energy with respect to strain were used [11].

This work put forward a method of calculation of elastic properties of a small glassy system from first principles using the common window glass as a model. The method is based on the direct application of the Hook's law. Aim of this work is to quantify and discuss size limitations inherently involved in ab initio molecular simulations of glassy systems.

COMPUTATIONAL

The ab initio (Born-Oppenheimer) MD calculation using the Hellmann-Feynman forces of the NCS glass was performed with help of the Vienna ab-initio simulation package VASP [12]. The valence-electron wave-functions were expanded in plane waves. The Kohn-Sham equations of density-functional theory (DFT) were solved using generalized gradient approximation (GGA) adapted by Perdew, Burke and Ernzerhof (PBE). The projector augmented wave (PAW) pseudopotentials [13] were used. The pseudopotentials can be found in the VASP pseudopotential PAW_PBE database under the following designation: Si, Ca_sv, Na, O_s. The potential energy calculations were performed with the plane-wave cut-off of 213 eV. Brillouin-zone sampling was restricted to the Γ -point only. The default values of other VASP parameters were assumed.

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Three independent systems contained 110 atoms: 28 Si, 4 Ca, 12 Na, and 66 O. It corresponds to 15.8 wt.% Na₂O, 10.5 wt.% CaO, and 73.7 wt.% SiO₂. Atoms were randomly placed into the cubic computational box adjusted to the temperature dependent densities of the studied systems (Table 1). The time-step of the numerical integration of the equations of motion was set to 0.002 ps. Temperature was rescaled in every 20 time-step.

Table 1. Scheme of cooling of the simulated NCS glassy systems.

Temperature (K)	Density (g/cm ³)	Box length (Å)	Time (ps)
5000	2.12	12.129	4
4000	2.12	12.129	10
2500	2.12	12.129	10
1000	2.43	11.590	10
300	2.50	11.481	10
300	2.50	11.481	10

Ionic positions and computational cell vectors of the glassy systems were optimized to obtain equilibrium structures at zero temperature and stress. This was done by the conjugate gradients method with the extended plane-wave basis expansion (368 eV) and VASP parameters adjusted for accurate calculations. The Hellmann-Feynman forces converged below 10⁻³ eV/Å. The optimized structures were achieved in about 200 iteration steps.

The optimized structures were used in the calculation of the elastic constants, mechanic moduli, and other elastic properties. This was done by calculating of (Hellmann-Feynman) stresses acting on distorted systems. Generally speaking, glass is isotropic solid medium which is characterized by only two elastic constants, c_{11} and c_{12} . However, a small computational cells employed in ab initio MD simulations contain hardly more than several hundred atoms. Thus, the simulated systems are quasi-periodic and substantially anisotropic.

In this work, we have chosen two independent strains, e_{comp} and e_{trig} , this way [14]:

$$e_{comp} = \begin{bmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{bmatrix}, \quad e_{trig} = \begin{bmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{bmatrix} \quad (1)$$

where e_{comp} is a compressive strain, e_{trig} is a trigonal strain, and δ is the strain parameter, $\delta = 0.003n$, where $n = 0, \pm 1, \pm 2$ that ensures retaining of the elastic regime. Ionic positions were re-optimized (relaxed) whenever dimensions of the computational cells had changed. The stresses, $\tau_j(\delta)$, where $j = 1, 2, \dots, 6$, responding to strains, $e_{comp}(\delta)$ and $e_{trig}(\delta)$, were tabulated and fitted by regression lines. A typical result is seen in Figure 1.

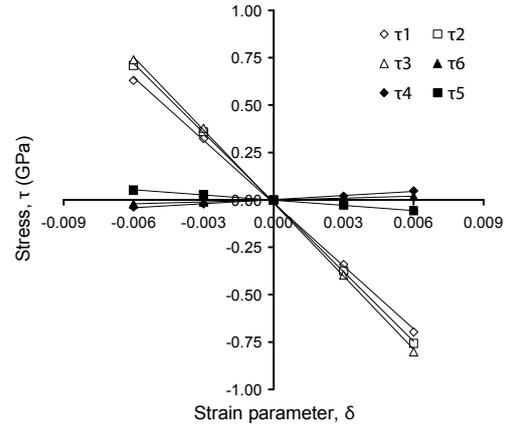


Figure 1. Stress-compressive strain dependence in the system cnf-1.

The elastic constants, c_{11} and c_{12} , and bulk and shear moduli, B and G , were calculated as follows:

$$k_{comp} = \frac{1}{3} \sum_{i=1,2,3} \frac{\partial \tau_i(e_{comp})}{\partial \delta} = c_{11} + 2c_{12} = 3B, \quad (2)$$

$$k_{trig} = \frac{1}{3} \sum_{i=4,5,6} \frac{\partial \tau_i(e_{trig})}{\partial \delta} = \frac{c_{11} - c_{12}}{2} = 2G \quad (2)$$

Young modulus, E , Poisson ratio, ν , and longitudinal and transversal sound velocities, v_l and v_t , were calculated according to usual relationships:

$$E = \frac{9GB}{3B + G}, \quad \nu = \frac{c_{12}}{c_{11} + c_{12}} \quad (3)$$

$$v_l = \sqrt{\frac{c_{11}}{\rho}}, \quad v_t = \sqrt{\frac{c_{12}}{\rho}} \quad (4)$$

The stress tensor components, τ_1, τ_2, τ_3 , in case of the compressive strain, and τ_4, τ_5, τ_6 , in case of the trigonal strain, were used to estimate variances within one configuration caused by anisotropy.

RESULTS AND DISCUSSION

The optimized cell parameters (corresponding to the minimum system energy) are collected in Table 2. It is seen that all systems expanded approx. by 7 % and lost their cubic cell symmetry.

Figure 1 shows stress response to the compressive strain, as obtained from the system cnf-1. A similar plot was obtained also for the system cnf-3. On the other hand, the stress-compressive strain relation in the system cnf-2 was not linear but v-shaped being centered at $\delta = 0$. This behavior can be explained by relaxation of some structural instability during expansion and its

Table 2. Optimization of ionic positions and cell parameters.

System	Density (g/cm ³)	Energy (kJ/mol)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
cnf-1	2.351	-1991.51	11.295	11.857	12.046	87.4	89.6	86.9
cnf-2	2.335	-1990.61	11.775	11.857	11.664	95.5	89.0	90.0
cnf-3	2.327	-1992.15	11.717	11.830	11.756	91.8	86.9	89.7
mean	2.337	-1991.06	11.596	11.848	11.822	91.6	88.5	88.9
st. dev.	0.013	0.77	0.262	0.015	0.199	4.1	1.4	1.7
max-min	0.025	1.54	0.480	0.027	0.381	8.1	2.7	3.1

transformation into diagonal stress components. In case of trigonal deformation, all graphs looked similar to the one in Figure 1. The slopes, k_{comp} and k_{trig} , are collected in Table 3. In the isotropic solid, the diagonal and off-diagonal stress tensor elements should be the same, i.e. for e_{comp} : $\tau_1 = \tau_2 = \tau_3 = \tau_{\text{comp}}$; $\tau_4 = \tau_5 = \tau_6 = 0$ and for e_{trig} : $\tau_1 = \tau_2 = \tau_3 = 0$; $\tau_4 = \tau_5 = \tau_6 = \tau_{\text{trig}}$. It is not the case of the small glassy systems presented in this work. Here, differences among respective matrix components can be used to quantify non-isotropic character of the system under study.

Table 3. Slopes k_{trig} and k_{comp} (GPa).

	Compressive deformation			Trigonal deformation		
	cnf-1	cnf-2	cnf-3	cnf-1	cnf-2	cnf-3
$\partial\tau_1/\partial\delta$	110.6	95.0	98.0	1.5	-17.2	17.6
$\partial\tau_2/\partial\delta$	122.2	65.0	99.2	1.5	2.5	4.5
$\partial\tau_3/\partial\delta$	128.5	102.3	97.6	-5.7	-30.3	-15.7
$\partial\tau_4/\partial\delta$	-3.4	3.3	11.3	54.3	26.0	46.0
$\partial\tau_5/\partial\delta$	-7.1	-8.3	-6.1	44.0	36.7	53.3
$\partial\tau_6/\partial\delta$	9.2	-15.7	-2.3	44.2	37.3	35.6

Average values of the slopes k_{comp} and k_{trig} , elastic constants, elastic moduli and sound velocities are presented in Table 4. This table is also completed with experimental values of elastic moduli. It can be seen that the simulated elastic moduli are in all cases underestimated comparing with the experimental ones by 10-20 %. The major part of such discrepancy can be attributed to the electronic structure model adopted in this work. We have found that PBE/PAW as implemented in

the VASP package gives longer and weaker Si-O bonds in the silicate glasses [3]. Other models e.g. PBE/US-PP or CA/PBE would improve results significantly.

It can be also seen that the variance of data within the simulated systems is quite large. It is caused by poor statistics of small atomic systems. To improve statistics of results and check size effects, additional simulations of a binary glass (close in stoichiometry), Na₂O·3SiO₂, was performed using the classical molecular dynamics with the empirical Buckingham-type potential. The cooling procedure was the same, only the force-field differed. Number of atoms, *N*, gradually increased from 110 up to 798. Averages and deviations of physical quantities were calculated from 14 independent configurations at each *N* (Figure 2). It is clearly seen that the standard deviations of the elastic moduli exceed 10 GPa for the smallest systems and the elastic moduli are nearly size-insensitive with respect to the error-bars. It is rather surprising because the medium range order of glass expressed by the silicate ring statistics (Figure 3) reveals strong dependence on the number of atoms.

CONCLUSION

One may deduce that elastic properties of MD simulated glasses are determined most by the short range ordering, i.e. the atomic local structure. Therefore, small glassy systems can be used to obtain reasonable elastic constants providing that more independent calculations are carried out to improve statistics. This is important result because computer time-consumption scales linearly with the number of independent configurations

Table 4. Elastic constants and moduli of the simulated NCS glasses (in GPa).

	cnf-1	cnf-2	cnf-3	this work [†]	experim.*
k_{comp}	120.4 ± 9.1	87.4 ± 19.8	98.3 ± 19.8	109.4 ± 13.4	
k_{trig}	47.5 ± 5.9	33.3 ± 6.4	45.0 ± 8.9	46.2 ± 6.9	
c_{11}	71.8 ± 7.0	51.4 ± 10.8	62.8 ± 6.2	67.3 ± 13.6	
c_{12}	24.3 ± 5.0	18.0 ± 4.5	17.8 ± 3.2	21.0 ± 6.8	
B	40.1 ± 3.0	29.1 ± 6.6	32.8 ± 6.6	36.5 ± 4.8	41.3
G	23.8 ± 3.0	16.7 ± 3.2	22.5 ± 4.5	23.1 ± 3.8	28.6
E	59.5 ± 9.0	42.0 ± 12.9	54.9 ± 7.3	57.2 ± 16.2	69.8
ν	0.253 ± 0.043	0.260 ± 0.063	0.221 ± 0.035	0.237 ± 0.069	0.218
v_1 (m/s)	5527 ± 269	4690 ± 493	5193 ± 256	5360 ± 542	5248
v_t (m/s)	3216 ± 331	2779 ± 347	2763 ± 249	2989 ± 485	3363

[†] averages of the cnf-1 and cnf-3 configurations

* compiled from [16] using a method described in [15].

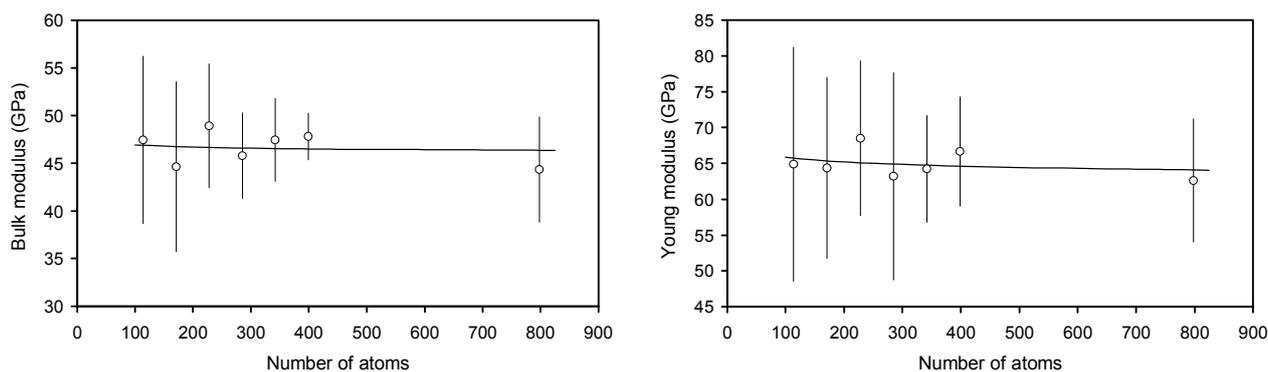


Figure 2. Elastic moduli of $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glass. A classical molecular dynamics simulation. Data points are fitted by the function $M(N)=M_0+c/N^n$, where M is a modulus, N is the number of atoms, and M_0 , c , n are parameters. The data can be easily completed with $B(1536) = 45.33$ GPa and $E(1536) = 63.22$ GPa obtained for the same system and referenced in [11].

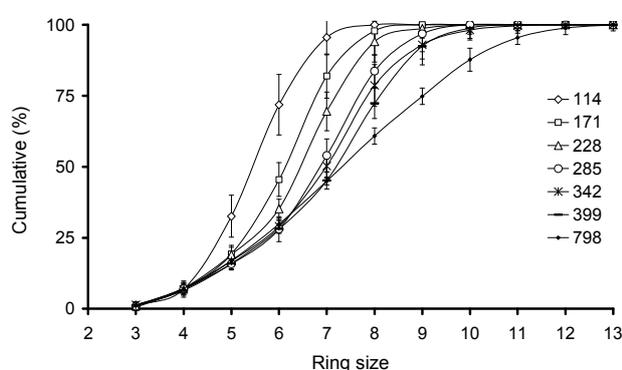


Figure 3. Silicate ring statistics in $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glass. A classical molecular dynamics simulation. A small system generates small ringselectron wave-functions were expanded in plane waves.

but increasing of the number of atoms scales quadratic at best. It was shown that differences among some stress tensor components can be used to quantify deviations from isotropic solid. The first principles model used in this work underestimates elastic constants; however this can be improved by using other models better adapted to glassy silicates.

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