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## Abstract

We investigate the diffusion of sodium ions in an artificially frozen amorphous silica matrix via molecular dynamics simulations. The motion of the Si and O atoms is stopped at different temperatures  $T_{fr}$  and we study the activation energy  $E_a$  of the diffusing Na atoms. We observe an abrupt change in  $E_a$  around the glass transition temperature  $T_g$ : for  $T_{fr} < T_g$  high values of  $E_a$  are found whereas low values of  $E_a$  exist for  $T_{fr} > T_g$ . By studying the probability of the available sodium volume to percolate we show that due to the closing of the intertetrahedral SiOSi angle with increasing  $T_{fr}$ , this volume percolates for the high values of  $T_{fr}$  which explains thus the easy diffusion of the sodium ions.

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## I. INTRODUCTION

The question of how ions diffuse in an amorphous host [1,2], is far from being elucidated and therefore it is the subject of numerous experimental [3,4] and numerical [5–9] studies and the topic of lively and animated sessions during the 5th IDRMCS. Prototypical systems are for example the sodium-silicate glasses since they contain the essential ingredients: the amorphous matrix (silica) and the mobile ions (sodium). Hence they represent a first step in the simulation of more complex glasses closer to real glasses or of higher practical interest.

In previous studies [10–12], we have shown by means of classical molecular dynamics simulations of  $\text{Na}_2\text{O}-4\text{SiO}_2$  (NS4), that the sodium atoms diffuse through a well connected network of pockets (which represents only a limited fraction of the entire available space) that we have called “channels” to be coherent with the literature. The existence of the channels, which are not due to micro-segregation effects [6,7], has been confirmed by the existence of a pre-peak in the partial Na-Na structure factor at a wave-vector  $q = 0.95 \text{ \AA}^{-1}$  [13]. This pre-peak has also been observed experimentally [14] and numerically [15,16] in other studies. Since the sodium dynamics appeared to be related to that of the underlying silica network [15] we have recently performed classical molecular dynamics simulations of a series of “toy” systems in which the atomic masses of both the oxygen and silicon atoms have been systematically changed after artificially multiplying their experimental values by a common factor  $\mu$  varying from 0.5 to infinity [17]. Contrarily to what is observed in a standard NS4 system ( $\mu = 1$ ), these simulations have shown that in a *frozen* silica matrix ( $\mu = \infty$ ) the diffusion of the sodium atoms is impossible. This result highlights the importance of the vibrations of the matrix atoms (Si and O) in the diffusion process of the ions (Na). The aim here is to extend this study by forcing the Na atoms to diffuse inside a silica matrix frozen at a temperature  $T_{fr}$  and to investigate the evolution of the sodium activation energy  $E_a$  as a function of  $T_{fr}$ . The values of  $T_{fr}$  are chosen between 4000K (liquid phase) and 0K (glassy phase). Since the matrix is frozen, if a dependence

of  $E_a$  on  $T_{fr}$  is detected, this would indicate that changes in the inherent structure of the silica matrix occur as  $T_{fr}$  is varied. This is indeed the case, and the changes in the structure are studied in terms of percolation theory together with an analysis of the intertetrahedral angle as a function of  $T_{fr}$  which permits to explain the observed changes. The paper is organized as follows: in section II the modus operandi is presented. The results are presented in section III and the major conclusions are summarized in section IV.

## II. MODUS OPERANDI

The classical molecular dynamics calculations are performed on NS4 systems containing 648 particles (86 sodium, 173 silicon and 389 oxygen atoms) confined in a cubic box of edge length 20.88 Å with periodic boundary conditions. This choice insures that the density is the experimental density of glassy NS4, *i.e.* 2.38 g.cm<sup>-3</sup> [18]. The interactions between the particles are given by a modified version of the so-called “BKS” potential [19,20] which is able to reproduce the structure as well as the dynamics of several sodium-silicate systems [10–13,21] (for more details see [11]). In this study we start from two standard NS4 samples previously generated and relaxed during 1.4 ns (10<sup>6</sup> steps) [17] at 8 different temperatures: 4000, 3050, 2500, 2325, 1900, 1675, 1025 and 0 K. We have shown in previous studies [10–13] that the properties of these samples are in good agreement with the available experimental data. Then, after these 1.4 ns of relaxation time, we have frozen all the movements of the silicon and oxygen atoms (including of course the vibrations) at these 8 “freezing” temperatures  $T_{fr}$ . In our previous work [17] we have shown that this implies that the sodium diffusion is impossible in these samples. In order to permit the sodium diffusion we have performed 3 additional simulations in which we have given a supplemental thermal energy to the sodium atoms in order to reach the diffusive regime after an additional 1.4 ns. As an example, for one of the samples frozen at  $T_{fr}=2325$  K the Na atoms have been successively put at  $T_{Na}=3235, 3800$  and

4700 K by rescaling their velocities accordingly. Thus for every couple  $(T_{fr}, T_{Na})$  we can calculate the sodium diffusion constant and plot it versus the inverse of  $T_{Na}$  on a linear-log graph like the one shown in Fig.1. Since the diffusion process is thermally activated we can reasonably assume that the diffusion constant follows an Arrhenius law. Therefore from this kind of graph we can, for each value of  $T_{fr}$ , extract the corresponding sodium activation energy  $E_a$  by fitting the data by an Arrhenius law. This procedure has been performed for two samples at 8 different  $T_{fr}$  temperatures for a total simulation time of  $2 \times 8 \times 3 \times 1.4 \text{ ns} = 67.2 \text{ ns}$ .

### III. RESULTS

In Fig.2 we have represented the activation energy  $E_a$  of the sodium atoms for both samples as a function of the freezing temperature  $T_{fr}$  of the matrix. We observe an abrupt change of behavior: for  $T_{fr} > 2600 \text{ K}$  the activation energy of the mobile ions is of the order of 1.25 eV whereas for  $T_{fr} \leq 2600 \text{ K}$ ,  $E_a$  is around 2.4-2.5 eV. It is worth noting that in order to detect aging effects on the value of  $E_a$ , we have performed a simulation in which  $E_a$  has been measured at  $T_{fr}=1900 \text{ K}$  in a sample that has been relaxed 14 ns instead of 1.4 ns. The obtained value (indicated by the cross in Fig.2) being only slightly lower than the ones obtained in the 2 samples relaxed during only 1.4 ns, we can conclude that the relaxation period has only a weak effect (increasing probably with decreasing  $T_{fr}$ ) on the activation energies of interest in this study.

In Fig.2 we have indicated by the horizontal dashed line, the average activation energy  $\approx 1.5 \text{ eV}$  obtained for Na atoms in a standard (not frozen) silica matrix. The fact that at low  $T_{fr}$  the Na activation energy is close to 2.5 eV indicates that the diffusion of the ions in a frozen matrix is possible only if a supplemental thermal energy is provided. This shows the fundamental role of the vibrations of the silica network in the diffusion process of the sodium atoms in the glassy phase. On the contrary, at high  $T_{fr}$ ,  $E_a$  is lower than the average activation energy in a regular NS4 sample. This indicates that in the

liquid phase, the diffusive motion of the matrix atoms in “real” NS4 samples hinders the diffusion of the sodium atoms.

Since in all cases the sodium atoms have been placed in the same physical conditions (they have reached the diffusive regime) it is reasonable to think that the abrupt change in the activation energy around 2600 K is due to a change in the inherent structure of the silica matrix. In order to address this point we have decided to study, as a function of  $T_{fr}$ , the available sodium volume. To do that we have virtually surrounded every Si/O atom of the silica matrix by a “hard” (impenetrable) sphere whose radius corresponds to the foot of the Si-Na/O-Na radial pair distribution functions [12] at the corresponding temperature. Indeed from the definition of the radial pair distribution function we know that the sodium atoms can not come closer to their neighbors than this distance. The rest of the volume defines the empty volume that can be used by the Na atoms to diffuse inside the frozen silica matrix. Once this available volume has been defined we have used an invasion algorithm in order to check if it forms an infinite cluster or not. In order to improve the statistics we have used, at a given temperature, for both samples, 2000 configurations. Then we can determine, for each  $T_{fr}$ ,  $P_{percol}$  which is the average probability that the available volume percolates (i.e. forms an infinite cluster) calculated as being the number of percolating configurations divided by the total number of configurations. This percolation probability is represented in Fig.3. We see that, with decreasing  $T_{fr}$ ,  $P_{percol}$  decreases. Though at 4000 K it reaches 60%, it drops to a few percents ( $< 1-3\%$ ) when  $T_{fr}$  approaches and becomes lower than the simulated glass transition temperature that is around 2400 K [12]. This explains the abrupt change in the activation energy of the modifiers observed in Fig.2: at high temperature, when the probability that the available sodium volume percolates is high, the mobile ions diffuse easily in the frozen matrix. On the contrary, at low temperature, when the available volume is finite and limited, the sodium atoms can not diffuse anymore except if they receive an additional thermal energy, which in a sense is similar to increasing the size of the available volume

and hence increasing  $P_{percol}$ . It appears therefore that the intrinsic structure of the silica matrix changes significantly when the temperature is lowered in that the interstitial volume forms an infinite volume or not. In our previous studies we did not detect, as a function of temperature, a clear signature of a change in the structure in the radial pair distribution functions of the matrix atoms [22]. In fact one has to look at the variation of the intertetrahedral angle to find a sign of this change. This is coherent with the fact that an angle, which describes 3-body correlations, is better suited to investigate medium range structural modifications than a 2-body correlation function like the radial pair distribution function. The variation of the intertetrahedral SiOSi angle is represented in Fig.4 as a function of  $T_{fr}$ . One can see that as  $T_{fr}$  decreases, the average intertetrahedral angle increases and opens up down to 2500 K and then stays approximately constant with further decreasing temperature. It seems therefore that, in the absence of vibrations, this slow opening of the network with decreasing temperature is at the origin of the closing of the available sodium volume and therefore hinders the diffusion mechanism of the sodium atoms at low temperature.

#### IV. CONCLUSION

With the use of classical molecular dynamics simulations we have studied the motion of sodium atoms in artificially frozen amorphous silica matrices (the position of the Si and O atoms is fixed). This motion is a forced motion since one needs to inject an additional thermal energy in order for the sodium atoms to reach the diffusive regime. As the freezing temperature of the silica matrix is lowered we observe an abrupt increase of the sodium activation energy around 2500 K which is close to the simulated glass transition temperature of  $\approx 2400$ K. By studying the topology of the space in which the Na atoms can diffuse we have shown that in the glassy phase this space forms finite clusters while in the liquid phase there is a high probability that this space forms an infinite cluster (percolates). This can explain the increase in the activation energy as one goes from

the liquid to the glassy phase. The modification of the topology of the available sodium volume can be due to the variation of the SiOSi intertetrahedral angle which opens up as the freezing temperature is lowered: this opening means that the silica network occupies globally more space and consequently that the available volume for the diffusion of the sodium atoms is diminished. An in depth study of the topology of the silica matrix and in particular the ring size distribution would be of great interest. Indeed one can imagine that the trapping of the sodium atoms in a matrix frozen at low temperature might be due to an increase of the proportion of large rings as the temperature decreases. This would confirm the strong connection between the diffusive characteristics of the modifiers and the structural properties of their host as shown in the present work using an adequate toy model.

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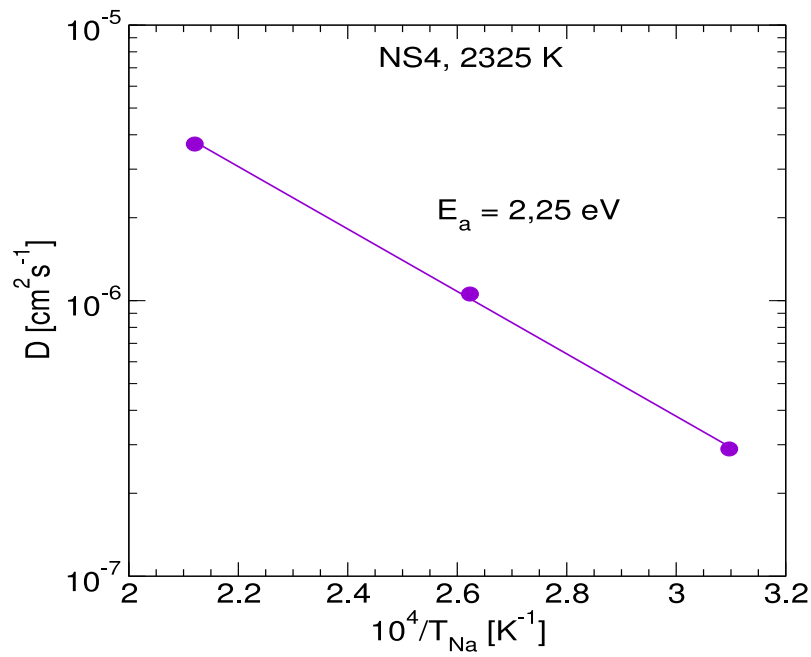


FIG. 1. Plot of the diffusion constant  $D$  as a function of the inverse sodium temperature  $T_{\text{Na}}$  for a NS4 matrix frozen at  $T_{\text{fr}}=2325 \text{ K}$ .

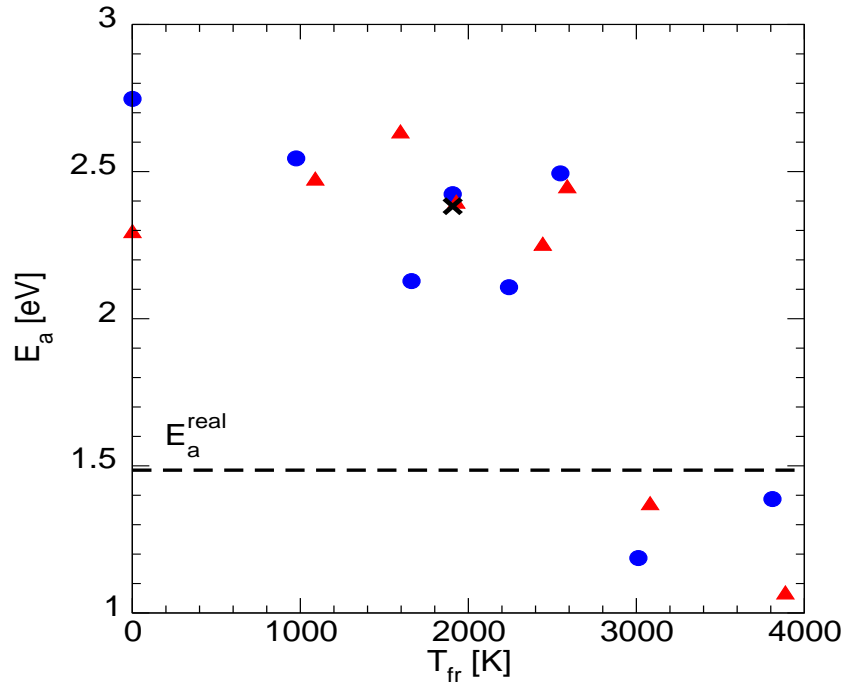


FIG. 2. Plot of the activation energy  $E_a$  of the sodium atoms as a function of  $T_{\text{fr}}$  ( $\bullet$ : sample 1;  $\triangle$ : sample 2;  $\times$ : sample relaxed 14 ns). The horizontal dashed line represents the average activation energy in real NS4 systems (not frozen).

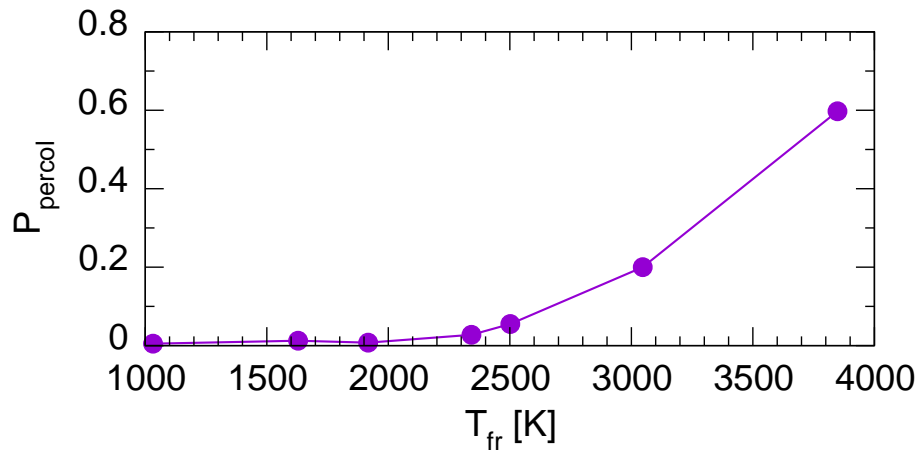


FIG. 3. Plot of the probability of the available sodium volume to percolate (see text for definition) as a function of  $T_{fr}$ .

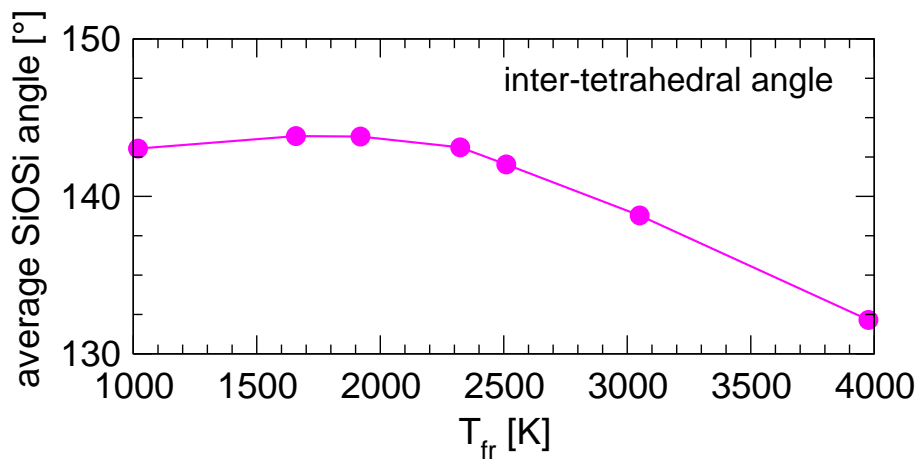


FIG. 4. Plot of the variation of the intertetrahedral angle as a function of  $T_{fr}$ .