



HAL
open science

Sodium diffusion through amorphous silica surfaces: A molecular dynamics study

Michael Rarivomanantsoa, Philippe Jund, Remi Jullien

► **To cite this version:**

Michael Rarivomanantsoa, Philippe Jund, Remi Jullien. Sodium diffusion through amorphous silica surfaces: A molecular dynamics study. *The Journal of Chemical Physics*, 2004, 120 (10), pp.4915-4920. 10.1063/1.1645511 . hal-00122365

HAL Id: hal-00122365

<https://hal.science/hal-00122365>

Submitted on 9 Jun 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Sodium diffusion through amorphous silica surfaces: A molecular dynamics study

Michaël Rarivomanantsoa^a, Philippe Jund^b and Rémi Jullien^c

^a*Dynamique et Thermodynamique des Milieux Complexes - UMR 5569 Hydrosciences- Université Montpellier 2, Place E. Bataillon Case MSE, 34095 Montpellier Cedex 5 France*

^b*Laboratoire de Physicochimie de la Matière Condensée - Université Montpellier 2, Place E. Bataillon Case 03, 34095 Montpellier Cedex 5 France and*

^c*Laboratoire des Verres - Université Montpellier 2, Place E. Bataillon Case 69, 34095 Montpellier Cedex 5 France*

(Dated:)

We have studied the diffusion inside the silica network of sodium atoms initially located outside the surfaces of an amorphous silica film. We have focused our attention on structural and dynamical quantities, and we have found that the local environment of the sodium atoms is close to the local environment of the sodium atoms inside bulk sodo-silicate glasses obtained by quench. This is in agreement with recent experimental results.

I. INTRODUCTION

Many characteristics of materials such as mechanical resistance, adsorption, corrosion or surface diffusion depend on the physico-chemical properties of the surface. Thus, the interactions between the surfaces with their physico-chemical environment are very important, and in particular for amorphous materials which are of great interest for a wide range of industrial and technological applications (optical fibers coating, catalysis, chromatography or microelectronics). Therefore a great number of studies have for example focused on the interactions between the amorphous silica surfaces with water, experimentally¹ and by molecular dynamics simulations^{2,3,4,5,6,7}.

On the other hand, the sodium silicate glasses entail great interest due to their presence in most of the commercial glasses and geological magmas. They are also often used as simple models for a great number of silicate glasses with more complicated composition. The influence of sodium atoms on the amorphous silica network is the subject of numerous experimental studies: Raman spectroscopy^{9,10}, IR^{9,11}, XPS^{12,13} and NMR^{13,14} from which we have informations about neighboring distances, bond angle distributions or concentration of so-called Qⁿ tetrahedra. In order to improve the insight about the sodium silicate glass structure and to obtain a good understanding of the role of the modifying Na⁺ cations, Greaves *et al.* have used new promising investigation techniques like EXAFS and MAS NMR^{15,16}. Despite all these efforts, the structure of sodo-silicate glasses is still a subject of debate. Another means to give informations about this structure is provided by simulations, by either *ab initio*¹⁷ or classical^{18,19,20,21,22,23} molecular dynamics (MD). In the present work, we are using classical MD simulations, but *a contrario* to previous simulations, the sodium atoms are not located before hand inside the amorphous silica sample.

Recent experimental studies of the diffusion of Na atoms initially placed at the surface of amorphous silica, using EXAFS spectroscopy²⁴, showed that the Na atoms diffuse inside the vitreous silica and once inside the amor-

phous silica network, the local environment of the Na atoms is characterized by a Na - O distance $d_{\text{Na-O}} = 2.3$ Å and by a Na - Si distance $d_{\text{Na-Si}} = 3.8$ Å. These values are close to the distances characterizing the local environment of Na atoms in sodium silicate glasses obtained by quench.

In this study we have used classical MD simulations in order to reproduce the diffusion of sodium atoms inside a silica matrix and to check that the local environment of the sodium atoms is close to what is found for quenched sodo-silicate glasses. The sodium atoms have been inserted at the surface of thin amorphous silica films under the form of Na₂O groups in order to respect the charge neutrality.

II. COMPUTATIONAL METHOD

To simulate the interactions between the different atoms, we use a generalized version²⁵ of the so-called BKS potential²⁶ where the functional form of the potential remains unchanged:

$$\phi(|\vec{r}_j - \vec{r}_i|) = \frac{q_i q_j}{|\vec{r}_j - \vec{r}_i|} - A_{ij} \exp(-B_{ij} |\vec{r}_j - \vec{r}_i|) - \frac{C_{ij}}{|\vec{r}_j - \vec{r}_i|^6}.$$

The potential parameters A_{ij} , B_{ij} , C_{ij} , q_i and q_j involving the silicon and oxygen atoms (describing the interactions inside the amorphous silica network) are extracted from van Beest *et al.*²⁶ and remain unchanged (in particular the partial charges $q_{\text{Si}} = 2.4e$ and $q_{\text{O}} = -1.2e$ are not modified). The new parameters, devoted to describe the interactions between the sodium atoms and the silica network are given by Kramer *et al.*²⁵ and are adjusted on *ab initio* calculations of zeolites except the partial charge of the sodium atoms whose value $q_{\text{Na}} = 0.6e$ is chosen in order to respect the system electroneutrality. However, this sodium partial charge does not reproduce the short-range forces and to this purpose, Horbach *et al.*²² have proposed to vary the charge q_{Na} as follows:

$$q_{\text{Na}}(r_{ij}) = \begin{cases} 0.6 \left(1 + \ln \left[C (r_c - r_{ij})^2 + 1 \right] \right) & r_{ij} < r_c \\ 0.6 & r_{ij} \geq r_c \end{cases}$$

where r_{ij} is the distance between the particles i and j . The parameters C and r_c are adjusted to obtain the experimental structure factor of $\text{Na}_2\text{Si}_2\text{O}_5$ (NS2) and their values are included in Ref²². It is important to note that using this method to model the sodium charge, the system electroneutrality is respected for large distances (in fact for distances $r \geq r_c$). Next we assume that the modified BKS potential describes reasonably well the system studied here, for which the sodium atoms are initially located outside the amorphous silica sample. In addition other simulations have shown that this interatomic potential is convenient for various compositions, in particular for NS2, NS3 ($\text{Na}_2\text{Si}_3\text{O}_7$)²² and NS4 ($\text{Na}_2\text{Si}_4\text{O}_9$)²³ and we assume it is adapted to model any concentration of modifying Na^+ cations inside sodo-silicate glasses.

Our aim here is to obtain a sodo-silicate glass by deposition of sodium atoms at the amorphous silica surface, as it was done experimentally²⁴. Using the *modus operandi* described in a previous study²⁸ we have generated Amorphous Silica Films (ASF), each containing two free surfaces perpendicular to the z -direction. These samples have been made by breaking the periodic boundary conditions along the z -direction, normal to the surface, thus creating two free surfaces located at $L/2$ and $-L/2$ with $L = 35.8 \text{ \AA}$. In order to evaluate the Coulomb interactions, we used a two-dimensional technique based on a modified Ewald summation to take into account the loss of periodicity in the z -direction. For further technical details see Ref²⁸. Then, instead of initially positioning the sodium atoms inside the silica matrix, like it was done before^{18,20,21,23,27}, we have deposited 50 Na_2O groups inside two layers located at a distance of 4 \AA of each free surface as depicted in FIG. 1.

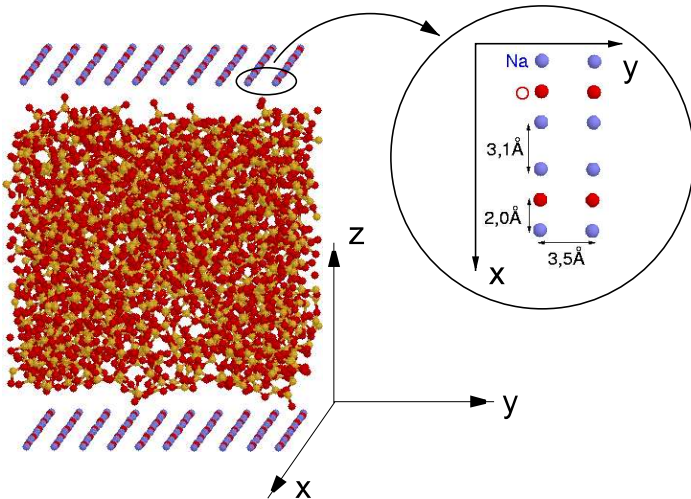


FIG. 1: Initial configuration: two layers containing 50 Na_2O groups each placed at 4 \AA of the two free surfaces of an amorphous silica film. The way the Na_2O groups are arranged within the layers is shown in the blow up.

Within the layers, the Na_2O groups are assumed to be

linear, with $d_{\text{Na-O}} = 2 \text{ \AA}$ ²⁹, and arranged on a pseudoperiodic lattice represented in the zoom of FIG. 1. Hence the system is made of 100 Na_2O groups for 1000 SiO_2 molecules, corresponding to a sodo-silicate glass of composition NS10 ($\text{Na}_2\text{Si}_{10}\text{O}_{21}$) and contains 3300 particles. Since our goal is to study the diffusion of the sodium atoms placed at the amorphous silica surfaces, we fixed the initial temperature of the whole system at 2000 K. Indeed, the simulations of Smith *et al.*²⁰ and Oviedo *et al.*²¹ of sodo-silicate glasses have shown that there is no appreciable sodium diffusion for temperatures below $\approx 1500 \text{ K}$. On the other hand, it is worth noticing that Sunyer *et al.*³⁰ have found a simulated glass transition temperature $T_g \simeq 2400 \text{ K}$ for a NS4 glass. Therefore we thermalized the sodium layers at 2000 K and placed them at the ASF surfaces, also thermalized at 2000 K.

We have used repulsive 'walls' at $z = -30 \text{ \AA}$ and $z = +30 \text{ \AA}$ in order to avoid that some Na_2O groups evaporate along the z direction, where the periodic boundary conditions are no more fulfilled. The energy of the repulsive 'walls' has an exponential shape, $E = E_0 \exp[-(z_w - z)/\sigma]$ where z_w is the wall position, $\sigma = 0.1 \text{ \AA}$ the distance for which the repulsion energy is diminished by a factor e and $E_0 = 10 \text{ eV}$ the repulsion energy at the plane $z = z_w$. The value of 30 \AA for z_w was chosen in order to place the repulsive walls at a reasonable distance from the Na_2O layers and not too far from the ASF surfaces.

We have then performed classical MD simulations, with a timestep $\Delta t = 0.7 \text{ fs}$, using ten statistically independent samples. Since the interactions between the surfaces and the Na_2O layers are relatively weak, some Na_2O groups may evaporate just before being reflected toward the thin films by the repulsive walls. During this time frame, the system temperature increases up to a temperature of approximately 2800 K. As described by Athanasopoulos *et al.*³¹ this temperature rise is likely due to the approach of the adatoms to the surface of the substrate, dropping in the potential well of the substrate atoms, thus increasing their kinetic energy. This kinetic energy is then transmitted to the substrate with the adsorption. Contrarily to Athanasopoulos *et al.*³¹ and Webb *et al.*³² we have not dissipated this energy excess with a thermal sink region, in fact we have not controlled the temperature at all. Using this device we are able to perform MD simulations of the diffusion of the sodium atoms deposited *via* Na_2O groups at the ASF surfaces. In the following section, we will present the structural and dynamical characteristics of the sodo-silicate film (SSF) obtained in this way.

III. RESULTS

The observation of the sodium diffusion in the silica network is an important goal of this molecular dynamics simulation. This can be carried out by analyzing the behavior of the density profiles along the normal direc-

tion to the surface (the z -direction). The density profiles represent the mass densities within slices, of thickness $\Delta z = 0.224 \text{ \AA}$, parallel to the surfaces²⁸. The time evolution of the sodium density profile is represented in FIG. 2(a) and FIG. 2(b) and the time evolution of the total density profile in FIG. 2(c) and FIG. 2(d).

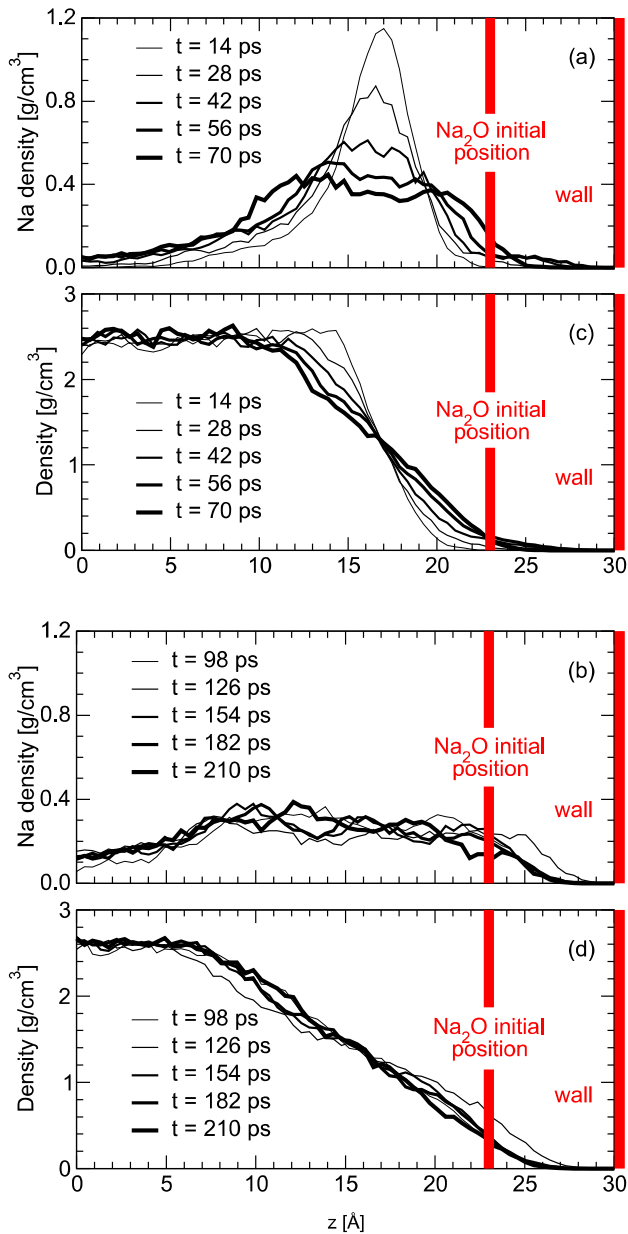


FIG. 2: Time evolution of the Sodium (a) and (b) and total (c) and (d) density profile.

The sodium atoms enter inside the silica network in the time range 14 - 70 ps (FIG. 2(a)) and during this time interval the sodium profile exhibits a diffusion front. After 42 ps, the sodium atoms are observed in the entire system illustrating that they have diffused within the whole ASF, as observed experimentally²⁴. This result contrasts

with that of MD simulations of the diffusion of platinum (electrically neutral)³¹ and potassium^{36,37,39} but is similar to that of the diffusion of lithium^{36,37,39} at the surface of amorphous silica. Moreover, the sodium profiles (FIG. 2(a) and (b)) show outward rearrangement at the surface as already pointed out by Zirl *et al.*³³ for glassy sodium aluminosilicate surfaces. This agrees with ion scattering spectroscopy³⁴ and simulations of sodium silicate glasses³⁵ in which high concentrations of sodium ions are found at the surface. For larger times, $t \geq 98$ ps represented in FIG. 2(b), the sodium density seems to stabilize around a mean value of 0.3 g.cm^{-3} which corresponds to ~ 2 Na atoms per slice ($\Delta z = 0.224 \text{ \AA}$).

The surface of the system is identified as being the large linear region in which the total density profile decreases. For the short times (FIG. 2(c)) the surface is located approximately in the range 15 - 20 Å and for larger times ($t \geq 98$ ps, FIG. 2(d)), the surface lies in the range 7 - 25 Å. Hence, the introduction of the sodium atoms in the ASF is likely to increase the surface thickness of the system. On the other hand, as observed for the adsorption of platinum atoms on the surface of amorphous silica³¹, the surface position does not seem to vary with time. We have also calculated the silicon and oxygen density profiles, but since they behave like the total density profile, they are not represented here. The non bridging oxygen (NBO) density profile is not represented in FIG. 2 as well since it is close to the Na density profile.

In the time range 98 - 210 ps, the total and sodium density profiles do not evolve with time. In particular, in the region $z \lesssim 5 \text{ \AA}$ (FIG. 2(d)), the total density value remains fluctuating around a mean value of 2.6 g.cm^{-3} and the atom composition is approximately of 370 Si, 760 O and 40 Na which is usually written $\text{Na}_2\text{O}(\text{SiO}_2)_{18.5}$ or 'NS18.5' (it should be noticed that the above mentioned density is significantly larger than the one expected for a "real" NS18.5 glass ($\approx 2.3 \text{ g.cm}^{-3}$)). Therefore it seems reasonable to consider that the system is in a *quasi permanent* regime after 210 ps and the forthcoming quantities, structural and dynamical, are calculated for the following 70 ps. It is worth remembering that all the quantities are determined for a system containing 3300 particles and averaged over 10 statistically independent samples.

As usual when studying the structural and dynamical characteristics of free surfaces, the system is divided into several subsystems: here six slices of equal thickness 10 \AA . But in order to increase the statistics, the contributions to the physical quantities of the negative and positive slices are averaged. Hence, the system is actually subdivided into three parts, named respectively from the center to the surface, interior, intermediate and external region.

In order to improve the characterization of the local environment of the atoms, we have calculated the radial pair distribution functions for all the pairs $(i, j) \in [\text{Si}, \text{Na}, \text{O}]^2$ within the three subsystems defined previously. The Na - Na, Na - O and Si - Na pair distribu-

tion functions are represented in FIG. 3(a), 3(b) and 3(c) respectively and represent the local environment of the sodium atoms for $t \geq 210$ ps.

At the surfaces of the system the distances are $d_{\text{Na-O}} \simeq 2.2$ Å, $d_{\text{Si-Na}} \simeq 3.5$ Å and, due to a lack of statistics, the Na - Na distance is included in the interval $3.3 \lesssim d_{\text{Na-Na}} \lesssim 3.9$ Å. While slightly smaller, these distances are close to the experimental values found by Mazzara *et al.* ($d_{\text{Na-O}} = 2.3$ Å and $d_{\text{Si-Na}} = 3.8$ Å)²⁴. Moreover, the values found in the present work agree with the distances, calculated by MD, corresponding to the sodium environment in sodo-silicate glasses, of several sodium compositions (NS2^{15,20}, NS3²² and NS4¹⁷), obtained by quench. Therefore, as observed experimentally by Mazzara *et al.*²⁴, once within the amorphous silica network, the sodium atoms have the same local environment as in the sodo-silicate glass obtained by quench. This fact is confirmed by the distributions of the $\overline{\text{NaONa}}$ and $\overline{\text{SiONa}}$ bond angles (not shown) which are close to those determined in quenched sodo-silicate glasses^{21,30}. In particular, the most probable angles are 90° for $\overline{\text{NaONa}}$ and 105° for $\overline{\text{SiONa}}$, in agreement with the values found by Oviedo *et al.*²¹ and Sunyer *et al.*³⁰.

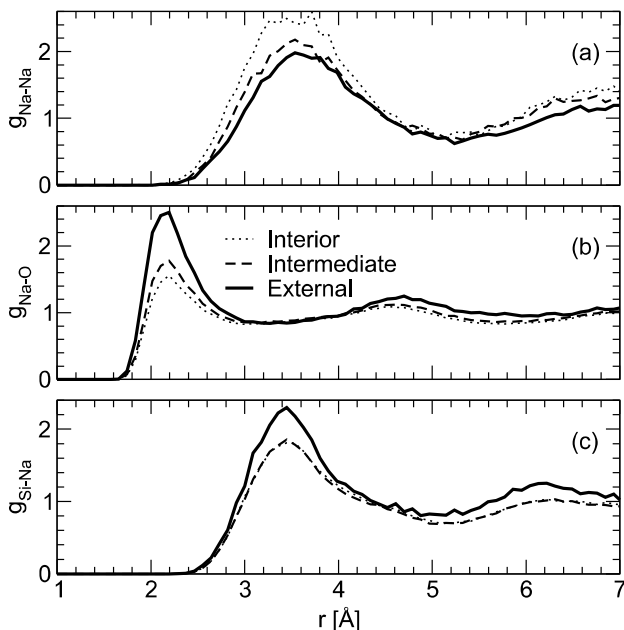


FIG. 3: (a) Na - Na, (b) Na - O and (c) Si - Na radial pair distribution functions for the (\cdots) interior, ($- -$) intermediate and ($-$) external region.

The intermolecular distances corresponding to the amorphous silica network structure are $d_{\text{Si-Si}} \simeq 3.1$ Å, $d_{\text{Si-O}} \simeq 1.6$ Å and $d_{\text{O-O}} \simeq 2.6$ Å. On the other hand, the most probable values exhibited by the distributions of the $\overline{\text{OSiO}}$ and $\overline{\text{SiOSi}}$ bond angles (not shown) are re-

spectively $\sim 109^\circ$ and $\sim 145^\circ$. These distances and bond angle distributions are very similar to those found experimentally or by MD simulations in bulk amorphous silica. The shoulder exhibited at 2.5 Å by the distribution $g_{\text{Si-Si}}$ at amorphous silica surfaces²⁸ and interpreted as the signature of the twofold rings is not present in the SSF. The absence of the shoulders at 80 and 100° depicted at ASF surfaces^{2,28,38} by the $\overline{\text{OSiO}}$ and $\overline{\text{SiOSi}}$ bond angle distributions confirms that the small sized rings have disappeared as suggested by the radial pair distributions. This result is expected for R_2O (with R belonging to the column I) adsorption on glassy silicate surfaces and observed *via* MD simulations for $\text{R} = \text{H}, \text{Li}, \text{Na}$ and K ^{2,3,6,35,36,37,39}. Note that this also occurs for platinum adsorption on sodium aluminosilicate surfaces^{31,32} and for H_2 adsorption on amorphous silica surfaces⁸. The small rings like two and threefold rings are known to be some of the most reactive sites on the surfaces of silicate glasses since they include strained siloxane bonds that react with water or other adsorbates^{40,41}.

Since the sodium introduction weakens the amorphous silica network, one important question is to measure the proportion of non bridging oxygens (NBOs). To this purpose, oxygen coordination with silicon was calculated. As expected, there is an important proportion of defective oxygens due to the presence of modifying cations Na^+ (8.9 % for the SSF to be compared with 1 % for the ASF²⁸), illustrated by the similarities between the NBO and Na density profiles mentioned previously. Moreover, the NBO concentration is coherent with the concentration of 11 % of NBO calculated by MD simulations in a NS9 system²⁷. The latter concentration is higher than the one found in this study because of the greater proportion of Na atoms in NS9 compared to 100 Na_2O for 1000 SiO_2 in the present SSF. At the surface ($z \geq 20$ Å), the BOs disappear and correlatively, the defective oxygens become preponderant, as observed for amorphous silica (36.2 % of NBOs at the SSF surfaces, 15 % at the ASF surfaces²⁸ and 10 % at the nanoporous silica surfaces⁴²). When analyzing the silicon coordination with oxygen, we can state that the silicon atoms remain coordinated in a tetrahedral way, revealing that the sodium introduction does not modify the silicon environment. The modifications created by the Na^+ cations are not able to break the SiO_4 tetrahedra which are very stable in the amorphous silica network. This agrees with the usual models for the sodo-silicate glasses, *ie* the CRN model of Zachariassen⁴³ and the MRN model of Greaves¹⁶.

One possible way to analyze more precisely the silicon environment consists in calculating the Q^n tetrahedra proportion. A Q^n structure is a SiO_4 tetrahedra which contains n BOs. The Q^n proportion is often determined by NMR experiments^{44,45}, XPS^{13,46} or by molecular dynamics simulations²⁰, in order to describe the local environment around the silicon atoms. In the SSF, the Q^2 and Q^3 concentrations (6.8 % and 25.4 % respectively) are weak compared to those determined for NS2, NS3 and NS4 glasses. This result is coherent since the NS2,

NS3 and NS4 glasses contain more Na^+ cations than the SSF studied in this work. At the surface, the Q^3 proportion is 45.9 % which is comparable to the proportions obtained by MD (using the BKS potential) in NS2, NS3 and NS4 glasses and to the experimental proportions in NS3^{13,14} and NS4^{45,46} glasses. Moreover, it is worth noting that some Q^1 appear at the surface. In fact, these structural entities do not allow to create a network but it is conceivable to find those defects forming 'dead ends' at the surface.

A direct method to confirm the previous assumption concerning the disappearance of small rings consists in analyzing directly the ring size distribution. A ring is a particularly interesting structure because it can be detected using infrared and Raman spectroscopy. In particular the highly strained twofold rings result in infrared-active stretching modes^{41,47} at 888 and 908 cm^{-1} . In order to determine the probability P_n for a given Si atom, whose coordinate along the normal direction to the surface is in one of the three regions, to be a member of a n -fold ring we have used the algorithm described in⁴⁸. A ring is defined as the shortest path between two oxygen atoms, first neighbors of a given silicon atom and made by Si - O bonds. The ring size is given by the number of silicon atoms contained in the ring.

The probability P_n is reported in FIG. 4(a) for $n = 2, \dots, 9$ and for the three different regions. For comparison, we have also reported P_n determined at the ASF surface and interior²⁸. In order to improve the medium range order characterization, we have investigated the orientation of the rings computing $\langle \cos^2 \theta \rangle$ for a given ring size, within the three regions of the system, where θ is the angle between the normal of the surface and the normal of the ring²⁸. The results are reported in FIG. 4(b) for the three regions and for $n = 2, \dots, 9$ together with the results obtained for the ASF surface (dashed line) and interior (dotted line).

For the three regions, the distributions of the sodo-silicate film (FIG. 4(a)) are closer to the ASF interior than to the ASF surface distributions. Particularly, the probability of a silicon atom to belong to a small sized ring (2, 3 or 4-fold ring) is weak. This confirms the previous conclusion about the disappearance of the small strained sized rings which react with the sodium ions during their adsorption at the amorphous silica surface. As observed for the ring size distributions, the orientation of the rings (FIG. 4(b)), in the three regions of the sodo-silicate film is similar to that obtained in the interior of the pure silica films²⁸ which means that even at the surface the rings have an isotropic orientation with respect to the surface. This is related to the disappearance of the small sized rings at the surface. Nevertheless, it is worth noting that in the external region the probability of a Si atom to belong to a 5-fold ring is greater than the probability to belong to a 6-fold ring (FIG. 4(a)) as observed at the ASF surfaces²⁸. In a sense, the 5-fold

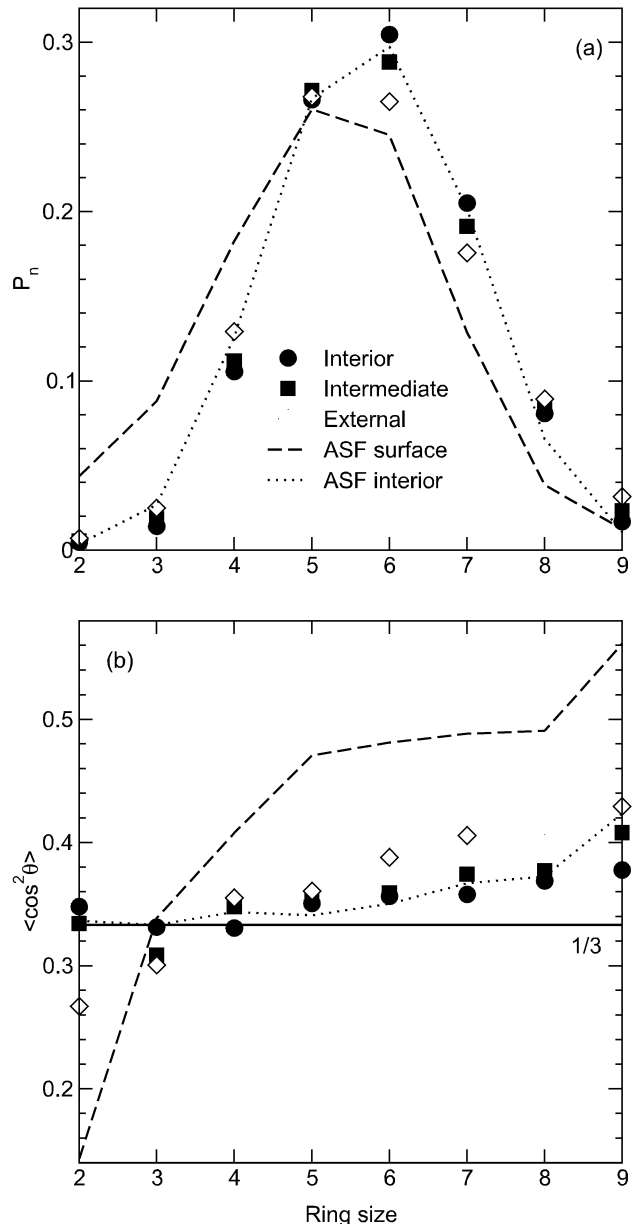


FIG. 4: Ring probabilities (a) and mean orientations (b) as a function of their size for the \bullet interior, \blacksquare intermediate and \diamond external regions. The same quantities calculated for the ASF surface (---) and ASF interior (···) regions²⁸.

rings are not affected by the sodium adsorption in contrast to the small sized rings which disappear with the introduction of the sodium atoms. Also in the external region, the 2 and 3-fold rings (that are still present) are oriented perpendicularly to the surfaces (FIG. 4(b)) as observed at the ASF surfaces^{28,49}.

We have also analyzed the dynamics of the Na^+ cations and compared the results obtained in the present 'NS10' system with those obtained in a NS4 glass. To this purpose, the mean square displacements (MSD) $\langle r^2(t) \rangle =$

$\langle |r_i(t) - r_i(0)|^2 \rangle$ have been calculated for each species composing the SSF. FIG. 5 represents the MSD for the BO, NBO, Na and Si atoms within the time frame 0.7 fs - 70 ps after the first 210 ps together with the MSD calculated by Sunyer *et al.*³⁰ for NS4 ($t \geq 1.5$ ps).

At ~ 2800 K, the MSD of each species exhibits three regimes. For the short times, we observe the so-called ballistic regime where $\langle r^2(t) \rangle \sim t^2$. In this regime, the differences between the species are not really important. For the long times, we recognize the so-called diffusive regime in which $\langle r^2(t) \rangle \sim t$ and in which the Si atoms are the ones that diffuse the less. Similarly to the pure ASF²⁸, the NBOs diffuse more than the BOs. The origin of this feature lies in the fact that the NBOs form only one covalent bond with the Si atoms instead of two for the BOs. The Na atoms diffuse much more (one order of magnitude) than the other species. Between the two former regimes, the MSD exhibits the so-called β -relaxation, clearly observable for the oxygen and silicon atoms. The phenomenon is not as clear for the sodium atoms, but between $\sim 10^{-1}$ and ~ 1 ps, the Na MSD does not behave like t (sub-diffusion) and it is reasonable to consider that the sodium atoms are submitted to the so-called cage effect characterizing the β -relaxation.

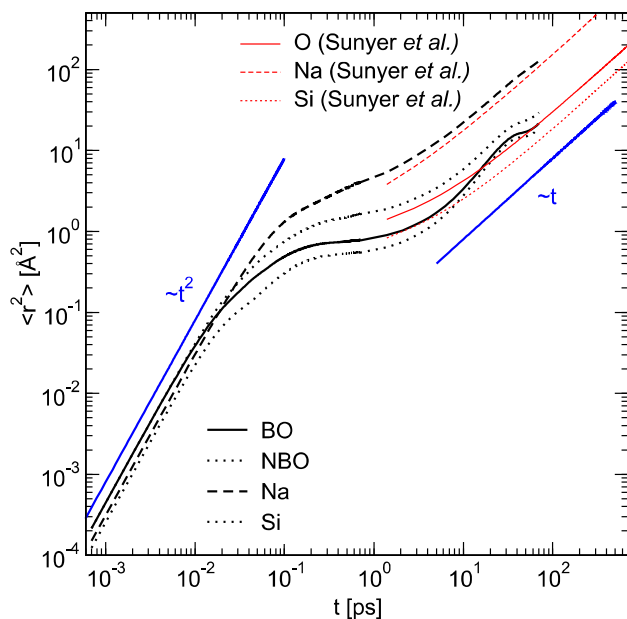


FIG. 5: Mean square displacements for the BO (—), NBO (···), Na (---) and Si (- · - ·) at ~ 2800 K. The thin lines represent the results obtained by Sunyer *et al.*³⁰ for a NS4 system at 3000 K.

These results are consistent with the observations made for different sodo-silicate systems^{20,21,22} for temperatures close to 2800 K. More precisely the mean square displacements in the SSF are close to those cal-

culated by Sunyer *et al.*³⁰ for a quenched NS4 glass at 3000 K. This is somewhat surprising since in a NS10 system, one expects smaller diffusion constants for all the species compared to the diffusion constants obtained in a NS4 system. The modus operandi of the present system (diffusion of the cations through the surface) could explain this observation.

IV. CONCLUSION

This work was motivated by a recent experimental study²⁴ of the local environment of diffusing sodium atoms deposited at the surfaces of thin amorphous silica films. We have reproduced numerically this experiment by classical molecular dynamics simulations after putting Na₂O groups at the surfaces of amorphous silica thin films.

We have quantitatively analyzed the temporal evolution of the sodium and total densities and we have checked that the sodium atoms are diffusing inside the amorphous silica network. After a given time, the density profiles are no longer evolving, and we have calculated the structure of the resulting sodo-silicate glass.

Our attention has been focused on the local environment of the sodium atoms. Once inside the thin film, they are preferentially bound to NBOs as predicted by the MRN model of Greaves¹⁶. The distances and bond angle distributions show that the sodium atoms have a local environment corresponding to the local environment of the sodium atoms in sodo-silicate glasses made by quench, as observed by Mazzara *et al.*²⁴. Moreover, the distances $d_{\text{Na-O}} = 2.2$ Å and $d_{\text{Si-Na}} \simeq 3.5$ Å are close to the experimental values.

Concerning the amorphous silica network, we have observed *via* the corresponding distance and bond angle distributions that its short range order is not modified by the introduction of the Na⁺ cations. We have also calculated the ring size distributions and the orientation of the rings which show that the introduction of the sodium atoms has an influence on the silica network but on larger scales compared to those corresponding to the local environment. The ring size distributions and the orientations are close to the results obtained in the bulk of thin amorphous silica films. This is due to the decrease of the proportion of small rings (particularly two and threefold) which interact with the Na₂O groups since they are known to be highly reactive sites for the adsorption of species on amorphous silica surfaces.

Finally concerning the dynamics of the different atoms we find results similar to those obtained in a NS4 glass at a slightly higher temperature.

Acknowledgments Calculations have been performed partly at the “Centre Informatique National de l’Enseignement Supérieur” in Montpellier.

-
- ¹ D. W. Sindorf and G. E. Maciel, *J. Am. Chem. Soc.* **105**, 1487 (1983); D. M. Krol and J. G. van Lierop, *J. Non-Cryst. Solids* **63**, 131 (1984); D. M. Krol and J. G. van Lierop, *J. Non-Cryst. Solids* **68**, 163 (1984); C. J. Brinker, E. P. Roth, G. W. Scherer and D. R. Tallant, *J. Non-Cryst. Solids* **71**, 171 (1985); I.-S. Chuang, D. R. Kinney, C. E. Bronnimann, R. C. Zeigler and G. E. Maciel, *J. Phys. Chem.* **96**, 4027 (1992); L. Dubois and B. R. Zegarski, *J. Phys. Chem.* **97**, 1665 (1993); D. R. Kinney, I.-S. Chuang and G. E. Maciel, *J. Am. Chem. Soc.* **115**, 6786 (1993); I.-S. Chuang, D. R. Kinney and G. E. Maciel, *J. Am. Chem. Soc.* **115**, 8696 (1993); A. Grabbe, T. A. Michalske and W. L. Smith, *J. Chem. Phys.* **99**, 4648 (1995)
- ² S. H. Garofalini, *J. Chem. Phys.* **78**, 2069 (1983); S. M. Levine and S. H. Garofalini, *J. Chem. Phys.* **86** 2997 (1987)
- ³ B. P. Feuston and S. H. Garofalini, *J. App. Phys.* **68**, 4830 (1990)
- ⁴ V. A. Bakaev and W. A. Steele, *J. Chem. Phys.* **111**, 9803 (1999)
- ⁵ B. P. Feuston and S. H. Garofalini, *J. Chem. Phys.* **91**, 564 (1989)
- ⁶ S. H. Garofalini, *J. Non-Cryst. Solids* **120**, 1 (1990)
- ⁷ M. M. Branda and N. J. Castellani, *Surf. Sci.* **393**, 171 (1997)
- ⁸ N. Lopez, M. Vitiello, F. Illas and G. Pacchioni, *J. Non-Cryst. Solids* **271**, 56 (2000)
- ⁹ S. A. Brawer and W. B. White, *J. Chem. Phys.* **68**, 242 (1975)
- ¹⁰ P. F. Mc Millan and G. H. Wolf, *Rev. Mineral.* **32**, 247 (1995); N. Umekasi, N. Iwamoto, M. Tatsumisago and T. Minami, *J. Non-Cryst. Solids* **106**, 77 (1988)
- ¹¹ J. Wong and C. A. Angell, *Glass Structure by Spectroscopy*, M. Dekker, New York (1976)
- ¹² R. Bruckner, H. U. Chun, H. Goretzki and M. Sammet, *J. Non-Cryst. Solids* **42**, 49 (1980)
- ¹³ D. Sprenger, H. Bach, W. Meisel and P. Gütlich, *J. Non-Cryst. Solids* **159**, 187 (1993)
- ¹⁴ A. H. Silver and P. J. Bray, *J. Chem. Phys.* **29**, 984 (1958); J. F. Stebbins, *Rev. Mineral.* **18**, 405 (1988)
- ¹⁵ G. J. Baker, G. N. Greaves, M. Surman and M. Oversthuizen, *Nucl. Instr. and Meth. in Phys. Res. B* **97**, 375 (1995)
- ¹⁶ G. N. Greaves, *J. Non-Cryst. Solids* **71**, 203 (1985)
- ¹⁷ S. Ispas, M. Benoit, P. Jund and R. Jullien, *Phys. Rev. B* **64**, 214206 (2001); T. Uchino and T. Yoko, *J. Phys. Chem. B* **102**, 8372 (1998)
- ¹⁸ T. F. Soules, *J. Chem. Phys.* **71**, 4570 (1979)
- ¹⁹ B. Vessal, M. Leslie and C. R. A. Catlow, *Mol. Phys.* **3**, 123 (1989); B. Vessal, A. Amini, D. Fincham and C. R. A. Catlow, *Philos. Mag. B* **60**, 753 (1989); B. Vessal, G. N. Greaves, P. T. Marten, A. V. Chadwick, R. Mole and S. Houde-Walter, *Nature* **356**, 504 (1992)
- ²⁰ W. Smith, G. N. Greaves and M. J. Gillan, *J. Chem. Phys.* **103**, 3091 (1995)
- ²¹ J. Oviedo and J. F. Sanz, *Phys. Rev. B* **58**, 9047 (1998)
- ²² J. Horbach, W. Kob and K. Binder, *Philos. Mag. B* **79**, 1981 (1999)
- ²³ P. Jund, W. Kob and R. Jullien, *Phys. Rev. B* **64**, 134303 (2001)
- ²⁴ C. Mazzara, J. Jupille, A.-M. Flank, and P. Lagarde, *J. Phys. Chem. B* **104**, 3438 (2000)
- ²⁵ G. J. Kramer, A. J. M. de Man and R. A. van Santen, *J. Am. Chem. Soc.* **64**, 6435 (1991)
- ²⁶ B. W. H. van Beest, G. J. Kramer and R. A. van Santen, *Phys. Rev. Lett.* **64**, 1955 (1990)
- ²⁷ C. Huang and A. N. Cormack, *J. Chem. Phys.* **93**, 8180 (1990)
- ²⁸ M. Rarivomanantsoa, P. Jund and R. Jullien, *J. Phys.: Condens. Matter* **13**, 6707 (2001)
- ²⁹ S. D. Elliott and R. Ahlirchs, *J. Chem. Phys.* **109**, 4267 (1998)
- ³⁰ E. Sunyer, P. Jund and R. Jullien, unpublished.
- ³¹ D. C. Athanasopoulos and S. H. Garofalini, *J. Chem. Phys.* **97**, 3775 (1992); D. C. Athanasopoulos and S. H. Garofalini, *Surf. Sci.* **273**, 129 (1992)
- ³² E. B. Webb and S. H. Garofalini, *Surf. Sci.* **319**, 381 (1994)
- ³³ D. M. Zirl and S. H. Garofalini, *J. Am. Ceram. Soc.* **75**, 2353 (1992)
- ³⁴ J. Kelso, C. G. Pantano and S. H. Garofalini, *Surf. Sci.* **134**, L543 (1983)
- ³⁵ S. H. Garofalini and S. M. Levine, *J. Am. Ceram. Soc.* **68**, 376 (1985)
- ³⁶ S. H. Garofalini and D. M. Zirl, *J. Vac. Sci. Technol. A* **6**, 975 (1988)
- ³⁷ D. M. Zirl and S. H. Garofalini, *Phys. Chem. Glasses* **30**, 155 (1989)
- ³⁸ A. Roder, W. Kob and K. Binder, *J. Chem. Phys.* **114**, 7602 (2001)
- ³⁹ D. M. Zirl and S. H. Garofalini, *J. Non-Cryst. Solids* **122**, 111 (1990)
- ⁴⁰ C. J. Brinker, R. J. Kirkpatrick, D. R. Tallant and B. C. Bunker, *J. Non-Cryst. Solids* **99**, 418 (1988); B. C. Bunker, D. M. Haaland, T. A. Michalske and W. L. Smith, *Surf. Sci.* **222**, 95 (1989); J. Tossell, *J. Non-Cryst. Solids* **120**, 13 (1990)
- ⁴¹ B. C. Bunker, D. M. Haaland, K. J. Ward, T. A. Michalske, W. L. Smith, J. S. Binkley, C. F. Melius and C. A. Balfe, *Surf. Sci.* **210**, 406 (1989)
- ⁴² J. L. V. Beckers and S. W. de Leeuw, *J. Non-Cryst. Solids* **261**, 87 (2000)
- ⁴³ W. H. Zachariasen, *J. Am. Chem. Soc.* **54**, 3841 (1932)
- ⁴⁴ I.-S. Chuang and G. E. Maciel, *J. Am. Chem. Soc.* **118**, 401 (1996)
- ⁴⁵ H. Maekawa, T. Maekawa, K. Kawamura and T. Yokokawa, *J. Non-Cryst. Solids* **127**, 53 (1991)
- ⁴⁶ J. F. Emerson, P. E. Stallworth and P. J. Bray, *J. Non-Cryst. Solids* **113**, 253 (1989)
- ⁴⁷ B. A. Morrow and A. Devi, *Trans. Faraday Soc.* **68**, 403 (1972); B. A. Morrow and I. A. Cody, *J. Phys. Chem.* **80**, 1995 (1976)
- ⁴⁸ J. Horbach and W. Kob, *Phys. Rev. B* **60**, 3169 (1999)
- ⁴⁹ D. Ceresoli, M. Bernasconi, S. Iarlori, M. Parinello and E. Tosatti, *Phys. Rev. Lett.* **84**, 3887 (2000)