



Is ergodicity in an oxide glass ionic conductor a matter of time?

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HIGHLIGHTS

- Ergodicity lost: a critical point for the proper use of statistical mechanics.
- Ergodicity lost: the observation time and the relationship with dynamic diversity.
- Graphical representation to search for the broken ergodicity in an oxide glass.

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ABSTRACT

From the results of molecular dynamic simulations of lithium metasilicate glass – at temperatures above and below their transition temperature (T_g) – we propose a simple graphical representation to search for the broken ergodicity in an ionic oxide glass. Knowing when ergodicity is lost is critical for the proper use of statistical mechanics as a tool for measuring dynamical and structural properties through molecular dynamic simulation. This work shows how an abrupt qualitative transformation occurs in the way the system explores its possible states when it goes down below the glass transition temperature range. We revise the broken ergodicity phenomena through its relationship with the observation time and the dynamic diversity of their atoms.

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1. Introduction

When referring to glassy systems we need to consider that they belong to a more general scientific classification: “they are complex systems”. Although this material has been known for thousands of years, scientific researchers are still looking for an accurate definition of glass. A glass system can be considered as a frozen disordered state, originated from a high temperature thermodynamic favorable state, arrested kinetically. Monasson says that the system that reaches a quasi-breaking of ergodicity coincides with the appearance of non vanishing density fluctuations; thus, the system becoming partially frozen in metastable states with very large relaxation times when its temperature is a little higher than its T_g [1].

Another much more general definition of glassy systems has been proposed: “a solid having a non-crystalline structure, which continuously converts to a liquid upon heating” [2]. We can infer some ideas about its structure but this definition does not give much information about the dynamical features of its components. Therefore, a universal law for a total description of their properties (structural and dynamical) has not been achieved yet in this field.

One relevant question of glassy systems is related to the loss of ergodicity when a super-cooled liquid passes through the glass transition temperature to become a glass. Since statistical physics is built on the ergodic hypothesis, this is a relevant issue to understand before analyzing any simulation data set.

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One of the most prevalent, and often unstated, assumptions in statistical mechanics is that ergodicity asserts the equivalence of time and ensemble averages of the thermodynamic properties of a system. Ergodicity implies that, given enough time, a system will explore all allowable points of phase space. The term “broken ergodicity”, introduced by Bantilan and Palmerin 1981, denotes the loss of ergodicity that is common in many systems such as spin and structural glasses [3].

If we revise some related theoretical aspects, we find that close to the end of the XX century, D.L. Stein said that non-ergodicity calls for a new paradigm that must go beyond equilibrium statistical mechanics [4]. In order to understand this statement, it is convenient to go some steps backwards in time and review some basic concepts on statistical mechanics, as O. Lombardi and M. Labarca have suggested in their works [5,6]. It is common to find in the literature that glass are systems that lose their ergodicity and are *trapped* inside a region of their state space for a long time and this is why it is useful to understand some dynamical and thermal properties. In the Mode Coupling Theory scenario when a liquid is cooled, it breaks its ergodicity. Then, their molecules are kinetically arrested and are prevented from trying different states, even though those states are thermodynamically available. That is explained through the formation of “cages” – spatial zones limited by their nearest neighbors – inside of which the particles have to spend increasingly more time until they find a way to move around neighbors and rearrange their positions [7,8].

If we approach the essential microscopic dynamic of the phase transition in statistical terms, the dynamic changes suggest that phase transitions can be understood through unexpected qualitative transformations in the way a system explores its achievable states [9]. Some works show that the formation of glass is governed by kinetics rather than thermodynamics; therefore, glass transition is based on the slowing down of its kinetics [10–12]. Also, it is well known that the glass transition temperature varies with the system’s thermal history, *i.e.* different cooling rates involve changes on the T_g which tell us that the structure keeps some information about the way in which it reached its frozen state.

In the present work, we show in a simple graphical way (through a paradigmatic ionic conductor oxide glass as is lithium metasilicate) that there is a change into system’s dynamical features when it passes through the glass transition. But the loss of its ergodicity is a matter of time scale or of how we explore the system.

In a very recent paper, a different kind of labeling of the system’s particles has been done. In this work, the authors consider the relationship between the system in terms of its particles’ distinguishability and their relationship to broken ergodicity. They emphasize that the distinguishability of the particles (the probability of a particle to be identified among the other particles of the system) depends on the observation time at a fixed temperature: “in the limit of zero observational time, the particles of any classical system are fully distinguishable. For any positive temperature, as the observation time increases, the distinguishability of the particles always decreases monotonically” [13]. These authors point out that the issue of ergodicity is a question of time scale. Additionally, they note that the loss of ergodicity is accompanied by a concurrent loss of configurational entropy. In another recent work, about granular material, they pay attention to the necessity to understand the time scale where the assumption of the ergodic hypothesis can be done. Additionally, they distinguish between global and local ergodicity and use this approach to test this assumption by verifying its consequences. The theoretical approach computes what the occupation of the different states should be if ergodicity holds and then verifies if the real system is indeed equally likely to be found in all of its states. In a few words, it checks if the assumption of the ergodic approach has consequences in the property of the system which they are computing [14].

In the present work, from our molecular dynamic simulation results, we analyze the experimental data looking for evidence to support the fact that the loss of ergodicity in glassy systems depends on the time scale and moreover, on the way the system is considered. We show that it is necessary to understand the lithium metasilicate as a combination of two different “dynamic systems” contained in a homogeneous phase of matter. This is not a new idea. In fact, during the last century, it has been proposed that this kind of systems (with very mobile ions in a glassy matrix) should be understood as a *liquid phase* flowing through a solid one [15–17]. Therefore, in our proposal, we regard the lithium metasilicate glass systems as two different dynamic phases, one is made up of lithium cations and the other by a more freezing dynamic phase where the lithium cations move; *i.e.* a potential landscape given by the glassy silicate matrix. The main difference, compared to different previous proposals, is that some features of the lithium dynamics are controlled by the matrix dynamic features when the temperature is lower than its T_g . Finally, we show an example where the glassy system of this work is trapped in single minimum of energy and, because of that, when we make a very short time dynamic analysis of the mobile ions, it shows distinct features which vanishes soon as the system can pass over an energy barrier in its landscape.

2. Methodology

A system formed by 3456 particles (1152 Li, 570 Si and 1728 O) has been used. A procedure has been applied to equilibrate the system. It allows us to reach the same density as the experimental data for any temperature, taking into account the experimental error. The three-dimensional system was built by the pair potential of Gilbert–Ida type [18] including the r^{-6} term:

$$U_{ij}(r) = \frac{q_i q_j e^2}{4\pi \epsilon_0 r} - \frac{c_i c_j}{r^6} + f_0(b_i + b_j) \exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right). \quad (1)$$

The first term in Eq. (1) is the Coulomb interaction with the effective charge numbers q_i ; the second term is a dispersive interaction and it presents those involving only oxygen ions; and the last term is a Born–Meyer type potential that takes

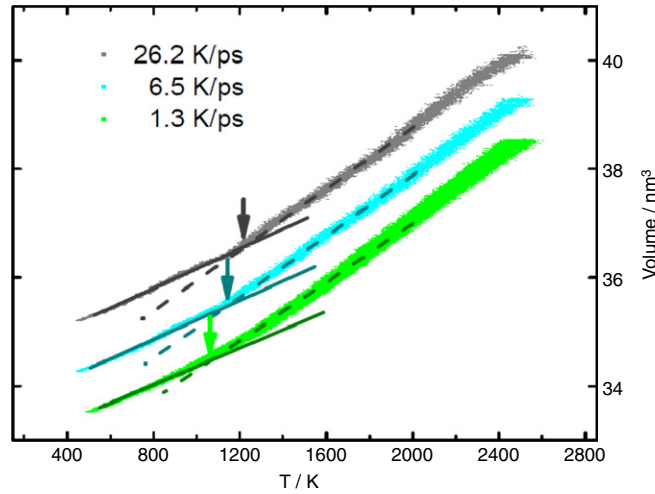


Fig. 1. Volume variation as a function of temperature.

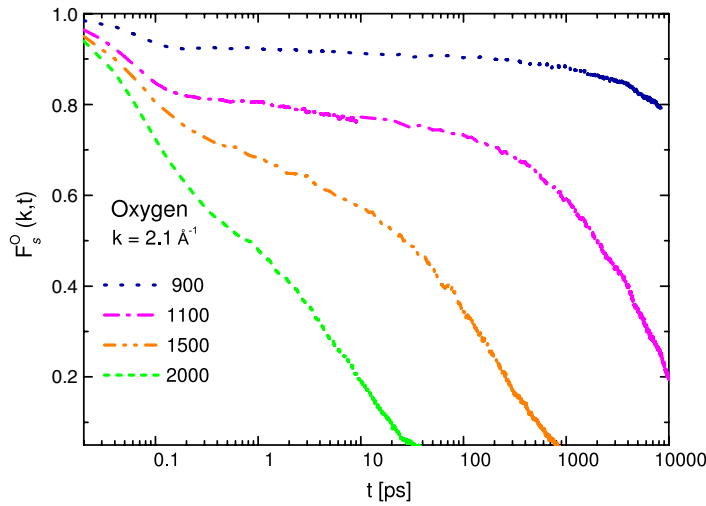


Fig. 2. Incoherent intermediate scattering function of the oxygen atoms of the system at each studied temperature.

into account the repulsive short-range interactions. We applied the potentials parameters derived on the basis of *ab-initio* molecular orbital calculations by Habasaki [19–21]. Then, we assigned to each atom its corresponding velocity drawn from a Maxwell–Boltzmann distribution according to a temperature of 3000 K. The Verlet Algorithm with a time step of 1 fs was used to integrate the motion equations. Periodic boundary conditions were applied in the software LAMMPS [22]. The complete equilibration procedure of the system was: 0.5 ns/3000 K/NVE starting from a random atoms configuration. After that, the temperature was slow down up to 2000 K and followed by 2 ns/2000 K/NPT; 1 ns/2000 K/NVT and 1 ns/2000 K/NVE to ensure the absence of a drift in pressure and temperature. Finally, the NVE trajectories with a step of 1 fs were used to perform the analysis. The same protocol was repeated for each temperature: 1500 K, 1100 K, 900 K and 700 K.

The mean square displacement for each atom type: $\langle r_j^2(t) \rangle$, MSD, is defined as:

$$\text{MSD} = \langle r_j^2(t) \rangle = N_j^{-1} \sum_{j=1}^N |\vec{r}_j(t) - \vec{r}_j(0)|^2 \quad (2)$$

where $\vec{r}_j(t)$ is the position vector of atom j at time t .

The mean square displacement between configurations: $\langle R^2(t) \rangle$, MCSD_{ox}, is defined as:

$$\text{MCSD}_{\text{oxygen}} = R^2(t) = N_{\text{ox}}^{-1} \sum_n \sum_i [r_i(t + n \cdot \Delta t) - r_i(t)]^2 \quad (3)$$

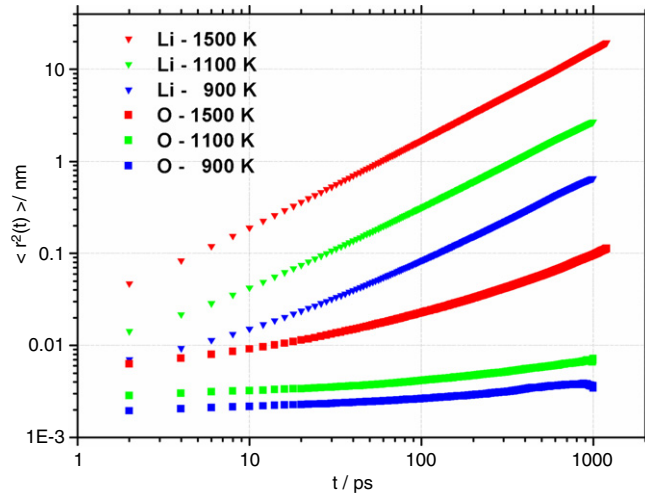


Fig. 3. MSD of lithium and oxygen atoms at 1500 K, 1100 K and 900 K.

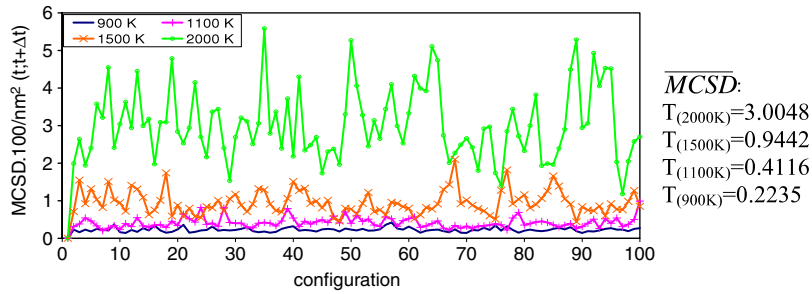


Fig. 4. MCSD_{ox} (Eq. (3)) between consecutive configuration (t ; $t + 10$ ps).

where $\Delta t = 10$ ps. Therefore, we have taken 100 n -configurations for each temperature that are equivalent to 1 ns window time and i mean oxygen atoms. We have also performed a long trajectory for $T = 900$ K with a 100 configurations with a $\Delta t = 100$ ps to analyze a 20 ns window time.

Finally, the incoherent intermediate scattering function $F(q, t)$ is defined as:

$$F_s(q, t) = \frac{1}{N} \left\langle \sum_{j=1}^N \exp(i \vec{q} \cdot (\vec{r}_j(t) - \vec{r}_j(0))) \right\rangle \quad (4)$$

where \vec{q} is the wave vector (2.1 \AA^{-1}). Eq. (4) characterizes the mean (space and time) relaxation of the system.

Isoconfigurational method developed in Ref. [23] performs is a set of equal length MD runs (IC ensemble) which start from the same initial configuration (the same point in its space state) but with different initial particle momentum taken randomly from a Maxwell–Boltzmann distribution at the appropriate temperature. Then, the propensity of each particle for a fixed time interval t , is defined as:

$$\langle \Delta r_i^2 \rangle_{\text{IC}} = \langle [r_{i(t)} - r_{i(0)}]^2 \rangle \quad (5)$$

where $[r_{i(t)} - r_{i(0)}]^2$ is the squared displacement of particle i and $\langle \rangle_{\text{IC}}$ indicates the average over the IC.

3. Results

Fig. 1 shows the volume variation as a function of temperature at three different quenching speeds. From this figure, we learn that for this simulated lithium metasilicate system the glass transition temperature is somewhere between the range (970–1250) K – characterized by a change in the slope (in the plot showed with an arrow) – which is acceptable compared to the lower experimental T_g obtained by DSC or DTA. Considering the simulation's limitations, this T_g value is commonly accepted for simulated lithium metasilicate [23–26]. Therefore, we assume that 900 K is a good temperature to make our analysis because it is possible to consider that the system has reached the glassy state.

In Fig. 2, we see that when the system goes down through the interval temperature noticed in Fig. 1 as the T_g range, this glassy matrix freezes in a solid glass state and its relaxation time is greater than 10 ns for temperatures lower than 900 K.

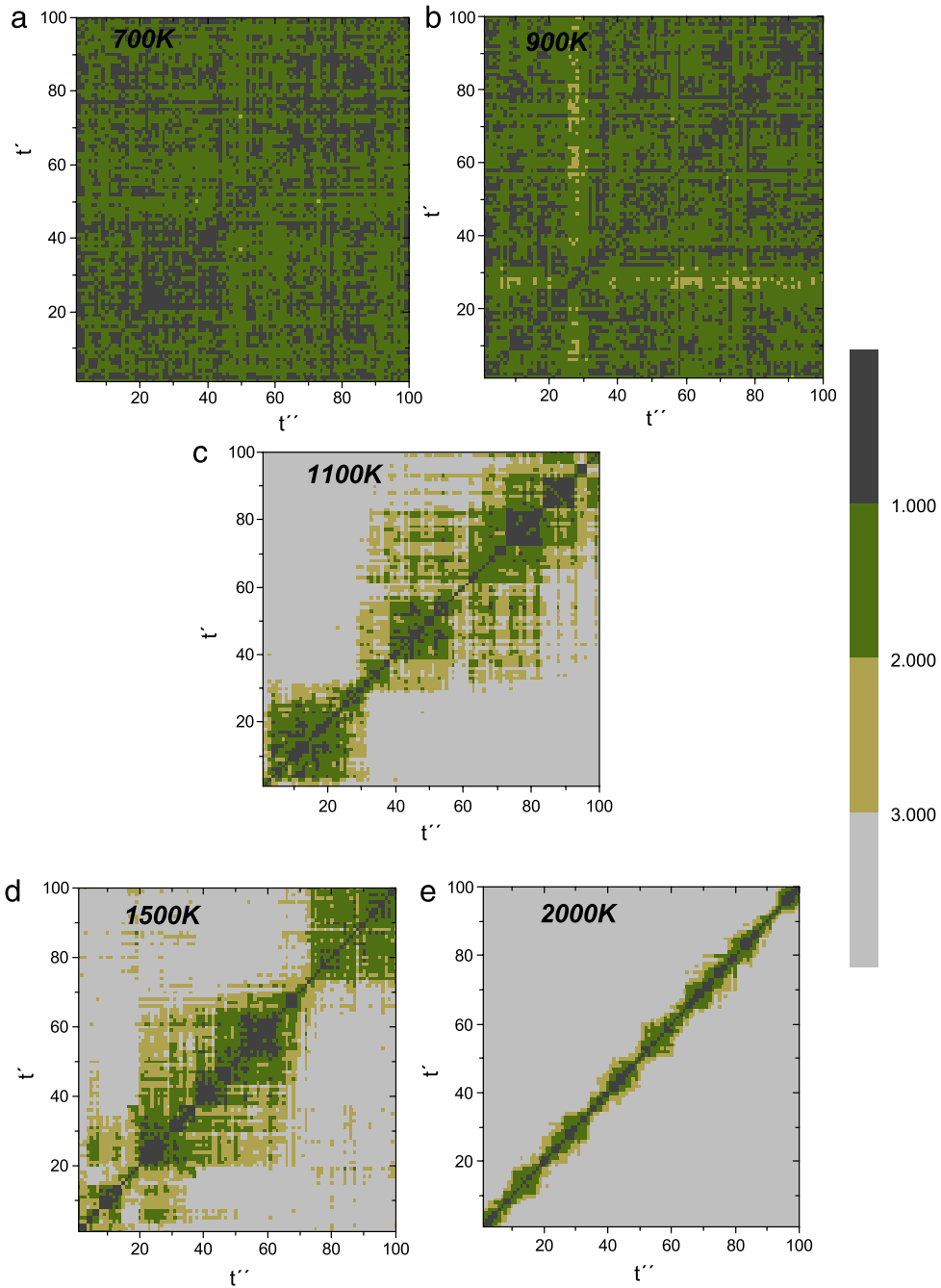


Fig. 5. 2D representation of $[\text{MCSD}_{\text{ox}}/\overline{\text{MCSD}}]$ (Eq. (3)) at each studied temperature (t' and t'' are configuration number units). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3 shows the MSD of lithium and oxygen atoms at every temperature in the present work. From this figure we learn that the system at 1 ns reaches the diffusive behavior for lithium ions while oxygen remains almost frozen at 900 K; while for 1500 K, the oxygen atoms are much more mobile.

Fig. 4 shows the MCSD_{ox} between consecutive configurations ($t; t + \Delta t$) obtained with Eq. (3). In these plots we observe, as it is expected, that below the T_g of the system one configuration (*i.e.* structure at time t) is very similar to the next, and because of that, its MCSD_{ox} value is very small and close to the average value, $\overline{\text{MCSD}}$. However, this behavior is completely different for the highest temperature. Far above the T_g , where two consecutive configurations are quite different, its MCSD_{ox} is large and has a high probability of being different from its average value. The system atoms coordinate changes very much above its T_g temperature.

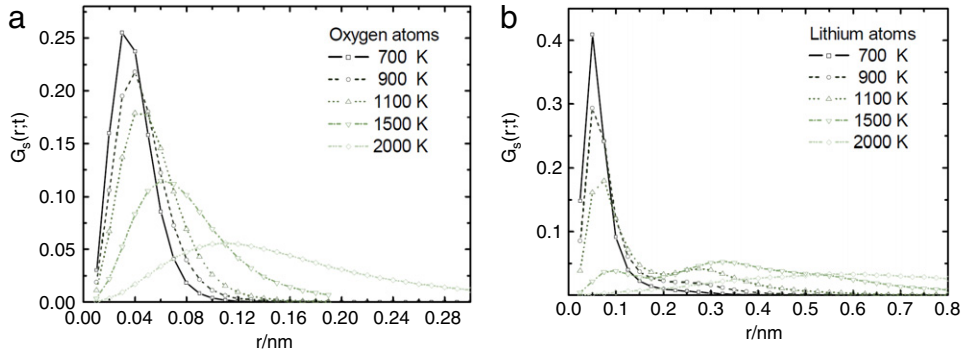


Fig. 6. (a) Self-part of the van Hove functions for oxygen atoms and (b) for lithium atoms.

Fig. 5(a)–(e) shows the 2D representation of $\text{MCSD}_{\text{ox}}/\overline{\text{MCSD}}$ (normalized for each temperature by the average value showed in Fig. 4). To build these plots, we have selected a box of $l = 10 \text{ \AA}$ immersed in the center of the whole system ($L = 30 \text{ \AA}$) in order to avoid artifacts in the analysis because of effects caused by boundaries conditions. In these representations, each coordinate of the square plot corresponds to one configuration, i.e. the structure given by the atoms coordinates that the system reaches at time t during its trajectory of MD simulation. With Eq. (3), we obtain the representation that Fig. 5 shows. The “normalized quadratic distance between two configurations (i.e. the average distance between the oxygen coordinates of two configurations, t' and t'' taken from 1 to 100–” ($\text{MCSD}_{\text{ox}}/\overline{\text{MCSD}}$) for all different window times (e.g., $\sum \{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t)\}/\overline{\text{MCSD}}$; $\sum \{\mathbf{r}_i(t + 2\Delta t) - \mathbf{r}_i(t)\}/\overline{\text{MCSD}}$; $\sum \{\mathbf{r}_i(t + 3\Delta t) - \mathbf{r}_i(t)\}/\overline{\text{MCSD}}$; . . .) is represented through a color scale, in which, the darker the color, the more similar the structures (for instance, one configuration against itself has a zero value, this result corresponds to the main diagonal in the square, the dark gray). This kind of plot has been used in many works to evidence particular events along the temporal evolution of a system [27–29].

4. The dynamics of different ion types

In this kind of representation, we easily understand that when the temperature is lower than T_g the different structures visited by the system are very similar among them (i.e. the color scale in Fig. 5(a) is dark all the way thorough). But, when the temperature is well above T_g , the system has the opportunity to visit very different structures. The oxygen atom coordinates change very much and the system reaches extremely different structures during its dynamics and because of that, the graphs in our representation (plots c to e) are dominated by a lighter color. Equivalent results (not shown in this work) are obtained if these plots are built by adding the silicon movements, which is what one expects since oxygen atoms resemble the skeleton of the glassy matrix.

Fig. 6(a) and (b) shows the self-part of the van Hove function (Eq. (6)) for oxygen and lithium atoms, in each of the temperatures studied:

$$G_s(r;t) = \frac{1}{N_a} \sum_{i=1}^{N_a} \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_{i(0)}|) \rangle. \quad (6)$$

Comparing Fig. 6(a) and (b), it is easy to realize that oxygen atoms are quite slower dynamically compared with lithium atoms which can travel along further distances. What is more, two distinct peaks related to two distinctive lithium jumps (Δt is 10 ps window time) can be observed in Fig. 6(b), in good agreement with what was previously observed in other works [30–33].

5. Looking for the broken ergodicity

In the present work, we develop an easy computational experiment to show how the graphical way presented above is useful to identify what the literature notices: *how to understand a glass system as a broken ergodic system*.

In a very descriptive paper about broken ergodicity related to the dynamics of disordered systems, D.L. Stein and C.M. Newman [4] have explained that for a system with metastable states the typical timescale to escape from it grows exponentially and its lost ergodicity depends on observational times. The state space can be decomposed into “components” which are not intrinsic to the system. They have also proposed a probability of confinement on some timescales and assuming that, while the system is restricted to that timescale, it is ergodic (within a “component”). Therefore, the system has the opportunity to visit a set of states whose average on state space equals the average in time provided that average involves the component’s states. These concepts are easy to visualize through the 2D representation given by Eq. (3). Additionally, they have proposed that the timescale where the system remains in the same component should diverge as the temperature decreases.

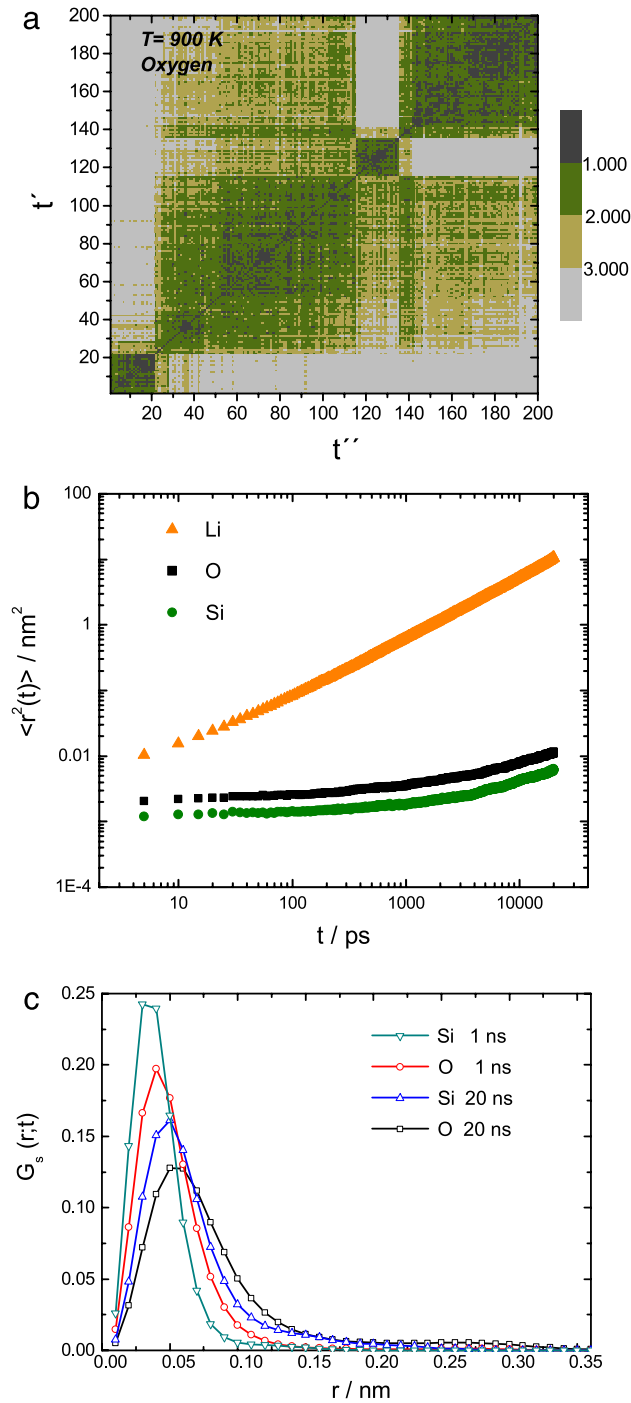


Fig. 7. (a) 2D representation of $\text{MCSD}_{\text{ox}}/\overline{\text{MCSD}}$ (Eq. (3)) (normalized by the average value), (t' and t'' are configuration number units). (b) MSD of lithium, oxygen and silicon atoms at 900 K; (c) the self-part of the van Hove function for oxygen and silicon atoms; for a larger window time of 20 ns at $T = 900 \text{ K}$.

Other works have showed evidence that when the structures reached by a system during its dynamics are quite similar (in this work, small values of MCSD_{ox}) these structures go down to the same minimum on the potential landscape; in other words, they belong to the same metabasin [29,34–38]. Although, the authors in those papers have reached their conclusions through molecular dynamic simulations of the binary 80/20 Lennard-Jones system and others, we assume here that the same behavior is obtained in other kinds of supercooled liquids and also in glassy systems.

Therefore, we could accept that the matrix of the paradigmatic oxide glass in the present work (lithium metasilicate) is a broken ergodic system when its temperature is below its T_g . Taking into account that the system is limited to visit very near

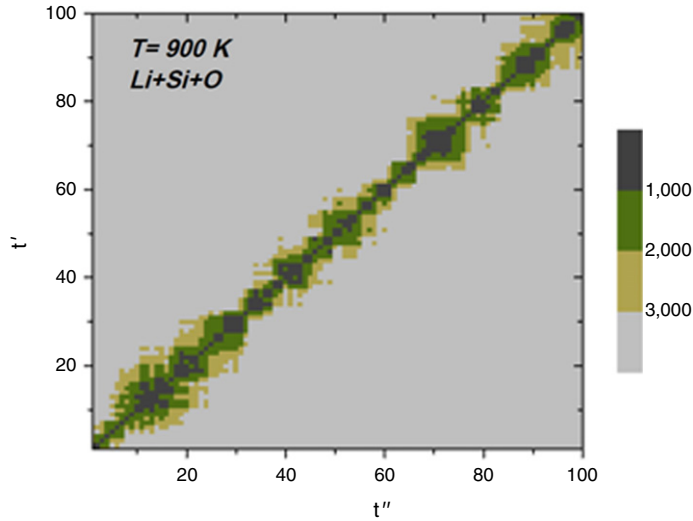


Fig. 8. 2D representation of $\text{MCSD}_{(\text{Li+Si+Ox})}/\sqrt{\text{MCSD}}$ (see Eq. (3)), but, in this case, for the whole system, i.e. i = lithium + silicon + oxygen atoms at the same time, in a window time of 1 ns, (t' and t'' are configuration number units).

configurations in the state space (as Fig. 5(a) and (b) shows) and given that all the structures visited during this window time are very similar, all of them will belong to the same minimum on the potential landscape. While above its T_g , but not so far from it ($T = 1100$ K) as in Fig. 5(c), the configurations explored by the system are different enough among themselves. Since the system has visited different “components”, or more generally speaking, it has explored its state space more and more extensively, those configurations will belong to different minimums in the landscape. Then, we should have to accept that the system is not more a broken ergodic system.

As we have mentioned before and as intuitive as it may be, all of these are of uppermost importance at the moment of deciding the window time for measuring a property in this kind of systems in order to apply the statistical mechanic tools.

Another interesting observation made by Stein and Newman is that given a fixed temperature, there is a cut off on the timescale above which the confinement mechanism breaks down. However, this time is not always the same. For Fig. 7 we test this statement through the same method used in Fig. 5. We observe there a larger window time of 20 ns (in this case each configuration was taken every 100 ps) and now, we see that the system is not confined to a single set of similar structures anymore. The system is exploring different configurations showing several transitions to different sets of self-similar configurations. In the words of Stein and Newman again, the system can visit different components or, by comparison with the results proposed in simulations for the Lennard-Jones systems [29,34,35,38], the system can visit several metabasins that belong to different minimums in its potential landscape. Then, at least from this point of view, it is not obvious that the glassy matrix has lost its ergodicity since the system still behaves as a glass where it is clear that the atoms which built the matrix are still almost frozen. Something similar has been recently shown by B. Ruta et al., in sodium silicate. In their work, they have provided experimental evidence showing that glasses display fast atomic rearrangements within a few minutes, even in the deep glassy state [39].

In order to complete this search for ergodicity lost, we have analyzed the system in the same way (2D representation of $\text{MCSD}_{\text{ox}}/\sqrt{\text{MCSD}}$) but now taking into account all the types of atoms that constitute this system, i.e. considering lithium, silicon and oxygen atoms at the same time. Fig. 7 shows these results and it is easy to realize that the system is not confined to any set of configurations. It is able to explore its state space much more freely (at this time it is useful to compare Figs. 8 and 5(b)).

Therefore, all the results in the present work allow us to assume that ionic conducting glasses made by oxides, where one oxide is the glass former (SiO_2) and a modifier oxide provides the mobile ions (Li_2O), are broken ergodic systems “only” for their matrices and at temperatures below their T_g . When we analyze the system without distinguishing between the mobile atoms from the almost frozen ones in the matrix, we see that the system does not remain confined during a large window time. This is why, it is crucial to do a complete characterization of each system before valuating statistically a property on it. Moreover when the analysis is made in the context of what is commonly denominated “short time dynamic of the system”.

Consequently, if one is interested in the dynamics of mobile ions in a glassy system, e.g. its ionic diffusion coefficient (on laboratory observable times), these systems can always be considered ergodic systems because their confinement to a metabasin, or to an only minimum on the potential landscape, it is not a relevant issue. We should bear the aforementioned observation in mind when we analyze the simulation data through statistical mechanics. Similar proposals, but in different contexts, are presented in referenced works [40,41]. Those papers, which clearly show evidence that there is a bridge between experimental (laboratory) and computational results, tell us that we should revise some issues if we want to find the best way to join the macroscopic and microscopic views in order to reach a complete understanding of the properties behavior of glassy systems.

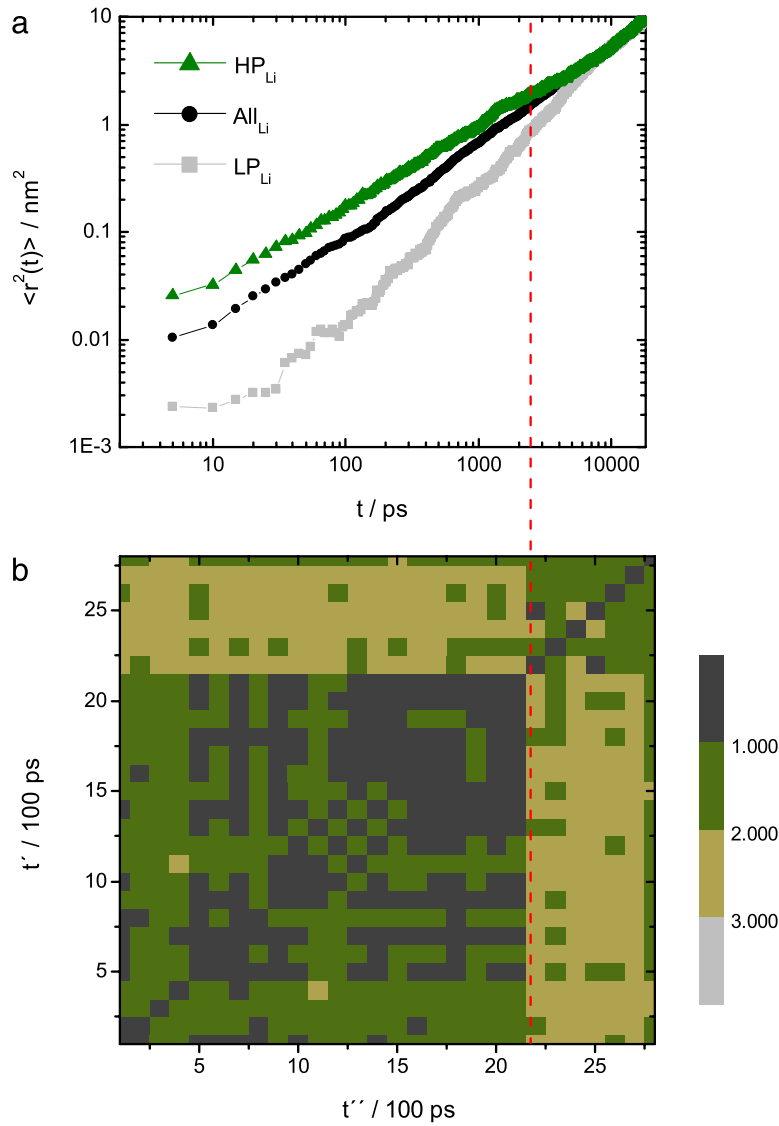


Fig. 9. (a) Mean square displacement of the labeled lithium atoms in the lithium metasilicate. (b) Zoom of 2D representation of $\text{MCS}_{\text{D}_{\text{ox}}} / \overline{\text{MCSD}}$ (Eq. (3)) (normalized by the average value) shown in Fig. 7.

6. Illustrative example

In 2004, Widmer-Cooper, Harrowell and Fynewever proposed a very interesting statistical tool called isoconfigurational ensemble (IC) to study the relationship between particle motion and initial structural configuration. This method allows us to find the propensities of the system's particles. This procedure provides a link between a given configuration and its dynamics [23]. This quantity named propensity allows us to label the particles in the system as very mobile (high propensity particle: HP) or almost motionless (low propensity particle: LP) regarding their position in the glassy matrix, according to Eq. (5). With this idea in mind, in a previous work, we showed the existence of regions which are potential candidates for hosting the ionic conduction channels [42].

Considering the above mentioned procedure, we compare the mean square displacement of the labeled lithium atoms in the lithium metasilicate. Fig. 9(a) shows those results for the system at 900 K. In this figure this differentiation between HP and LP before 2 ns is clear but it is not after that window time. These results are consistent with a transition from one metabasin to the following as it is easy to see in Fig. 7 and clearer in Fig. 9(b) where we have zoomed that window time. The hypothesis of the present work is clearly evidenced in this example; some properties can change according to the window time where they are evaluated. Then, it is important to know if the system under study has or has not lost its ergodicity in order to understand the statistical results that are obtained from the simulation data.

7. Summary

From the results of molecular dynamic simulation of lithium metasilicate glasses, we have found a simple way to establish the windows time in which broken ergodicity of an oxide glassy matrix could be considered. It is important to take this particular behavior of the system into account when one is analyzing dynamical and structural properties using statistical mechanics in different scale times. The glass transition temperature is a sign of a sudden qualitative change in the exploration of the potential landscape. The broken ergodicity phenomenon is clearly seen through the easy graphical representation used in this work. It is important to note that the confinement in a reduced area of the space states of the system is associated to the glassy matrix although this is not strictly true neither when the very mobile ions (lithium ions in this system) are considered in the analysis of the data nor when the window time where the system is analyzed is long enough.

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