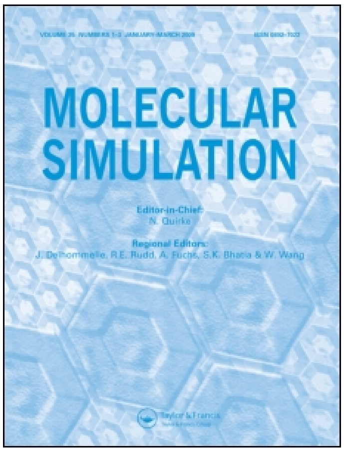

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NUMERICAL INVESTIGATION OF THE INFLUENCE OF THE HISTORY ON THE LOCAL STRUCTURE OF GLASSES

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By means of molecular dynamics simulations and the Voronoï tessellation, we study the influence of the history on the low temperature characteristics of soft sphere and silica glasses. The quench from the liquid is interrupted at an intermediate temperature T_i for a given relaxation time, and then the cooling process is continued down to 0 K. The local structure at 0 K depends on the temperature T_i and the effect is larger for T_i close to the glass transition temperature T_g. This dependence, coherent with recent results, is expected in the strong glass former where the characteristics of a particular state depend on its history. In the soft-sphere case, because of crystallization effects, the dependence of the local structure of the glassy samples on their history can only be detected in the supercooled liquid region.

Keywords: Numerical simulation; glass; structure; aging effects

PACS numbers: 61.43.Fs, 02.70.Ns, 61.20.Lc, 61.43.-j

I. INTRODUCTION

Experimentally, from the study of slow dynamics in disordered solids, it is now well established that the time evolution of certain systems depends on the manner these systems were prepared. This phenomenon called usually "aging" has been observed in structural (polymer) glasses [1], spin-glasses [2] or orientational glasses [3]. Recently theoretical work concerning aging effects in a structural Lennard-Jones glass has been published [4]. Through classical molecular dynamics (MD) simulations the authors show that the

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*Corresponding author.

dynamical behavior of this system depends on the initial temperature before the quench and exhibits the same scaling features than the one observed in spin-glasses. Several theoretical explanations have been proposed to account for this apparent universal behavior of the out-of-equilibrium dynamics in various glasses [5].

Since it has been shown that aging effects occur in a model glass, we want here to address this question from the structural point of view by using a combination of classical micro-canonical MD calculations and the Voronoï tessellation. An in-depth description of our Voronoï tessellation scheme can be found in a previous paper [6]. For the sake of generality, we consider two very different systems, a soft sphere glass and a silica glass, representative of amorphous metals and vitreous oxides, respectively.

II. METHODOLOGY

The soft sphere system is a very simple monoatomic model (without any particular experimental counterpart) described by the purely repulsive potential introduced by Laird and Schober (LS) [7]. This potential is basically a modified inverse 6th power potential similar to those very often used in computer simulations of liquids and glasses. Here we use the same parameters (arbitrarily equal to the Lennard-Jones parameters of Argon) as in previous studies [6, 8] and consequently the glass transition temperature T_g and melting temperature T_m are respectively $T_g \simeq 10.3$ K [7] and $T_m \simeq 22.7$ K [9]. In the present MD calculations we have considered, as before [6, 8], 1000 soft spheres in a cubic box of edge length 34.05 Å. The silica system is described by the more sophisticated potential first introduced by van Beest, Kramer and van Santen (BKS) [10] and justified by *ab initio* calculations. Though designed originally for the crystalline phases of silica, it has been shown to describe quite well the structural [11] and vibrational [12] properties of vitreous silica. In that case also we make use of the same parameters as in a previous study [13] in which we have performed micro-canonical MD calculations (treating the Coulomb interactions using the Ewald summation method [14]). The Voronoï tessellation procedure has been straightforwardly adapted to this two component system and it is worth noting that we did not include any weighing factor to distinguish silicon from oxygen atoms [13]. The estimated value for the glass transition temperature [11 – 13] is $T_g \simeq 3500$ K, subsequently larger than the experimental one partly because of the very fast cooling rate ($2.3\ 10^{14}$ K/s) imposed by numerical calculation limitations. But the value of T_g is consistent with its dependence with the cooling rate proposed by Vollmayr *et al.* [11] in which a Vogel-Fulcher dependence of the relaxation time τ^* of the system on the temperature is assumed. As in [13], our silica system consists of 216 silicon and 432 oxygen atoms confined in a cubic box of edge 21.48 Å corresponding to a density close to the experimental one. In the following the soft sphere and silica systems will be called LS and BKS, respectively.

The purpose of the present work is to study the influence of the sample history on the low temperature structural properties of our two model glasses. To achieve this goal we follow in both cases a very simple *modus operandi*, which is illustrated in Figure 1 in the LS case. We start from well equilibrated liquid samples at a well defined temperature T_ℓ (point A). We have chosen $T_\ell = 45\,\mathrm{K}$ in the LS case and 7000 K in the BKS case. At this point two paths can be followed: either the liquid is quenched to an intermediate temperature T_i (point B) then relaxed in a microcanonical ensemble during a time τ (point C′) and finally quenched to zero temperature (point D) or the liquid is quenched to 0 K directly (point C) relaxed during τ

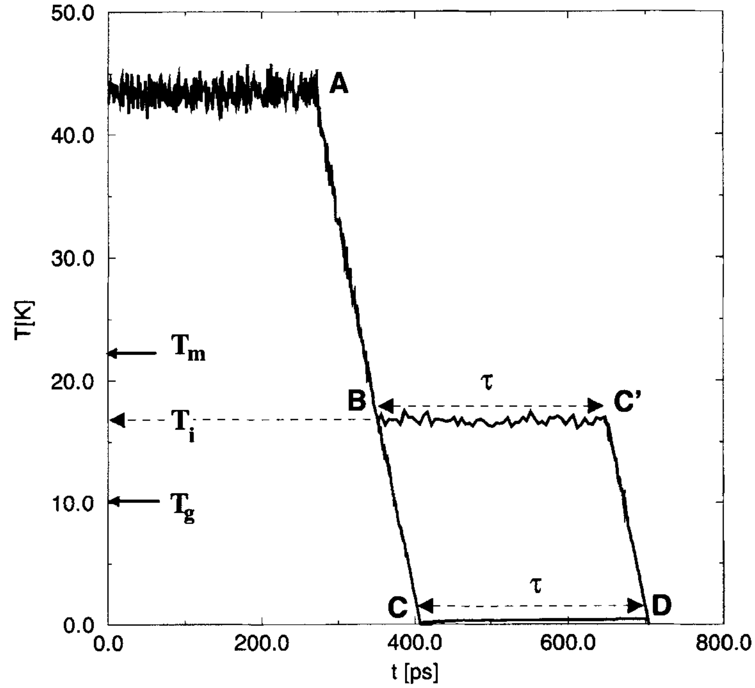

FIGURE 1 Example of the quenching procedure used in this study: a relaxed liquid (point A) is quenched to 0 K following either the path ACD or the path ABC′D.

and finally cooled to 0 K (point D). This last cooling procedure is necessary because of the slight temperature increase following the direct quench to 0 K since our system evolves at constant energy. From a structural point of view we have checked that this short quench is not really necessary but we have included it anyway in the second path to have a unique final state (point D).

III. SOFT-SPHERE GLASS

In the LS case, the quenching rate γ has been chosen equal to the "ideal" quenching rate of 10^{12} K/s for which the glass stability at 0 K compared to the crystalline state has been shown to be maximum [8] and the local structure at point D has been studied using the fraction of pentagonal faces f_5 of the Voronoï cell attached to each particle. We have previously shown that this parameter is a very sensitive tool: a high value of f_5 (typically 0.45) is a sign of strong icosahedral order, characteristic of amorphous metallic glasses, while a small value of f_5 (<0.2) indicates the onset of crystal nucleation. Indeed, depending on τ, one has to be careful in order to distinguish between pure glassy state relaxation and recrystallization effects. Here we have considered two different values of τ: 100 and 300 ps. These values of τ should be compared to the value of the typical relaxation time of the system, τ^*. This relaxation time depends on the quenching rate. It is generally admitted that the system falls out of equilibrium when its relaxation time is on the order of the time scale of the cooling process *i.e.*, $\tau^* \approx T_g/\gamma \approx 32$ ps where γ is the effective cooling rate deduced from Figure 1. The values of τ used in our study are therefore large enough to permit a complete relaxation of the systems for $T_i \geq T_g$. Of course this is no more the case in the solid phase.

Concerning T_i, for each sample we saved configurations (positions and velocities) along the quench at fixed time intervals corresponding approximately to a difference of temperature of 2 K. The corresponding results have then been averaged over ten different samples generated from ten independent liquid configurations. It is interesting to note in Figure 1 that the amplitude of the temperature fluctuations during the relaxation procedure follows the usual $\sqrt{T}$ behavior and are almost inexistent at very low temperature.

In Figure 2 we show the variation of f_5 as a function of T_i for $\tau = 100$ and $\tau = 300$ ps. The error bars show the temperature dependent dispersion of our statistical ensemble containing ten samples. The first information

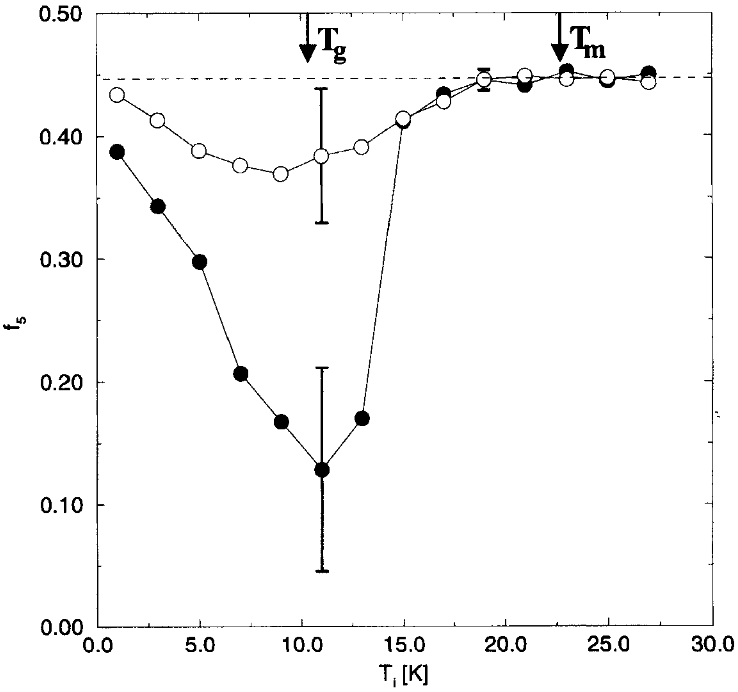

FIGURE 2 Variation of the fraction of pentagonal faces, f_5, as a function of the intermediate temperature T_i for $\tau = 100\,\text{ps}$ (○) and $\tau = 300\,\text{ps}$ (●). The horizontal dashed line is a guide for the eye and indicates the value of f_5 in the reference structure at 0 K.

concerns the high temperature behavior. Figure 2 points out that if T_i is above a temperature $T_{\text{sup}} \approx 19\,\text{K}$ (lower than T_m), the structure obtained at 0 K is the same whichever path the system followed during the quench. This structure is symbolically represented in Figure 2 by the horizontal dashed line. Indeed the points for $T_i \geq 19\,\text{K}$ lie nicely on this line as well as the extrapolated value for $T_i = 0$ (due to averaging, the value $T_i = 0$ can not be reached exactly). This structure is without any doubt a glassy arrangement and exhibits a value of f_5 close to 0.45 which is a sign of strong icosahedral local order. This first information tells us that the low temperature structure following the quench will be the same whatever the initial liquid temperature is, as long as it is above T_{sup}. In the picture representing the whole system as a point evolving on a complex multi-valleyed energy "surface" [15], it means that as long as the temperature T_i is above T_{sup}, the kinetic energy of the system is greater than all the energy barriers on that surface. Therefore if $T_i \geq T_{\text{sup}}$ the system explores the whole configuration space and the low temperature sample does not depend on T_i. From a purely practical point of view it means also that quenches from the liquid state can be started at temperatures just above the melting temperature without the system remembering the characteristics of this liquid state.

The curves in Figure 2 depart from the horizontal dashed line (which represents in a sense the "reference" structure) for T_i below ≈ 19 K. It is interesting to note that the two curves corresponding to the two values of τ are superimposed down to ≈ 15 K. Then these two curves split and exhibit a minimum for $T_i \approx 10$ K. This minimum is close to 0.38 for $\tau = 100$ ps and is much lower for $\tau = 300$ ps ($f_5 \approx 0.12$). This is a direct consequence of the relaxation, the system after 100 ps being on its way to the equilibrium configuration reached after 300 ps. What is the meaning of this minimum? As said earlier a small value of f_5 is a sign of the onset of crystallization. Moreover looking at the results obtained for the individual samples it appears that some systems exhibit values of f_5 as small as 10^{-2} indicating an almost perfect crystalline character. This can also be verified by direct visualization of these samples. These results indicate that if T_i is chosen close to the glass transition temperature T_g ($T_g = 10.3$ K), the propensity to crystallize is maximum. This means that our model glass exhibits a maximum of instability with respect to the crystalline state when its temperature is close to T_g. Below T_g, f_5 increases again and the low temperature glass stability is recovered as shown previously for this quenching rate [8]. The fact that the tendency to crystallize increases when T_i increases up to T_g can be explained using the same kinds of arguments than the ones developed in [8]. When T_i increases, the local density fluctuations increase and therefore the probability to find crystal germs in the samples increases. Of course, as in [8], this explanation remains qualitative since it does not take into account the ability of the existent germs to grow. To explain the existence of a minimum around T_g in the f_5 curve *i.e.*, that the stability increases when T_i increases above T_g, one can argue that the crystal germ nucleation is now outweighed by the fact that the energy difference between the super-cooled state and the crystal state increases, making the crystallization process more difficult to happen. Let us discuss again in terms of relaxation times. When crystal nucleation occurs the nucleation rate has to be taken into account introducing an extra time scale, $\tau_n(T)$. τ_n is a very rapidly varying, non monotonous function of the temperature: it first decreases as T is lowered from the liquid state, due to the decrease in the free energy barrier and then increases again due to the liquid becoming more sluggish. This variation is shown in the so-called "TTT" diagrams [16]. The curves in Figure 2 can then be interpreted in the following way: the waiting time $\tau = 100$ ps is always smaller than τ_n while $\tau = 300$ ps becomes larger than τ_n between 12.5 and 15 K. Hence the samples relaxed at $T_i \lesssim T_{\text{inf}} \approx 13$ K exhibit crystal nucleation. The maximum crystalline order is reached when the nucleation rate is maximum *i.e.*, around T_g [16].

When the curves in Figure 2 depart from the horizontal dashed line, it means that the glass "remembers" its past history and has a different structure depending on the path (ABC′D or ACD) which it followed during the quench. Nevertheless most of these differences are due to recrystallization effects which are interesting but are not aging effects (the term aging was in fact introduced to "distinguish glassy state relaxation from other time-dependent processes such as recrystallization" [1]). To make this distinction we report in Figure 3 the variation for $\tau = 300$ ps of f_5 as a function of T_i (full circles) but also as a function of T_f (open squares). T_f is the temperature of the system at point C′ in Figure 1. It corresponds to the

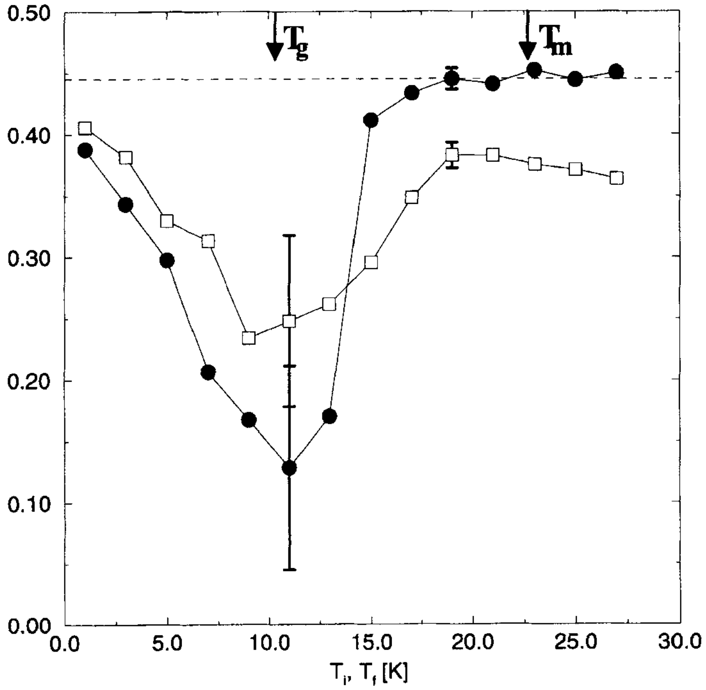

FIGURE 3 f_5 as a function of T_i (●) and T_f (□). T_f is the final temperature after a relaxation time $\tau = 300$ ps (temperature at point C' in Fig. 1). The horizontal dashed line is a guide for the eye and indicates the value of f_5 in the reference structure at 0 K.

final temperature after the waiting time τ and can be compared directly to the temperature used in the work done on the Lennard-Jones glass [4]. As can be seen in Figure 3, these temperatures are almost identical which permits to compare the f_5s in the system at C′ and D. The difference between these two states is an additional quench to lower the temperature from T_f to 0 K. In fact the time spent during this quench can be viewed as an extra relaxation time. Therefore if the system evolves towards a crystalline state this supplemental relaxation time should lead to a decrease of the f_5s at D compared to the results obtained at C′. In Figure 3 this is the case for temperatures between 2 K and the crossover temperature T_{inf}. This indicates that the departure from the reference structure in that temperature range is simply due to crystallization effects. In the liquid region for temperatures above T_{sup} the smaller values of f_5 at T_f are a consequence of thermal effects [17] and therefore it is expected that once the system is cooled down the values of f_5 increase towards the values obtained in the reference structure. Let us now examine the last temperature interval which goes from T_{inf} to T_{sup}. In Figure 3 we see that the additional relaxation time induces an *increase* of the f_5s in that temperature region (as an example at 15 K, f_5 is equal to 0.28 at C′ while at D $f_5 = 0.42$). Therefore no onset of crystallization is present in the samples. On the contrary the additional quench makes them even more amorphous. Nevertheless in that temperature interval the curve of f_5 as a function of T_i is *not* superimposed with the horizontal dashed line. Therefore the glassy structures obtained are different from the reference structure indicating the effect of the history on the local structure of the amorphous phase. The differences are admittedly small but they exist and are larger than the error bars in that temperature range. This effect exists between T_{inf} and T_{sup} *i.e.*, roughly in the supercooled liquid region. It may exist also at lower temperatures but to us it will remain hidden by the recrystallization effects. In that temperature region the system does not explore the whole configuration space anymore and therefore the glassy systems obtained are different from the ones obtained at higher temperatures. Locally they appear less disordered (f_5 is smaller than the value obtained for the reference structure) because the system has not access to the full variety of possible configurations but it remains amorphous. In fact we have a picture of the configurational space corresponding to T_i in which the crystalline ground state is not accessible and which leads to glassy systems structurally different from the reference structure. This difference is quantified in Figure 3.

IV. SILICA GLASS

In the BKS case, the quenching rate γ has been chosen equal to 2.3 10^{14} K/s and a unique relaxation time $\tau = 42$ ps (corresponding to 60000 timesteps) has been considered. This choice for τ results from a balance between an upper limit imposed by our computing facilities and a lower limit necessary to obtain detectable effects, even after averaging over ten independent samples, as we did here. Also this value of τ is nearly three times larger than the typical relaxation time of the system, $\tau^* \approx 15$ ps, which permits a complete relaxation of the samples during the waiting time for $T_i \geq T_g$. The difficulty in obtaining these results is rewarded by the certitude that in the BKS case no crystallization tendency has ever been seen [11 – 13]. To detect the structural modifications in the case of vitreous silica we can no more make use of the f_5 parameter since it has a significance only for amorphous monoatomic glasses with spherical symmetry. Here we have chosen to present the standard deviations σ_O and σ_{Si} of the Voronoï cell volumes for the oxygen and silicon atoms over the whole sample. In fact we have calculated the dimensionless quantities $\Sigma_O = \sigma_O/\langle V_O\rangle$ and $\Sigma_{Si} = \sigma_{Si}/\langle V_{Si}\rangle$ in which the standard deviation has been divided by the corresponding averaged cell volume. The standard deviation of the cell volumes is a direct measure of the local density fluctuations around a given atom. As shown in a recent study [13] this quantity decreases when lowering the temperature from the liquid state and it is possible to extrapolate it to zero at 0 K as if the system would try to reach a crystalline state. This decrease slows down when T becomes lower than the glass transition temperature T_g, and finally the standard deviations saturate to a non zero value at 0 K, typical of glassy disorder. Therefore the lower the σ's are, the closer to an "ideal" glassy state the considered system is (as long as there is no crystallization). The variation of Σ as a function of T_i is plotted in Figure 4. Note that Σ_{Si} is smaller than Σ_O which reflects a larger disorder around the oxygen atoms, in agreement with the fact that the tetrahedral arrangement around the silicon atoms is quite well preserved, even in the liquid or amorphous states. In the case of silica also, the data obtained for a sufficiently large temperature ($T_i \geq T_{\text{sup}} \approx 6000$ K) correspond to the one obtained for $T_i = 0$ K (represented by the horizontal dashed lines in the figure) within the error bars. The small but significant data departure from the dashed line in the whole range $0 < T_i < T_{\text{sup}}$ is maximal when T_i is chosen close to T_g, similar to the behavior observed in the soft-sphere glass. How can this departure be interpreted in the case of silica in which no crystallization occurs? For a strong glass former, at sufficiently low temperature, the characteristics of a sample depend on the history of the sample (quenching rate, relaxation time) as shown previously [11]. Therefore we expect that the local structure of our silica glass depends on T_i and this is indeed the case as shown quantitatively in Figure 4. Nevertheless in that point of view the shape of the curve needs to be explained: why is there a minimum close to T_g? For temperatures below T_g, in the solid phase, the structural relaxation time exceeds by far 40 ps and therefore our waiting time τ is not sufficient to permit a complete relaxation of the systems and the situation gets worse as the temperature decreases. This explains why the curves in Figure 4 converge towards the reference lines at low temperature. At T_g, $\tau^* \approx 15$ ps and the waiting time is sufficient to let the systems relax closer to the underlying ideal glassy structure (with a smaller Σ). In terms of energy

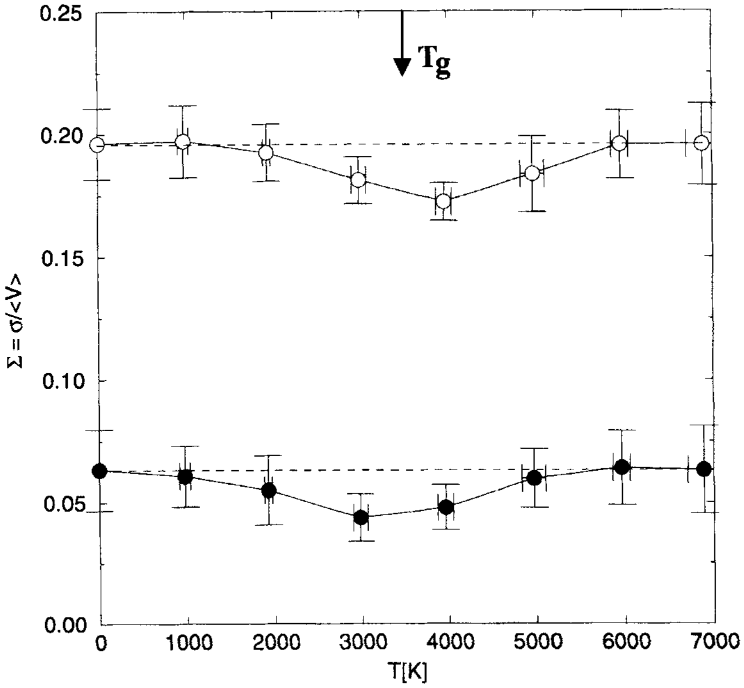

FIGURE 4 Variation of the reduced standard deviations $\Sigma = \sigma/\langle V\rangle$, for the oxygen (○) and the silicon (●) atoms in our silica system, as a function of the intermediate temperature T_i for $\tau = 42$ ps. The horizontal lines show the corresponding values in the reference structure at 0 K and are guides for the eye.

landscapes, at T_g the system has enough kinetic energy to overcome the barriers separating the metastable state characteristic of the considered quenching rate from the lower lying states, during the waiting time. At a higher temperature, the system explores more phase space during the time τ and therefore gets trapped after the quench in a state close to the metastable state characteristic of the cooling rate. With still higher temperatures, the system explores the same energy landscape during the waiting time and the low temperature structure (after the quench) is just a reflection of the fast cooling rate. The minimum in the curves in Figure 4 indicates that the structure obtained by stopping the quench to perform a long relaxation period at a temperature close to T_g is closer to the "ideal" glassy structure, since it corresponds to lower values for the standard deviations of the cell volumes than in the reference system (quenched at the same speed, but without interruption). This is consistent with the fact that, for a slower quench, the glass transition temperature would be smaller and so would be the standard deviations of the cell volumes (which have been shown to decrease with decreasing temperature in the liquid phase [13]). In practice, to obtain the same result, it is however more efficient to stop the quench and perform a relaxation at T_g, which is the procedure followed by the authors in [12], than to perform a slower purely linear quench.

V. CONCLUSION

This study combining MD simulations and the Voronoï tessellation in model glasses provides an other point of view in the study of the influence of the glass history on its properties. Here we tackle this question from the structural point of view. First of all the study as a function of temperature of the local structure in soft-sphere samples has shown that this model glass exhibits a maximum instability with respect to the crystalline state at T_g.

We have then shown that the structure of this model glass depends on its history. Indeed when a system is cooled to an intermediate temperature, relaxed and then quenched to zero temperature (and if it stays amorphous) its structure is different from the structure obtained by a direct quench to 0 K followed by the same relaxation period *if* the intermediate temperature is chosen roughly in the supercooled liquid region. Secondly we did the same kind of study in a model silica glass where the crystallization phenomenon is absent. In that case we find also, as expected, a dependence of the local structure on the glass history. This dependence is maximum when the intermediate temperature is close to T_g.

These results show that the Voronoï cell characteristics permit to clearly distinguish recrystallization from "true" glassy state relaxations in the case of the soft-sphere glass. In the case of silica an extension of this work would be to check if the change of the local structure observed close to T_g is detectable in other quantities.

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