Aging of Tetrahedral Structure in a Lennard-Jones Glass[1]

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Summary

We study the aging of a glassy Lennard-Jones binary mixture with molecular dynamics simulations. We follow the evolution of the packing as a function of the system's age t_w, the time passed since the system is quenched to below its glass transition temperature. We focus on simple properties of all tetrahedra formed by the majority of particles. We find that both the averages and the distributions of the edge length of tetrahedra and of their standard deviation monotonically evolve over time: they age. Specifically the aging process decreases the irregularity of tetrahedra while loosening them up. This is in stark contrast with previous experiments on slightly charged hard-sphere colloidal suspension where tetrahedral geometry was found to be a poor indicator of age. Furthermore, we confirm that tetrahedral packings sample microscopic structure in a non-trivial way.

1. Introduction

Amorphous materials are abundant both in Nature and as man-made substances, yet some of their fundamental properties remain poorly understood. One such puzzle is related to the glass transition [1, 2, 3, 4, 5] and the non-equilibrium behaviour of glasses [6]. As a liquid is quenched to temperatures near its glass transition temperature T_G its viscosity increases by many orders of magnitude. On the microscopic scale, long time diffusion of the molecules is inhibited and only localized, vibrational, motion survives. However a diverging structural length-scale which might explain such a slowing in the dynamics and increase in viscosity has not yet been identified.

Once in the glassy regime a second puzzling phenomenon surfaces: that of aging. Unlike for equilibrium systems, a dependence of dynamical properties of glasses on the waiting time (t_w) between vitrification and the measurement precludes the possibility of taking time averages, and statistics can only be improved by averaging over ensembles. This slow evolution slows as the glass ages, and again does not seem to be accompanied by increasing length-scales.

Thus far much attention has been focused on two-time quantities. The most basic of these is simply particle mobility. For example, experiments on dense colloidal suspensions [7, 8, 9] and simulations of Lennard-Jones (LJ) systems [10] have found that the positions of the most mobile and immobile particles are spatially correlated. Heterogeneity has been found also in the temporal domain [8, 11]: the rearrangements that occur during aging are intermittent. Other two-time correlation functions [12, 13] have shed some light on the microscopic processes at play in supercooled and glassy systems. Nevertheless, a structural tell-tale able to discern different ages of a glass would be valuable.

One possible approach is to analyze the structure of an aging glass in terms of tetrahedral packings. This is motivated by the fact that a regular tetrahedron is a highly dense object with a (hard-sphere) packing fraction that reaches $\phi_{\text{tet}} \approx 0.78$ at close packing. Even below this limit, tetrahedra's high packing efficiency would allow a collection of particles to increase local vibrational entropy thus distributing available volume more evenly throughout the system, perhaps with some cost in configurational entropy. A similar in-

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crease in vibrational entropy for organized packing is what drives a hard-sphere supercooled liquid to eventually crystallize. On the other hand, tetrahedra do not tile space, as could have been suspected by the fact that $\phi_{\rm tet}$ is greater than the highest packing fraction possible for hard spheres, hexagonal close packing at $\phi_{\rm hcp} \approx 0.74$. One can postulate that a glass is caught between the advantage to optimize local packing and increase its entropy, and the constraint that it must fill space. In this picture, aging could be seen as the gradual, and perhaps only partial, resolution of this *frustration* [14].

We previously analyzed the structure of an aging colloidal glass in terms of tetrahedral packings [15, 16]. In those experiments we found that while tetrahedral geometry was somewhat correlated with the aging dynamics, neither the averages or the distributions of promising static tetrahedral characteristics aged.

Here we present a similar study carried out on data from extensive Molecular Dynamics (MD) simulations of a quasi-realistic glass former [13]. We find that unlike in the case of colloidal experiments, the tetrahedra formed by the particles do age and moreover, they tend to become more regular with time.

2. Model and Computational Procedure

The MD simulation data we analyze here were generously provided to us by H. E. Castillo and A. Parsaeian [13].

The well known glass forming system first proposed in Ref. [17] consists of a collection of 8000 particles of identical mass m (an 80:20 mixture of particles A and B). Over time-scales accessible by MD, the binary nature of the system suppresses crystallization and, in fact, this same system has been used to study post-quench aging in the glassy regime [13, 18]. The particles interact via a LJ potential of the form $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}\right]$, with $\alpha,\ \beta \in \{A, B\}$. The values of $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ were $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$,$\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$ and $\sigma_{BB} = 0.88$. The potential is cut off and shifted at a distance $2.5\sigma_{\alpha\beta}$. Fifteen independent MD runs were simulated in a cubic box of length $L = 18.8$ with periodical boundary conditions. The system was equilibrated at a temperature $T_0 = 5.0$ and then instantly quenched to $T = 0.4 < T_C^{\rm MCT} = 0.435$ [17] (the Boltzmann constant is set to $k_B = 1.0$). All times are reported relative to $t_w = 0$, the time of the quench. Further details of the protocols can be found in Ref.[17].

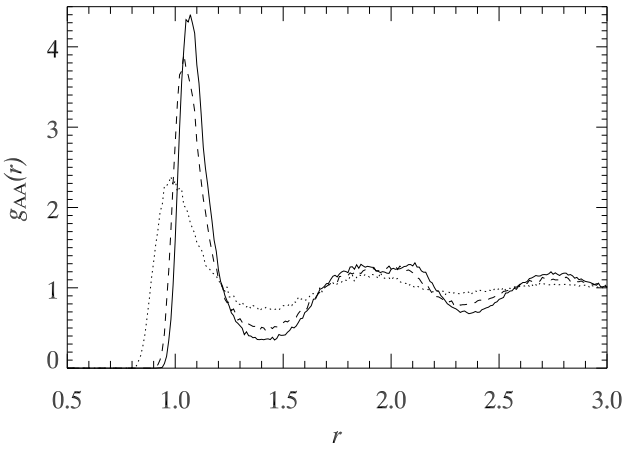

Fig.1 Aging of the pair correlation function $g_{AA}(r)$. The dotted, dashed and solid curves represent $t_w = 0, 10$, and 10^5 (reduced LJ units) respectively.

In what follows we report all quantities using reduced LJ units of energy (ϵ_{AA}) and length (σ_{AA}), with time in units of $\sqrt{m\sigma_{AA}^2/48\epsilon_{AA}}$.

3. Results

We focus our attention on the structure of the majority (80%, type A) particles in order to simplify the analysis. We start by calculating the pair correlation function $g_{AA}(r)$ as a function of system age t_w. In Fig. 1 we plot $g_{AA}(r)$ at the quench ($t_w = 0$) and for the first ($t_w = 10$) and last ($t_w = 10^5$) time points available after the quench.

We find that in contrast with our previous colloidal experiments [15, 16], the pair correlation function shows appreciable aging as has already been seen by Kob and co-workers [17]. We also note that most of the aging occurs within the first ten LJ time units of the quench although it continues for the duration of the simulation. Specifically, as the glass ages, the first peak narrows and shifts to larger values of r. At $t_w = 0$ the structure is that of a liquid at $T = 5$ with a wide range of accessible inter-particle distances. The position of the peak of $g_{AA}(r)$ reflect the most likely separation while its width tells us that thermal fluctuations are quite important. After the thermal quench, the change in r_{peak} reflects the new energetically favorable structure at the lower T. A qualitatively similar shift was observed in the evolution of $g_{BB}(r)$ and $g_{AB}(r)$ (data not plotted).

Note that the first minimum of $g_{AA}(r)$ remains

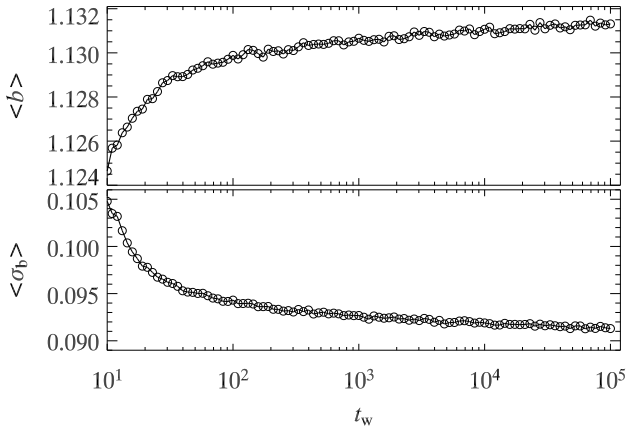

Fig.2 Aging of the average tetrahedral looseness $\langle b \rangle$ and irregularity $\langle \sigma_b \rangle$. The values $\langle b \rangle|_{t_w=0} = 1.105$ and $\langle \sigma_b \rangle|_{t_w=0} = 0.141$ are not shown to allow for a logarithmic t_w-axis.

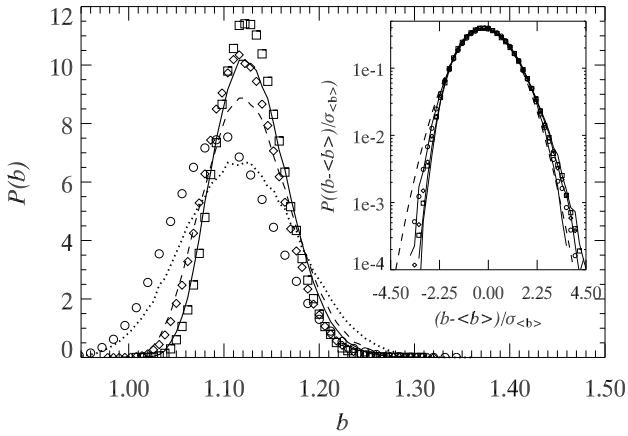

Fig.3 Probability distributions of tetrahedral looseness. $P(b)$ for $t_w = 0$: circles, $t_w = 10$: diamonds, and $t_w = 10^5$: squares. The dotted, dashed and solid lines are the corresponding reference curves $P_{\rm ref}(b)$ computed by considering sextuplets of random AA nearest neighbor bonds based on $g_{AA}(r)$. Inset: Rescaled tetrahedral (symbols) and reference (solid lines) probability distributions for the three ages. The dashed line is a Gaussian best fit.

at $r = 1.4$ for all ages. Following the procedure in Refs. [15, 16] we identify all particles of type A that are within $1.4\sigma_{AA}$ of each other and label them as nearest neighbors. We then define a tetrahedron as a quadruplet of particles which are all nearest neighbors. The average of the six edge lengths (or bonds) $b_{i=0\ldots5}$ is labeled b and represents the *looseness* of the tetrahedron. We also compute tetrahedral *irregularity* as the standard deviation σ_b of the b_i. Clearly there are other geometrical quantities that describe tetrahedra and we will mention a few before concluding. Here we concentrate on b and σ_b to allow for a clear comparison with our previous experiments on colloidal glasses [15, 16].

In order to determine whether these quantities also age we plot the time dependence of b and σ_b averaged over all tetrahedra (and all MD runs) in Fig. 2. Since in Fig. 2 we plot t_w on a logarithmic axis we cannot include the values $\langle b \rangle|_{t_w=0} = 1.105$ and $\langle \sigma_b \rangle|_{t_w=0} = 0.141$, but it is clear that the majority of the adjustment in these quantities happens within the first ten LJ time units. In fact the monotonic evolution of $\langle b \rangle$ and $\langle \sigma_b \rangle$ slows down as the system ages and after a few hundred LJ time units from the quench, the change is less than 0.1% over a decade in time. This is compatible with the virtually flat time-dependence of these quantities observed in colloidal experiments [15]. This is especially so given then unavoidable lag between the macroscopic stirring which rejuvenates those sample and $t_w^{\rm exp} = 0$ which is set when transient flows due to the stirring subside. In other words, this could mean that the current method of initializing aging experiments in colloidal glasses forces one to miss the crucial first few hundred time units. On the other hand, this decelerating evolution is indicating that as the glass ages, it is getting harder and harder to find better ways to pack tetrahedra, and more interestingly that the aging process increases the average regularity of tetrahedra. The binary nature of the system and the complex nature of the pair potentials (when compared to hard-spheres) make it difficult to assert whether the regularization of tetrahedra in the glass is due to entropy alone. Nevertheless, this constitutes a single-time structural property of a glass that shows clear signs of aging.

To get a more complete picture of the changes tetrahedra undergo during aging we now consider the evolution of the distributions $P(b)$ and $P(\sigma_b)$. We start by plotting the probability distribution of obtaining a tetrahedron with average edge length b in Fig. 3 for the ages $t_w = 0$ with circles, $t_w = 10$ with diamonds, and $t_w = 10^5$ with squares. Again in marked contrast with our experimental work, we find that the distribution changes with age: as t_w increases $P(b)$ shifts to higher values of b and narrows. Here also, the most drastic change occurs between the configuration at $t_w = 0$ and at the next available time $t_w = 10$. This change in $P(b)$ is consistent with the increase in

$\langle b \rangle$ and decrease in $\langle \sigma_b \rangle$ observed in Fig. 2. We also computed reference distributions $P_{\rm ref}(b)$ of the average of six random nearest neighbor bonds at the three different ages. These are shown as solid, dotted and dashed curves respectively in the main plot of Fig. 3. These distributions sample all nearest neighbor bonds randomly, without the constraint that they be an edge of a tetrahedron. We find that these reference distributions do not match the $P(b)$ at the same age indicating that tetrahedral bonds sample the set of nearest neighbor bonds in a non-random way. Nevertheless, the $P_{\rm ref}(b)$ also age by shifting to higher b and narrowing. In this sense, all nearest neighbor bonds age similarly. The aging of this reference distribution is also related to the aging of the pair correlation function $g_{AA}(r)$ which in fact samples all bonds in the sample.

To determine whether the aging of $P(b)$ can be entirely described by the aging of its first and second moments and whether the aging reference distributions $P_{\rm ref}(b)$ are qualitatively different from that of the tetrahedral $P(b)$ we plot the rescaled probability density functions $P(\frac{b-\langle b \rangle}{\sigma_{\langle b \rangle}})$ on a semi-logarithmic plot in the inset of Fig. 3. We use $\sigma_{\langle b \rangle}$ to denote the standard deviation of looseness values b of all tetrahedra at a given t_w; this is distinct from σ_b, the irregularity of a single tetrahedron. Both the tetrahedral and reference data from all three ages collapse very well indicating that $\langle b \rangle$ and $\langle \sigma_b \rangle$ are sufficient to describe the aging of the tetrahedral edge length and that these edge lengths age in a qualitatively similar manner to all nearest neighbor bonds. In the inset we also included a Gaussian best fit (dashed) curve which highlights that $P(b)$ is not a Gaussian distribution. The skewness of all of the plotted distributions is about 0.2 and can be attributed to the asymmetry of the LJ potential with respect to its minimum.

Next we turn to the distribution of tetrahedra irregularities $P(\sigma_b)$ which is plotted for the same three ages in Fig. 4. We find that the distribution ages significantly: Firstly the peak of the distribution shifts to lower irregularities, as could be predicted by looking at the decrease of $\langle \sigma_b \rangle$ in the bottom pane of Fig. 2. This implies that aging somehow homogenizes tetrahedra. On the other hand, the width of $P(\sigma_b)$ stays roughly constant as the glass ages. This means that the variability of tetrahedral irregularity relative to the average actually increases with age. In this relative sense aging is instead diversifying the structure of the

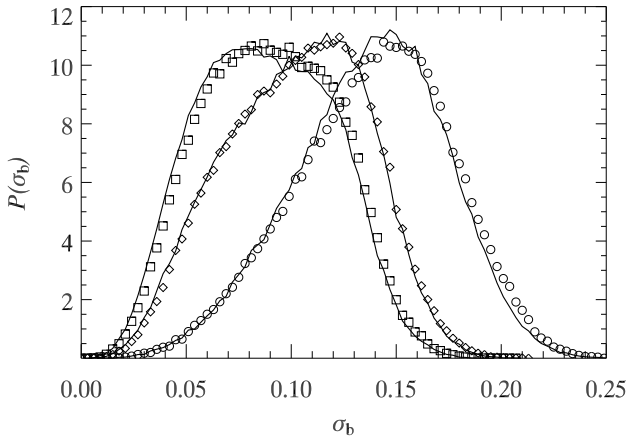

Fig.4 Probability distributions of tetrahedral irregularity. $P(\sigma_b)$ for $t_w = 0$: circles, $t_w = 10$: diamonds, and $t_w = 10^5$: squares. The solid lines are reference curves computed by considering sextuplets of random AA bonds based on $g_{AA}(r)$ without the constraint that they form tetrahedra.

sample. One more interesting observation is that the shape of the distributions is qualitatively changing (going from left-skewed to slightly right-skewed) with age. This is another static, one-time, description of the geometry of a glass that can tell the difference between a young and an old glass.

As we did for the distribution of looseness values, we also calculated a reference $P_{\rm ref}(\sigma_b)$ from the standard deviations of random sextuplets of nearest neighbor bonds. These reference curves are plotted with full lines in Fig. 4 and surprisingly, they match the tetrahedra curves fairly nicely, indicating that the aging effects described above affect all bonds at the same age in the same way.

4. Conclusion

We have analyzed the aging of a simple binary Lennard-Jones glass forming model in terms of tetrahedral structure and compared this model with an experimental colloidal glass.

Our findings here seem somewhat at odds with the colloidal suspension data. The present system shows aging even in one-time structural quantities such as the pair correlation function or the distributions of tetrahedral looseness values and irregularities. That was not the case in the colloidal samples. This discrepancy could be due to the rapidly decelerating pace of the aging of structure: it is possible that most of the aging occurs too quickly to be observable in

the experiments. Another possible source of deviation is the shape of the potential. Here we analyzed a Lennard-Jones system with both attractive and repulsive components, while the potential at work in the experiments is purely repulsive and quasi-hard sphere. To distinguish between these two possible causes further experiments are necessary which avoid transient flows while the glass is young and allow observation sooner. Another, complementary approach would be to simulate glasses with varying inter-particle potentials to determine whether it can affect the way structure ages.

We have also shown that, here as in our colloidal experiments, tetrahedral packing samples the microscopic geometry of the glass in a non-trivial way.

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