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An investigation of string-like cooperative motion in a strong network glass-former

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Abstract. The presence of string-like cooperative motion in silica, a strong network glass former, is investigated using large scale molecular dynamics simulations based on a realistic potential. We observe that dynamical heterogeneities and string-like motion in this strong glass-former show similarities with the results obtained by Donati et al. on a fragile model system. We observe that silicon and oxygen atoms are heterogeneously moving in a string-like fashion on different time scales corresponding to the maximum of their respective non-Gaussian parameter. We observe that the average string length increases when the temperature decreases. This result suggests that the length of the strings is not the determinant parameter for discriminating strong from fragile glass formers. We also observe that in silica the excess of cooperativity of mobile atoms is entirely due to the string-like motion of some of them.

PACS. 64.70.Pf Glass transitions – 61.20.Lc Time-dependent properties; relaxation

1 Introduction

The existence of increased cooperative motion in supercooled glass-forming liquids has long been speculated [1] as the likely explanation for the dramatic increase of the viscosity and of various time scales as the temperature is decreased. Cooperative motion is also commonly postulated in order to explain the non-exponential behavior of correlation functions and the non-Arrhenius behavior [2–4] of the viscosity of most glass-forming liquids.

Dynamical heterogeneities and associated cooperative behavior have been reported in various glass formers, either experimentally [2,5,6] near the glass transition temperature, or with molecular dynamics simulations [7–20] well above this temperature. Some of these heterogeneities were found to move in a string-like fashion [6–9]. Because a substantial increase of the static correlation functions is not observed, it is natural to speculate that the cooperative motions found in dynamic heterogeneities are related to an increase of cooperativity which is also supposed to be responsible for the non-Arrhenius behavior of fragile glass formers [2,4]. From this viewpoint, dynamic heterogeneities may be absent from strong glass formers or at least may be strongly different from the cooperative motions found in fragile glass formers.

On the other hand string-like motion in supercooled glass formers may be seen as a simple consequence of the cage effect. For example, among various possible mechanisms linking cage effect and string-like motion, if an atom finds its way outside the cage of its neighbors, it also opens a hole in a nearby cage at its previous position. This opportunity may then be used by another atom to escape the cage of its neighbors and enhanced by the mean field created by the other atoms, creating a string of cooperatively moving atoms. In this view, string-like cooperative motion has to be a universal characteristic of supercooled liquids just as the cage effect is.

In this article we investigate the cooperative motion of dynamic heterogeneities recently found in silica [20], a strong network glass former using large scale molecular dynamics simulations based on a realistic potential. We find that dynamical heterogeneities in this strong glass-former show similarities with the results of Donati et al. [7] in a fragile model system. We find string-like cooperative motion of atoms in silica on different time scales for the oxygen and silicon atoms. We also find that the mean length of the strings are of the same order as the string lengths found in the fragile model-glass former [7]. We find that the average string length increases when the temperature decreases. This result suggests that the length of the strings is not the determinant parameter for discriminating strong and fragile glass formers. Finally, we find that in silica the excess of cooperativity of mobile atoms is entirely due to the string-like motion of some of them. In accordance with this result, we find that the increase of

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the average string length versus time follows the increase of the non-Gaussian parameter versus time.

2 Simulations

The present simulations were carried out on a system of 9000 particles (3000 Si + 6000 O). The calculations used the molecular dynamics (MD) method with a Verlet algorithm [21] to integrate the equations of motion. The time step was chosen equal to 10^{-15} s. We used the modified [22] BKS potential [23] which is to our knowledge one of the best existing potentials to study the dynamics of silica [24–26]. In order to improve the algorithm efficiency the reaction-field method was employed to take into account long-range electrostatic interactions with a cutoff radius of 10 Å. The cutoff radius of the short range repulsive part of the potential was also set to 10 Å. A very short range repulsive part was also added, as described by Y. Guissani and B. Guillot [22], in order to eliminate the possible short range divergence of this potential. The use of the reaction-field method with this cutoff radius was found to decrease slightly the diffusion coefficients [27] in comparison with previous results of J. Horbach and W. Kob [26]. However, the diffusion was found to follow a very similar Arrhenius law [27] over the same temperature range [26] and to approach even slightly better the experimental data. A detailed study of the conditions used in our simulations will be found in reference [27]. The density was set constant at 2.3 g/cm^3. The box size is then constant at 50 Å. The system is heated to a temperature of 7000 K to insure homogenization. It is then cooled to the different investigation temperatures using a Berendsen thermostat [28]. The simulations are then aged during 20 ns in order to insure stabilization before any analysis.

In the Markovian approximation, the self part of the Van Hove correlation function $G_s(r,t)$ has a Gaussian form. This function is defined by

$$G_s(r,t) = \frac{1}{N}\sum_{i=1}^{N} \delta(r - (|\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0)|)), \qquad (1)$$

and $4\pi r^2 G_s(r,t)$ represents the probability for a particle to be at time $t+t_0$ at a distance r from its position at time t_0. This function does not depend on t_0 if the liquid is at equilibrium. N represents here the number of oxygen or silicon atoms. Departure from this Gaussian form has been found in various glass-forming liquids and they are thought to reflect the presence of dynamical heterogeneities. Such deviations are usually characterized by the non-Gaussian parameter (NGP):

$$\alpha_2(t) = 3\left\langle r^4(t)\right\rangle / 5\left\langle r^2(t)\right\rangle^2 - 1. \qquad (2)$$

The non-Gaussian parameter reaches a maximum for a characteristic time named t^*. t^* evolves with temperature and it is thought to be a characteristic of the heterogeneity. We define the mobility $\mu_{i,t_0}(t)$ of atom i at time t_0 within a characteristic time t, by the relation:

$$\mu_{i,t_0}(t) = |\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0)| / \left(\left\langle r^2(t)\right\rangle\right)^{0.5}, \qquad (3)$$

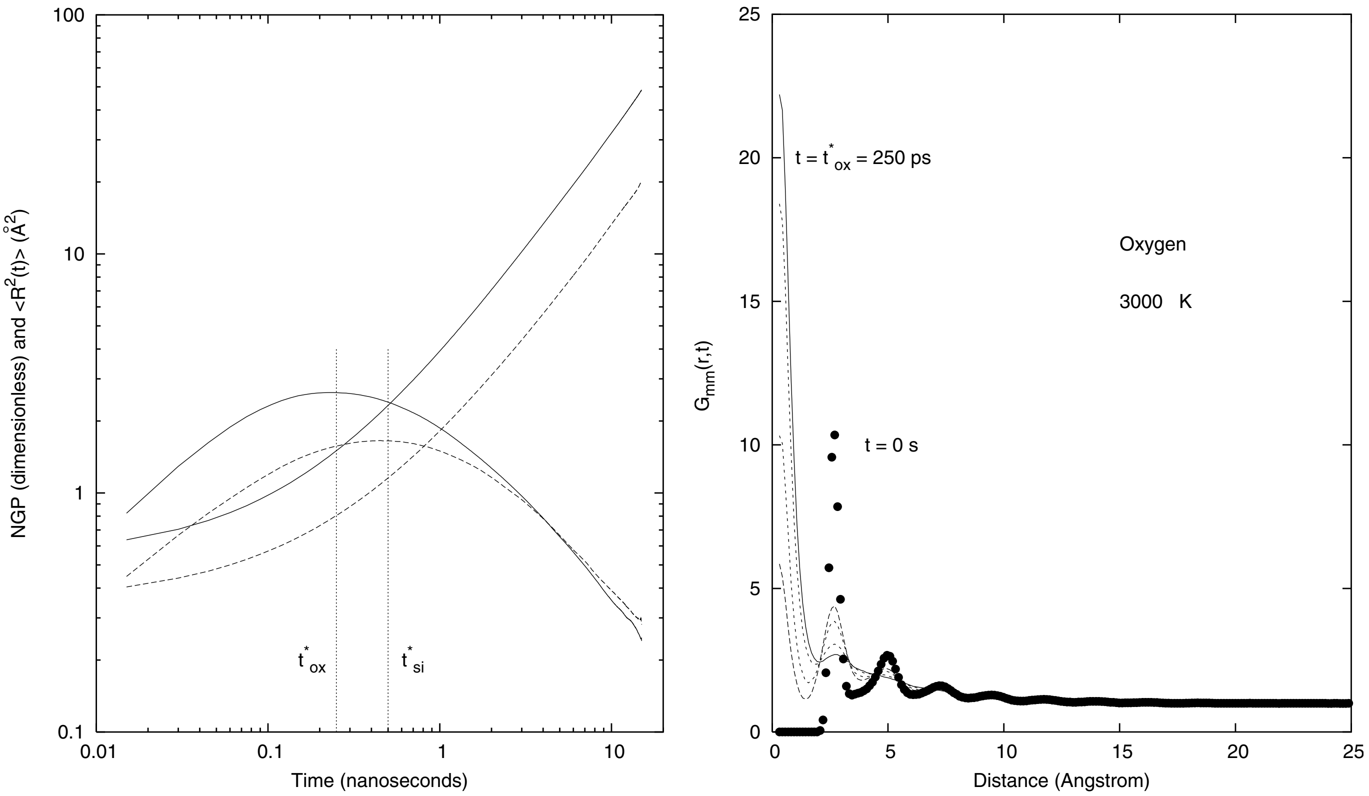
where $\langle r^2(t)\rangle$ is the mean-square displacement. The mobility of atom i at time t_0 is then defined as the normalized displacement of atom i during a time t. We will omit in further discussion the time t_0 which will disappear in the mean statistical values. We then select atoms of high mobility for the calculation of the dynamical heterogeneity. This selection is then dependent on the time t chosen in the definition of the mobility $\mu_i(t)$. When not specified, following Donati et al. [7] we use the time t^* corresponding to the maximum of the non-Gaussian parameter as the characteristic time in this procedure. However, we see in Figure 1a that the non-Gaussian parameter corresponding to oxygen atoms is different from the non-Gaussian parameter of silicon atoms. We then define t^*_{ox} and t^*_{si} as the times corresponding to the maximum of the non-Gaussian parameters of oxygen atoms and silicon atoms, respectively. We define here as mobile the 10 percent oxygen atoms with largest mobility on a time $t = t^*_{ox}$, and similarly the 4 percent silicon atoms with largest mobility on a time $t = t^*_{si}$.

3 Results

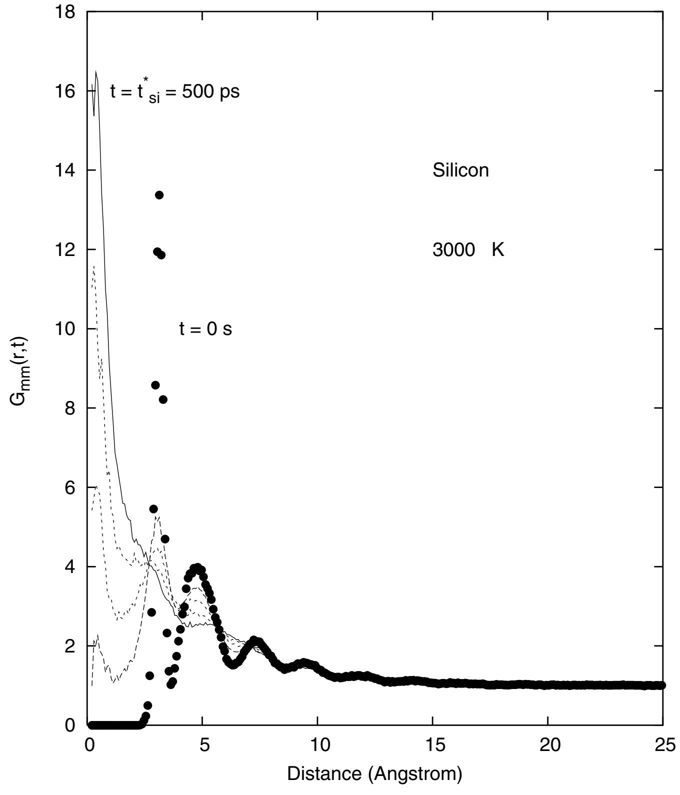
This section is organized in three parts. In the first part we show the presence of string-like cooperative motion for the oxygen and silicon atoms in silica. To ease the comparison with fragile glass formers, in this part we use the same correlation functions as Donati et al. [7]. In a second part, we investigate the temperature evolution of the mean string length and show that this length is not constant but evolves with temperature. This result is in contradiction with what may be predicted from a direct correlation between string length and fragility. Finally, we investigate the relation between string-like motion and cooperativity in silica. We show that cooperativity is directly related in this case with string-like motion.

Figure 1b shows the distinct part of the Van Hove correlation function $G_{mm}(r,t)$ between the 10 percent most mobile oxygen atoms at various times t. The function $G_{mm}(r,t)$ measures the probability to find at time t a mobile oxygen atom at a distance r from the position of another mobile oxygen atom at time zero. If some mobile oxygen atoms are moving string-like, the position of any mobile oxygen atom at time zero will have some probability to be occupied by another mobile oxygen atom at later time t. This will result in an increase of $G_{mm}(r,t)$ with time around $r = 0$ until t has reached the characteristic time of the string-like motion, as it can be seen in Figure 1b. An oxygen atom follows another one with a characteristic time equal to t^*_{ox} the time corresponding to the maximum of the oxygen non-Gaussian parameter (NGP). This effect leads then to string-like cooperative motion of oxygen atoms with a characteristic time t^*_{ox}.

Figure 1c shows the same Van Hove correlation function $G_{mm}(r,t)$ between the 4 percent most mobile silicon atoms. We also find in this figure string-like cooperative motion but with a different characteristic time t^*_{si} corresponding to the maximum of the NGP for silicon.



(a) (b)



(c)

Fig. 1. (a) Mean-square displacement and non-Gaussian parameter versus time at a temperature of 3000 K. The continuous lines correspond to oxygen atoms and the dashed lines to silicon atoms. The dotted lines mark the location of the maximum of the non-Gaussian parameter for oxygen (left) t^*_{ox} and silicon (right) t^*_{si}. We see on this figure that the times corresponding to the maxima of the non-Gaussian parameters correspond to the end of the plateau of the mean-square displacements where some atoms begin to escape the cage of their neighbors before the diffusion regime is reached for all atoms. (b) Distinct part of the Van Hove correlation function $G_{mm}(r,t)$ between the 10 percent most mobile oxygen atoms at a temperature of 3000 K for various t. Full circles correspond to $t = 0$ i.e. to the radial distribution function. The continuous line corresponds to $t = t^*_{ox}$ =250 ps (the time corresponding to the maximum of the non-Gaussian parameter for oxygen at a temperature of 3000 K). From top to bottom, the times are: 250 ps, 180 ps, 90 ps, 45 ps and 0 ps. (c) Distinct part of the Van Hove correlation function $G_{mm}(r,t)$ between the 4 percent most mobile silicon atoms at a temperature of 3000 K for various t. Full circles correspond to $t = 0$. The continuous line corresponds to $t = t^*_{si}$ =500 ps (the time corresponding to the maximum of the non-Gaussian parameter for silicon at a temperature of 3000 K). From top to bottom, the times are: 500 ps, 800 ps, 270 ps, 180 ps and 0 ps.

As seen in Figure 1a, t^*_{si} is larger than t^*_{ox} in relation with the difference between the respective diffusion coefficients. Moreover, the Van Hove correlation function shows a wider increase around $r = 0$ than for oxygen atoms. We then find two different string-like motions for oxygen and silicon evolving on different time scales. String-like motion is then present in liquid silica, a strong glass former, suggesting that this is a universal property of supercooled liquids. In both cases (silicon or oxygen) we have observed that a modification of the percentage of mobile or non-mobile atoms does not affect the characteristic time value. However, it affects the height of the peak at $r = 0$ which decreases when the percentage increases. This effect is clearly due to the contribution of more and more atoms non-participating to strings when the percentage of atoms that are defined as mobile is increased.

To measure the number of mobile oxygen atoms involved in the string-like motion with a typical time t, we define strings by connecting two mobile atoms i and j, if atom i is replacing atom j in a time t. More precisely, for a defined characteristic time t, atoms i and j will participate to the same string if $|G_{mm}(r_{ij}, t)| < 1.8$ Å, a distance shorter than the first maximum of the radial distribution function (RDF) between two oxygen atoms, and also shorter than the first maximum of the RDF between two silicon atoms. Figure 2a shows the percentage of mobile oxygen atoms $P(n)$ participating in a string of length n for various temperatures ($P(n)$ versus n). We observe that $P(n)$ decreases exponentially with n, a behavior similar to the results found in fragile liquids [7,8]. The slope of the exponential decreases with temperature and evolves also with the considered time t, reaching a minimum for t^*.

The corresponding mean length of the chain,

$$\langle n\rangle = \frac{\sum nP(n)}{\sum P(n)}, \tag{4}$$

displayed in Figure 2b ranges from approximately 1 at high temperature (1.7 at 3250 K, full triangles) to approximately 3 at a temperature of 3000 K (full circles). In the temperature range where the oxygen and silicon diffusion coefficients follow an Arrhenius law with this potential, the mean length of the chain is clearly increasing. This result suggests that the length of the strings is not the determinant parameter for discriminating strong and fragile glass formers, because in this case we should expect that the mean string length would not depend on temperature for a strong glass-former like silica. In other words we do not find the expected relation

$$D = D_0 \exp\left(-A(\langle n\rangle - 1)/T\right) \tag{5}$$

which has been obtained in the case of water [8]. For an Arrhenius glass former like silica, this relation would indicate that the mean string length $\langle n\rangle$ does not depend on temperature.

However, chains of different lengths may not contribute equivalently to the diffusion mechanism. Also, this calculation depends on the definition of mobile atoms, here the 10 percent most mobile ones. With the choice of Donati et al. [7] (5 percent most mobile) $\langle n\rangle$ will be increased here. In order to eliminate partly this effect we may, in the calculation of $P(n)$, weight each atom i involved in a chain of length n with the associated mean-square displacement $r^2(t^*, i)/\langle r^2(t^*)\rangle$. In this case we observe that the mean length increases slightly. However, even this choice is not perfect as an increase in t gives more importance to longer chains. Finally, we then find a mean length of the same order or even slightly higher than the length found for strings in fragile liquids for equivalent relaxation-time scales.

As seen in Figure 2b the maximum of the mean string length is reached at the same time than the maximum of the NGP t^* for the same atoms. We also see in Figure 2b an increase of the mean string length that follows roughly the increase of the non-Gaussian parameter. We define here the functions

$$A(r, t) = G_{mm}(r, 0)/G(r, 0) - 1, \tag{6}$$

and

$$A(r) = A(r, t^*_\alpha), \tag{7}$$

with $\alpha = \mathrm{O}$ or Si.

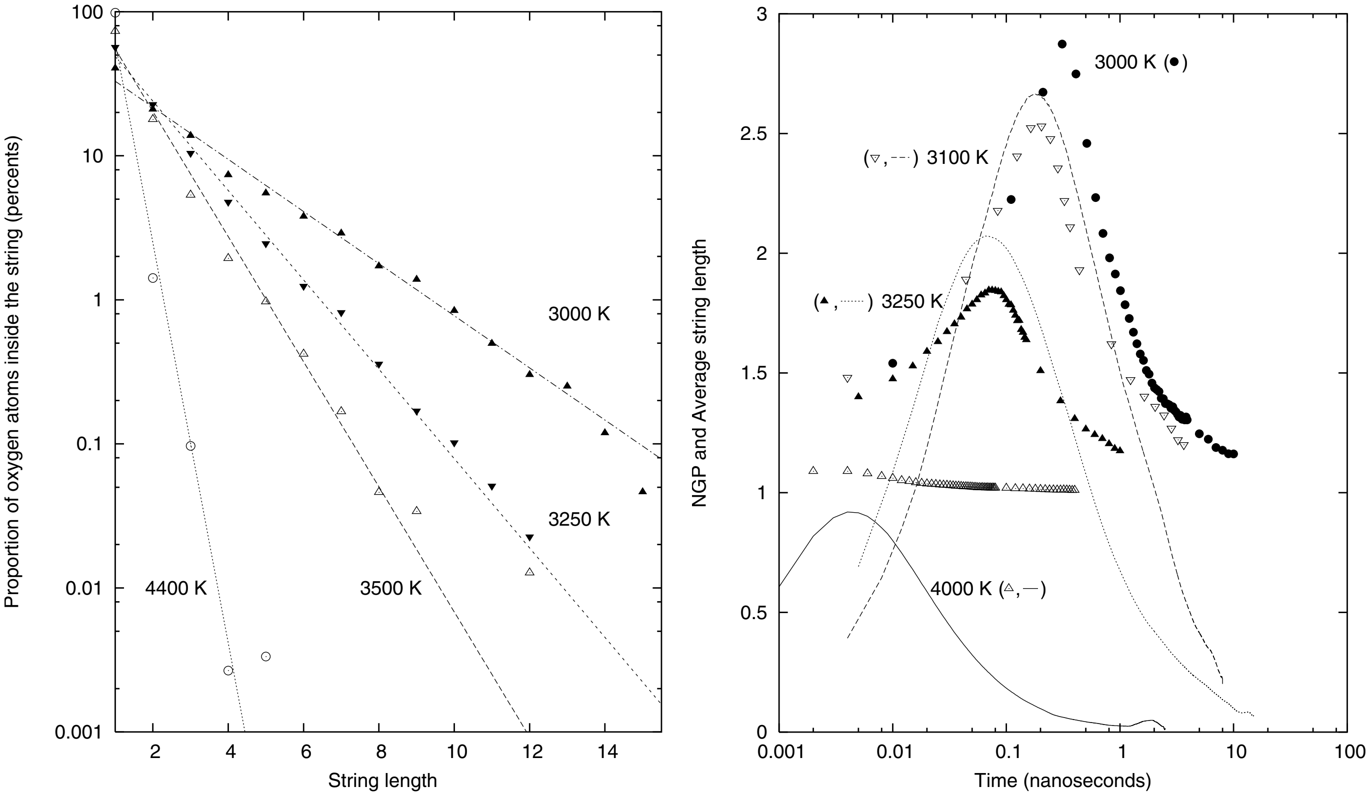
In this formula $G_{mm}(r, 0)$ is the radial distribution function between two mobile oxygen atoms, and $G(r, 0)$ is the mean radial distribution function between two oxygen atoms. Time t appears in this formula because the selection of the most mobile atoms depends on the time t chosen in the definition of the mobility $\mu_i(t)$ (Eq. (3)). In order to eliminate infinite values, we define $A(r, t) = 0$ and $A(r) = 0$ when $G(r, 0) < 0.05$. This definition implies that $A(r, t)$ is only meaningful above a certain cutoff distance defined by $G(r, 0) > 0.05$. The cutoff distance is here 2.2 Å for oxygen atoms and 2.7 Å for silicon atoms.

$A(r)$ gives a measure of the correlation increase between mobile oxygen atoms. When the considered mobile atoms have the same correlation than the mean atom, $A(r)$ is zero. The function $A(r)$ for the whole set of mobile oxygen atoms (first line in Fig. 3) is different from zero showing an increase in correlation for mobile atoms and then cooperative dynamics. This result that disappears at higher temperatures was found in various supercooled liquids and associated with dynamical heterogeneity.

Using the integral $I(t)$ of the function $A(r, t)$,

$$I(t) = \int_0^\infty A(r, t) 4\pi r^2 dr, \tag{8}$$

as a measure of cooperativity, we find that the time corresponding to the maximum of the cooperativity is also equal to t^*. These results suggest that the three corresponding mechanisms (non-Gaussian behavior of the Van Hove, cooperativity of the most mobile atoms, string motion) are linked to some extent. As seen in Figure 1a, the times t^* (t^*_{ox} for the oxygen atoms and t^*_{si} for the silicon atoms) correspond here to the end of the plateau of the mean-square displacement where some atoms begin to escape the cage of their neighbors before the diffusion regime is reached for all atoms.



(a) (b)

Fig. 2. (a) Probability of finding a mobile oxygen atom in a string of length n for various temperatures. A string of length 1 (the minimum) is a solitary mobile atom. From top to bottom the temperatures are: 3000, 3250, 3500, 4400 K. We have used the following characteristic times t^*_{ox} in these calculations: 250 ps for 3000 K, 70 ps for 3250 K, 22 ps for 3500 K and 2 ps for 4400 K. (b) Mean oxygen string length $\langle n \rangle = \frac{\sum nP(n)}{\sum P(n)}$ versus time for various temperatures (circles and triangles) together with the oxygen non-Gaussian parameter (lines) at the same temperatures. From top to bottom temperatures are: 3000, 3100, 3250, 4000 K (the NGP corresponding to 3000 K is not shown in order to improve legibility).

In Figure 3 we discriminate between mobile atoms participating in strings of different lengths. We show in this figure the function

$$A^n(r) = G^n_{mm}(r,0)/G(r,0) - 1 \qquad (9)$$

for mobile oxygen atoms participating in strings of different lengths. In this formula $G^n_{mm}(r,0)$ is the radial distribution function between mobile oxygen atoms participating in a string of length n, and $G(r,0)$ is the mean radial distribution function between two oxygen atoms. $A^n(r)$ gives a measure of the correlation increase between mobile oxygen atoms in a string of length n. We see in Figure 3 that the correlation increases dramatically with the length of the string. More interesting, we see that mobile oxygen atoms which are not included in strings have the same correlation than the mean oxygen atoms as $A^1(r) = G^1_{mm}(r,0)/G(r,0) - 1 = 0$. This result suggests that in silica the cooperative motion of mobile atoms is entirely due to the string-like dynamics. We then observe that mobile atoms which do not participate in strings are not cooperative in nature for silica.

4 Conclusion

In summary, our results support the hypothesis that string-like cooperative motion is a universal property of supercooled liquids, like the cage effect is. The mean length of the strings, which has been supposed to be a measure of the size of the cooperatively rearranging regions [8] in the context of Adam and Gibbs theory [1], is not significantly different in this strong glass former compared to fragile ones. In silica we do not find the expected relation (5) linking the diffusion coefficient with the mean string length. In an Arrhenius glass former this relation would imply a constant mean string length $\langle n \rangle$. On the other hand, we also observe that mobile atoms that do not participate in strings are not cooperative in nature for silica, suggesting that string-like motion is at the origin of the observed cooperativity of mobile atoms. In accordance with this view, the size of the string, the non-Gaussian parameter, and the cooperativity parameter $I(t)$ evolve in the same way. The size of the strings $\langle n \rangle$ is then a measure of the cooperativity of mobile atoms

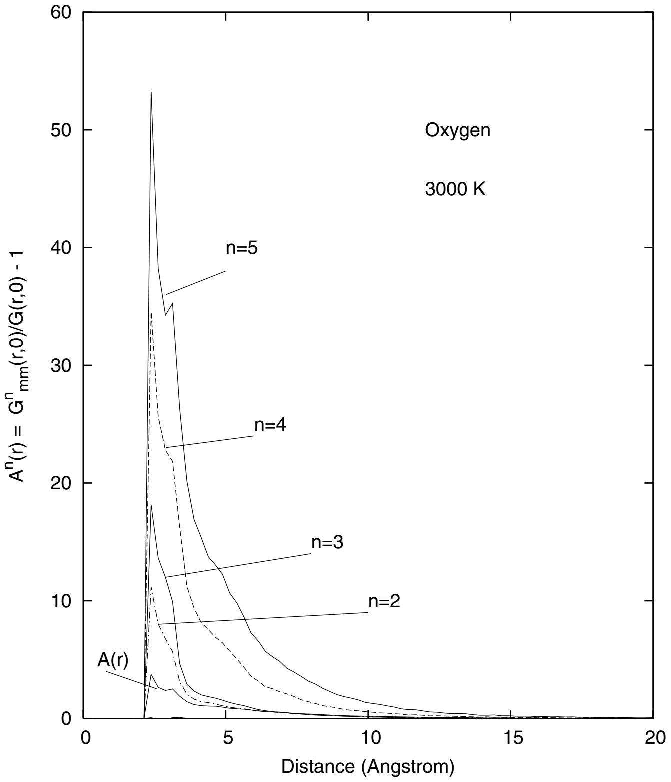


Fig. 3. $A^n(r) = G^n_{mm}(r,0)/G(r,0) - 1$ for various string lengths n, at a temperature of 3000 K for mobile oxygen atoms. From top to bottom the string length are: 5, 4, 3 and 2. The first line from the bottom corresponds to $A(r) = G_{mm}(r,0)/G(r,0) - 1$. It is not possible to see the string of length 1 (single atom) plotted here as $A^1(r) = 0$.

involved in dynamical heterogeneity, but it is not for silica a direct measure of the configurational entropy of the Adam and Gibbs theory.

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