The Dynamics of Non-Crystalline Silica: Insight from Molecular Dynamics Computer Simulations

Walter Kob, Jürgen Horbach, and Kurt Binder

Institute of Physics, Johannes Gutenberg University, Staudinger Weg 7, D-55099 Mainz, Germany

Abstract. Using a large scale molecular dynamics computer simulation we investigate the dynamics of a supercooled melt of SiO$_2$. We find that with increasing temperature the temperature dependence of the diffusion constants crosses over from an Arrhenius-law, with activation energies close to the experimental values, to a power-law dependence. We show that this crossover is related to the fact that at low temperatures the dynamics of the ions is dominated by hopping processes, whereas at high temperatures it shows the continuous flow-like motion proposed by the ideal version of mode-coupling theory (MCT). Finally we show that at low temperatures the dynamics of the system in the $\beta-$relaxation regime obeys the factorization property, in agreement with MCT.

INTRODUCTION

In the last few years a significant advance in our understanding of the dynamics of glass-forming liquids has occurred. By now it is well established that features like, e.g., the cage-effect, the slow dynamics in the $\beta-$relaxation regime, and the stretching of the relaxation curves in the $\alpha-$relaxation regime, are characteristic for the dynamics of supercooled liquids, and that many of these features are described well, or have even been predicted, by mode-coupling theory (MCT) [1]. For fragile glass-formers [2] there are even systems for which MCT describes the relaxation dynamics correctly not only on a qualitative level, but even on a quantitative one, such as colloidal particles or Lennard-Jones systems [3–5]. The dynamics of strong glass-formers is, however, understood in much less detail since it is, e.g., not yet clear whether the features predicted by MCT to be present in the $\beta-$relaxation regime, such as the critical decay or the von Schweidler law, do not exist in these system or are just obscured by other dynamical features, such as the boson-peak. In the present paper we therefore present some results of a large scale computer simulation in which we investigated the dynamics of a silica melt, the prototype of a strong glass former.
MODEL AND DETAILS OF THE SIMULATION

The silica model we study has been proposed by van Beest et al. (BKS) [6] and has been found in the past to reproduce well various structural properties of real silica [7]. In this potential the interaction between the ions is given by

$$\phi(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6}.$$  \hspace{1cm} (1)

Here $r_{ij}$ is the distance between ions $i$ and $j$, and the values of the partial charges $q_i$ and the constants $A_{ij}$, $B_{ij}$, and $C_{ij}$ can be found in Refs. [6,7]. The simulations have been done at constant volume using 8016 ions and a box size of 48.37Å, thus at a density of 2.37g/cm$^3$, close to the experimental value of the density. (Such a large system was needed to avoid finite size effect in the dynamics [8].) Using Ewald sums to evaluate the Coulombic part of the potential, the equations of motion have been integrated with the velocity form of the Verlet algorithm with a time step of 1.6 fs. The temperatures investigated were 6100 K, 5200 K, 4700 K, 4300 K, 4000 K, 3760 K, 3580 K, 3400 K, 3100 K, 3000 K, 2900 K and 2750 K, and in order to improve the statistics of the results we averaged at each temperature over two independent runs. At each temperature the system was first equilibrated over a time span which significantly exceeded the typical relaxation time of the system at this temperature. At the lowest temperature the runs had 13 million time steps, which is equivalent to about 20 ns of real time. The total CPU time used for this temperature was 13 years of single processor time on a CRAY-T3E.

RESULTS

The simplest quantity which characterizes the dynamics of a system is $\langle r^2(t) \rangle$, the mean squared displacement (MSD) of a tagged particle, which is calculated from the positions $\vec{r}_j(t)$ by means of

$$\langle r^2(t) \rangle = \frac{1}{N_{\alpha}} \sum_{j=1}^{N_{\alpha}} \langle |\vec{r}_j(t) - \vec{r}_j(0)|^2 \rangle \quad \text{with } \alpha \in \{ \text{Si, O} \}. \hspace{1cm} (2)$$

In Fig. 1 we show the time dependence of $\langle r^2(t) \rangle$ for the oxygen atoms for all temperatures investigated. (Qualitatively similar curves are found for the silicon atoms [9].) From this figure we see that at high temperatures the MSD crosses over from the ballistic motion of the particles, $\langle r^2(t) \rangle \propto t^2$, to the diffusive motion, $\langle r^2(t) \rangle \propto t$. At low temperatures we see in addition to these two regimes also a third one at intermediate time scales, in which the MSD stays essentially constant over 2-3 decades in time. In this time regime the particle is trapped in the cage formed by the atoms that surround it, and it takes the particle a long time before it is able to leave this cage. One of the main features of MCT is to give a self-consistent description of this motion, and below we will discuss some of these predictions.
(Self-consistency is needed since the particles forming the cage are trapped by their neighbors.)

Using the Einstein relation \( D = \lim_{t \to \infty} \langle r^2(t) \rangle / 6t \), it is simple to calculate the diffusion constant \( D \) from the MSD. The temperature dependence of \( D \) is shown in Fig. 2 for \( D_{Si} \) and \( D_{O} \) in an Arrhenius plot. We see that at low temperatures the diffusion constants show the Arrhenius dependence expected for a strong glass-former. The activation energies found, 5.18 eV and 4.66 eV for silicon and oxygen, respectively, are in very good agreement with the experimental values of Brébec et al. (silicon: 6 eV) and Mikkelsen (oxygen: 4.7 eV) [10]. Since a similar good agreement has been found for the temperature dependence of the viscosity [11] we thus conclude that the present model of silica is not only able to reproduce reliably the static properties of amorphous silica [7], but also the dynamic ones.

From the figure we also see that at high temperatures significant deviations from the Arrhenius law are observed. Such deviations are often found in fragile glass-formers and have been explained by means of MCT, which predicts that in supercooled systems there exists a critical temperature \( T_c \) in the vicinity of which transport coefficients, such as the diffusion constant or the \( \alpha \)-relaxation time \( \tau \), show a power-law dependence on temperature, i.e.

\[
D \propto \tau^{-1} \propto (T - T_c)^\gamma ,
\]  

(3)
where the exponent $\gamma$ is a system universal parameter, i.e. is independent of the transport coefficient. Motivated by this theoretical prediction we thus have attempted to fit the temperature dependence of the diffusion constants with such a power-law and have included the results of these fits in Fig. 2 as well (dashed lines). Note that in these fits the critical temperature $T_c$ was not used as a fit parameter but fixed to 3330 K, a value we obtained from fits to the relaxation times $\tau$ of the intermediate scattering function for different values of the wave-vector $q$ (which will be discussed below). From the figure we can see that the so obtained fits reproduce the data very well over a temperature range in which the diffusion constants change by about 1.5 decades. This range is significantly smaller than the one typically found in fragile glass-formers (3-4 decades [12]) and it is often argued that such a small range is related to the dominant presence of activated processes, the so-called hopping processes, which are taken into account only in the “extended” version of MCT [13] and not in the “ideal” version [1].

One way to see the mentioned hopping processes directly is to study the self part of the van Hove correlation function, $G_s(r, t)$, which is given by

$$G_s^\alpha(r, t) = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \langle \delta(r - |\vec{r}_i(t) - \vec{r}_i(0)|) \rangle \quad \alpha \in \{\text{Si, O}\} .$$  \hspace{1cm} (4)
FIGURE 3. $r-$dependence of the self part of the van Hove correlation function for the oxygen atoms. The times are 0.16 ps, 1.44 ps and then increase by a factor of about 2.3. The last curves are 15.2 ns and 19.2 ns. Inset, the same curves in a lin-log plot. The arrow marks the location of the first peak in the radial distribution function between two oxygen atoms.

Thus $4\pi r^2 G_Q^O(r,t)$ is the probability to find a particle at time $t$ at a distance $r$ away from the place it was at $t=0$. In Fig. 3 we show the $r-$dependence of $4\pi r^2 G_Q^O(r,t)$ for different times for the lowest temperature investigated.

In the main figure we see that at intermediate times this function is peaked at around 0.4 Å and hardly depends on time. This observation can be understood by recalling that in this time regime, the $\beta-$regime, the particles are trapped in the above discussed cages formed by the surrounding particles. Only for times corresponding to the $\alpha-$relaxation this peak starts to decrease significantly and the function begins to show a secondary peak, or rather a shoulder, at a distance around 2.6 Å, the location of the first peak in the radial distribution function between two oxygen atoms [7,14]. This secondary peak can be better seen in a semi-logarithmic plot of this function, which is shown as an inset of the figure. Hence we conclude that at low temperatures the cage for the oxygen atoms breaks up because an atom jumps to the location of one of its six nearest oxygen neighbors, assuming that no other oxygen atom is at this position (see also Ref. [15]). Note that this type of motion is very different from the one found in the relaxation of a fragile glass-former (Lennard-Jones system [12]) since in that case the breaking up of the cage occurs in that the main peak observed in the $\beta-$relaxation becomes broader and moves
FIGURE 4. Time dependence of the incoherent intermediate scattering function for the oxygen atoms for different temperatures.

to larger distances and no secondary peak is observed at any time, thus showing that in these systems no jump processes are present.

The relaxation dynamics of the system can also be studied well by means of the (incoherent) intermediate scattering function $F_{s}^{\alpha}(q, t)$, which is given by a space Fourier-transform of $G_{s}^{\alpha}(r, t)$, i.e.

$$F_{s}^{\alpha}(q, t) = N_{\alpha}^{-1} \sum_{j=1}^{N_{\alpha}} \langle \exp \left( i \vec{q} \cdot (\vec{r}_{j}(t) - \vec{r}_{j}(0)) \right) \rangle. \quad (5)$$

The time dependence of $F_{s}^{O}(q, t)$ is shown in Fig. 4 for all temperatures investigated. The value of $q$ is 1.7 Å$^{-1}$, the location of the first peak in the static structure factor. We have found that the correlation functions for different wave-vectors as well as those for the silicon atoms are qualitatively similar to the one presented here. The same is true for the coherent intermediate scattering functions. From the figure we see that with decreasing temperature the $\alpha$–relaxation time increases quickly and we have found that its temperature dependence is very similar to the one of the diffusion constants (see Fig. 2) in that it shows an Arrhenius dependence at low temperatures and at high and intermediate temperatures a dependence which can be fitted well with the power-law given in Eq. (3) [11]. (It was from this temperature dependence that the critical temperature $T_{c} = 3330$ K was determined.) In particular we find that for temperatures above $T_{c}$, the product between $\tau$ and $D$
was essentially constant, as it is predicted by MCT, whereas below $T_c$ the product increases (which is not in contradiction to the extended version of MCT).

We see that also in $F_s(q, t)$ the cage effect is seen very well in that at low temperatures the relaxation function shows a plateau. Before the correlators reach this plateau, they show a pronounced dip, a feature not present in the dynamics of fragile glass-formers. This dip is the signature of the so-called boson-peak, a dynamical feature whose origin is still a matter of debate [9,16].

For the time-range of the $\alpha-$relaxation, MCT predicts that the so-called time-temperature superposition principle (TTSP) holds, i.e. that a time correlation function $\phi(t)$ can be written as

$$\phi(t) = \Phi(t/\tau(T)),$$

where $\Phi$ is a master function which will depend on $\phi$. This prediction of the theory can easily be tested by plotting the time correlation function versus the rescaled time $t/\tau$, which is done in Fig. 5 for the intermediate scattering function shown in Fig. 4. From the figure we see that in the $\alpha-$relaxation regime this type of scaling leads indeed to a nice collapse of the curves for the different temperatures, as predicted by the theory. In the time regime of the late $\beta-$relaxation, however, strong deviations from the TTSP are observed, in contrast to what has been found in many fragile glass formers. A detailed analysis of the curves has shown [14]
that the violation of the TTSP in this time regime is due to the presence of the boson-peak, since the intensity of this feature depends significantly on temperature and thus leads to a strong temperature dependence of the height of the plateau and hence to a violation of the TTSP in this time window. However, the *shape* of the curves was found to be essentially independent of temperature, in agreement with the prediction of MCT [14]. In particular we have found that in the late \( \beta \)-relaxation regime this shape, i.e. the time dependence, is described very well by the so-called von Schweidler law, i.e. \( F_s(q, t) = f_s(q) - h(q)t^b \), where according to MCT the exponent \( b \) is related to the critical exponent \( \gamma \) of Eq. (3) [1], a relationship which we have found to hold to within 10% for the present system.

It is sometimes argued that the ideal version of MCT does not hold below \( T_c \), since real systems will always show ergodicity restoring hopping processes, and since the details of the extended theory have not been worked out, the whole theory becomes useless at low temperatures. In the following we will demonstrate that such an attitude is overly pessimistic and does not correspond to reality. Although the extended version of MCT does not make predictions on the \( \alpha \)-relaxation regime, it makes useful and testable prediction in the \( \beta \)-relaxation regime. In particular the theory predicts that in this regime the so-called factorization property should hold. This means that any time correlation function \( \phi(t) \) can be written as follows:

\[
\phi(t) = \phi_c + h g(t) \tag{7}
\]

Here the constant \( \phi_c \) is the height of the plateau (see Fig. 4), also sometimes called nonergodicity parameter, and \( h \) is a constant which is called critical amplitude. Both quantities depend on \( \phi \). The important point is that the time dependence of \( \phi \) is given by the *system universal* function \( g(t) \), i.e. a function that does not depend on \( \phi \). One possibility to test whether the factorization property holds is to calculate the ratio

\[
R_\phi(t) = \frac{\phi(t) - \phi(t')}{\phi(t'') - \phi(t')} \tag{8}
\]

Here \( t' \) and \( t'' \neq t' \) are two arbitrary times in the \( \beta \)-relaxation regime. A trivial calculation shows that the quantity \( R_\phi(t) \) will be independent of \( \phi \) if \( \phi(t) \) can be written in the form given by Eq. (7). In order to test this prediction of the theory we therefore plot in Fig. 6 the time dependence of \( R_\phi \) for different correlators \( \phi(t) \) at \( T = 2750 \) K. In particular we use for \( \phi(t) \) the incoherent intermediate scattering function for oxygen at \( q = 2.8 \text{Å}^{-1} \), the coherent intermediate scattering function for the Si–Si correlation at \( q = 1.7 \text{Å}^{-1} \), the function \( b_s(t) = \int_0^{0.44} 4\pi r^2 G_s(r, t) dr \), and \( a_{\text{Si–O}}(t) = \int_{1.32}^{2.35} 4\pi r^2 \left[ G_{\text{Si–O}}(r, t) - 1 \right] \left[ g_{\text{Si–O}}(r) - 1 \right] dr \). Here \( G_{\text{Si–O}}(r, t) \) and \( g_{\text{Si–O}}(r) \) are the distinct part of the van Hove correlation function and the radial distribution function between Si–O atoms, respectively [17]. (These two last functions have been proposed by Roux et al. and have no deep physical meaning, but are just functions which can be calculated with relatively high accuracy [15]. The
FIGURE 6. The ratio $R_\phi(t)$, see Eq. (8), for different correlation functions $\phi$ as a function of time. $T = 2750$ K. See text for details.

occurring integration boundaries are related to the location of the minima in the radial distribution function [14].

From the figure we see that in the time scale of the $\beta$-relaxation regime the different curves collapse nicely onto a master curve, as it is predicted by MCT. For times outside this regime no collapse is observed, demonstrating that the existence of a master curve is a nontrivial feature. We emphasize that the curves are for a temperature which is considerably below $T_c$ and that, as demonstrated above by means of the diffusion constants and the van Hove correlation functions, at this temperature the hopping processes are very prominent. Thus we conclude that, although not all details of the extended version of MCT have been worked out, this theory is indeed able to make interesting and testable predictions also below $T_c$. Finally we mention that we have found that the factorization property also holds well at temperatures as high as $T = 4000$ K, i.e. above the critical temperature $T_c = 3330$ K, in agreement with the theory.

SUMMARY AND DISCUSSION

We have presented the results of a large scale molecular dynamics computer simulation of a realistic model, the BKS model [6], of supercooled silica, the prototype of a strong glass-former. Although we find that the time dependence of the mean
squared displacement of a tagged particle is roughly similar to the one in a fragile glass-former [12], important differences can be noted, such as, e.g., an overshoot which is related to the boson-peak as well as the temperature dependence of the long time behavior. The latter is related to the temperature dependence of the diffusion constant $D$ and we find that $D(T)$ shows at low temperatures an Arrhenius behavior with activation energies that agree very well with experimental values, thus giving evidence that this silica model is indeed quite realistic. With increasing temperature significant deviations from the Arrhenius-law are observed and we find that the temperature dependence of $D$ can be fitted well with the power-law proposed by MCT with a critical temperature $T_c$ around 3330 K. Thus we find that for this strong glass former $T_c$ is more than twice the experimental glass transition temperature $T_g$ which is at 1450 K. (We note that in Ref. [11] we have given evidence that the BKS model has an experimental glass transition temperature which is close to the real one.) Thus these results support the idea [18] that also for strong glass-formers there is a temperature range in which the predictions of the ideal version of MCT hold, that, however, for the case of silica this range is at temperatures which are currently difficult to access by experiments.

For temperatures below $T_c$ we find, by investigating the self part of the van Hove correlation function, that the motion of the particles is strongly influenced by jump like motions of the oxygen atoms, i.e. that instead of the flow-like motion of the particles proposed by the ideal version of MCT above $T_c$, it might be more appropriate to think of a quasi-frozen potential energy landscape in which the dynamics is mainly given by the hopping of the particles [19]. That the presence of these strong hopping processes does not exclude the possibility that MCT makes useful predictions also at low temperatures, is demonstrated by our investigation of the factorization property [see Eq. (7)]. We show that this property holds very well even at temperatures at which the dynamics of the system is strongly influenced by hopping processes. Furthermore we have found [11] that the master curve obtained, see Fig. 6, is in the late part given by the von Schweidler law with an exponent $b$, which fulfills the relation proposed by MCT between $b$ and the critical exponent $\gamma$ of the relaxation times [1].

Finally we have also investigated the time and temperature dependence of the incoherent intermediate scattering function. We find that the time-temperature superposition principle holds well in the late $\alpha$-relaxation regime that, however, quite large deviations are observed in the $\beta$-relaxation regime. The reason for these differences is the boson-peak, which leads to a temperature dependence of the height of the plateau. The form of the curves, however, is indeed independent of temperature, as can be seen from the factorization property.

Thus we can summarize by saying that many aspects of the dynamics of this strong glass-former can be understood by means of MCT, although the agreement between the ideal version of the theory and the results of the simulation is less satisfying as it has been found to be for fragile glass-formers. In particular the range over which the power-law for the diffusion constants can be observed is relatively small and the strong influence of the boson-peak onto the $\beta$-relaxation leads to a
breakdown of some, but not all, of the predictions of the theory in this time window. Nevertheless, the extended version of the theory is able to describe correctly some aspects of the dynamics also at low temperature, a result which should encourage to work out this version of the theory in more detail.

ACKNOWLEDGMENTS

This work was supported by BMBF Project 03 N 8008 C and by SFB 262/D1 of the Deutsche Forschungsgemeinschaft. We also thank the HLRZ Jülich and the RUS in Stuttgart for a generous grant of computer time on the T3E.

REFERENCES

1. W. Götze and L. Sjögren, Rep. Prog. Phys. 55, 241 (1992); W. Kob, p. 28 in Experimental and Theoretical Approaches to Supercooled Liquids: Advances and Novel Applications Eds.: J. Fourkas, D. Kivelson, U. Mohanty, and K. Nelson (ACS Books, Washington, 1997).
2. C. A. Angell, in Relaxation in Complex Systems, Eds.: K. L. Ngai and G. B. Wright (US Dept. Commerce, Springfield, 1985).
3. E. Bartsch, M. Antonietti, W. Schupp, and H. Sillescu, J. Chem. Phys. 97, 3950 (1992); W. van Megen and S.M. Underwood, Phys. Rev. E 49, 4206 (1994); W. Götze and L. Sjögren, Phys. Rev. A 43, 5442 (1991).
4. M. Nauroth and W. Kob, Phys. Rev. E 55, 657 (1997).
5. T. Gleim, W. Kob, and K. Binder, Phys. Rev. Lett. 81, xxxx (1998).
6. B. W. H. van Beest, G. J. Kramer, and R. A. van Santen, Phys. Rev. Lett. 64, 1955 (1990).
7. K. Vollmayr, W. Kob, and K. Binder, Phys. Rev. B 54, 15808 (1996).
8. J. Horbach, W. Kob, K. Binder, and C. A. Angell, Phys. Rev. E. 54, R5897 (1996).
9. J. Horbach, W. Kob, and K. Binder, Phil. Mag. B 77, 297 (1998).
10. J. C. Mikkelsen, Appl. Phys. Lett. 45, 1187 (1984);
    G. Brébec, R. Seguin, C. Sella, J. Bevenot, J. C. Martín, Acta Metall. 28, 327 (1980).
11. J. Horbach, W. Kob, and K. Binder, preprint 1998.
12. W. Kob and H. C. Andersen, Phys. Rev. Lett. 73, 1376 (1994); Phys. Rev. E 51, 4626 (1995); ibid. 52, 4134 (1995).
13. S. P. Das and G. F. Mazenko, Phys. Rev A 34, 2265 (1986); W. Götze and L. Sjögren, Z. Phys. B 65, 415 (1987); M. Fuchs, W. Götze, S. Hildebrand, and A. Latz, J. Phys.: Condens. Matter 4, 7709 (1992); R. Schmitz, J. W. Dufty, and P. De, Phys. Rev. Lett. 71, 2066 (1993).
14. J. Horbach, PhD Thesis, University of Mainz, 1998.
15. J. N. Roux, J.-L. Barrat, and J.-P. Hansen, J. Phys.: Condens. Matter 1, 7171 (1989).
16. A. Wischnewski, U. Buchenau, A. J. Dianoux, W. A. Kamitakahara, and J. L. Zarestky, Phys. Rev. B 57, 2663 (1998); P. Benassi, M. Krisch, C. Masciovecchio, V. Mazzacurati, G. Monaco, G. Ruocco, F. Sette, and R. Verbeni, Phys. Rev. Lett. 77,
3835 (1996); M. Foret, E. Courtens, R. Vacher, and J.-B. Suck, Phys. Rev. Lett. 77, 3831 (1996); S. N. Taraskin and S. R. Elliott, Europhys. Lett. 39, 37 (1997); Phys. Rev. B 56, 8605 (1997); J. Horbach, W. Kob, and K. Binder, J. Non-Cryst. Solids 235-238, 320 (1998); W. Schirmacher, G. Diezemann, and C. Ganter, Phys. Rev. Lett. 81, 136 (1998).

17. J.-P. Hansen and I. R. McDonald, Theory of Simple Liquids (Academic, London, 1986).
18. E. Rössler and A. P. Sokolov, Chemical Geology, 128, 143 (1996).
19. M. Goldstein, J. Chem. Phys. 51, 3728 (1969).