Molecular dynamics simulation of aging in amorphous silica

Holger WAHLEN[1] and Heiko RIEGER[2]

[1] *John von Neumann Institute for Computing, Forschungszentrum Jülich, 52425 Jülich, Germany*
[2] *FB 10.1 Theoretische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany*

(Received November 28, 2001)

By means of molecular dynamics simulations we examine the aging process of a strong glass former, a silica melt modeled by the BKS potential. The system is quenched from a temperature above to one below the critical temperature, and the potential energy and the scattering function $C(t_\mathrm{w}, t + t_\mathrm{w})$ for various waiting times t_w after the quench are measured. We find that both qualitatively and quantitatively the results agree well with the ones found in similar simulations of a fragile glass former, a Lennard-Jones liquid.

§1. Introduction

In the recent years aging effects have become a very active field of research in the study of non-equilibrium systems. Common features have been found in the aging behavior of spin and structural glasses in experiments and simulations, and similarities in the theories worked out indicate the possibility of a connection between the slow dynamics in both types of glasses.2)

Even though silica (SiO_2), a strong glass former, has been examined frequently both in theories and experiments, comparatively few simulations have been performed so far on the dynamics of systems like this that form an open network structure. In this paper we present several results of aging simulations for silica and compare them to those obtained for a model for a fragile glass former, a binary Lennard-Jones mixture.

§2. Simulation

2.1 BKS potential

The model we used in our simulations is given by the potential proposed by van Beest, Kramer and van Santen (BKS):1)

$$U_{jk}(r_{jk}) = \frac{\gamma q_j q_k}{r_{jk}} + A_{jk}\exp(-B_{jk} r_{jk}) - \frac{C_{jk}}{r_{jk}^6}$$

with $\gamma = e^2/(4\pi\varepsilon_0)$; the values of the parameters, taken from the original publication, are listed in tables I and II. As has been shown in previous calculations and simulations, this potential reproduces many of both the structural10) and dynamical properties of silica and has frequently been used for simulations of the amorphous phase. Moreover, it has the advantage of consisting of two-body interactions only, so that it can be implemented in a simulation more efficiently than some other potentials proposed for silica that also contain three-body terms. Considering that silica forms an open network where the silicon atoms are the centers of tetrahedra and the oxygen atoms work as bridges between them, it is not obvious at all that a potential without three-body interactions is suitable for a good description of the properties; it has been found, however, that the competing two-body forces indeed mimic the three-body ones, causing the formation of a network.11)

Previous simulations4) have shown that the critical temperature for this model is $T_\mathrm{c} = 3\,330$ K, which is a good approximation for the value found in experiments with real silica, $3\,221$ K.3)

Table I. Interaction constants in the BKS potential.

j–k	A_{jk} [eV]	B_{jk} [Å^{-1}]	C_{jk} [eV Å^6]
O–O	1388.7730	2.76000	175.0000
O–Si	18003.7572	4.87318	133.5381
Si–Si	0	0	0

Table II. Charges and masses of the ions.

	q_j	m_j [u]
O	−1.2	15.9940
Si	+2.4	28.0855

For the O–O and O–Si interactions, the BKS potential has the drawback that it shows an unphysical behavior for small distances by diverging towards minus infinity. To correct this, it was replaced by a harmonic potential for distances below the location of the potential maximum (1.4387 Å for O–O, 1.1936 Å for O–Si). We confirmed the observations made in earlier simulations11) already: because of the potential barrier the particles have to overcome in order to reach them, these small distances only occur in very few particle pairs, so the substitution of the potential is not likely to have a relevant effect on the quantitative results of the simulation.

2.2 Parameter choices

We performed molecular dynamics simulations in a cubic system of length $L = 25.11$ Å containing 1089 (363+726) particles, so that the density was fixed at 2.3 g/cm^3. To integrate the equations of motion, the velocity form of the Verlet algorithm with time steps of 1.6 fs was used. The non-Coulombic part of the potential was truncated and shifted at a distance of 5.5 Å. The Coulomb term was calculated by means of the Ewald summation,[8] splitting it into a sum in real space,

$$U' = \gamma \sum_{j<k} \frac{q_j q_k \mathrm{erfc}(\alpha r_{jk})}{r_{jk}}$$

(where erfc denotes the complementary error function, $\mathrm{erfc}(x) = 2\pi^{-1/2} \int_x^\infty \exp(-t^2)\,\mathrm{d}t$), and one in Fourier space,

$$U'' = \frac{\gamma}{2\pi L} \sum_{\boldsymbol{n}\neq 0} \frac{1}{n^2} \exp\left(-\frac{\pi^2 n^2}{\alpha^2 L^2}\right) \left| \sum_j q_j \exp\left(\frac{2\pi \mathrm{i}}{L} \boldsymbol{n}\boldsymbol{r}_j\right) \right|^2$$

($n \equiv |\boldsymbol{n}|$). We chose $\alpha = 6.5/L$; the real-space sum was truncated and shifted at 9 Å, the Fourier-space one at $|\boldsymbol{n}| = 5$. Further details about the simulation can be found elsewhere.[12]

2.3 Preparation and measurements

The simulations were done in the same way as previous ones for a Lennard-Jones potential:[5,6] a system is first equilibrated at a temperature above the critical one, then at $t = 0$ suddenly "quenched" to one below; there it is allowed to relax for various waiting times before measurements of the potential energy and the generalized scattering function

$$C(t_\mathrm{w}, t_\mathrm{w} + t) = \frac{1}{N} \sum_j \exp(\mathrm{i}\boldsymbol{q} \cdot [\boldsymbol{r}_j(t + t_\mathrm{w}) - \boldsymbol{r}_j(t_\mathrm{w})]).$$

(where N is the number of particles and $\boldsymbol{q}$ is a wave vector) are started, so that examples for both an equilibrium constant and a two-time correlation function are examined.

To improve the statistics of the results, we averaged over three independent initial configurations consisting of randomly distributed particles. Each of those was used to produce equilibrium configurations at 6 000, 7 000 and 8 000 K by first rescaling the particle velocities periodically according to the desired temperature and then letting the system evolve freely for 55 000 time steps.

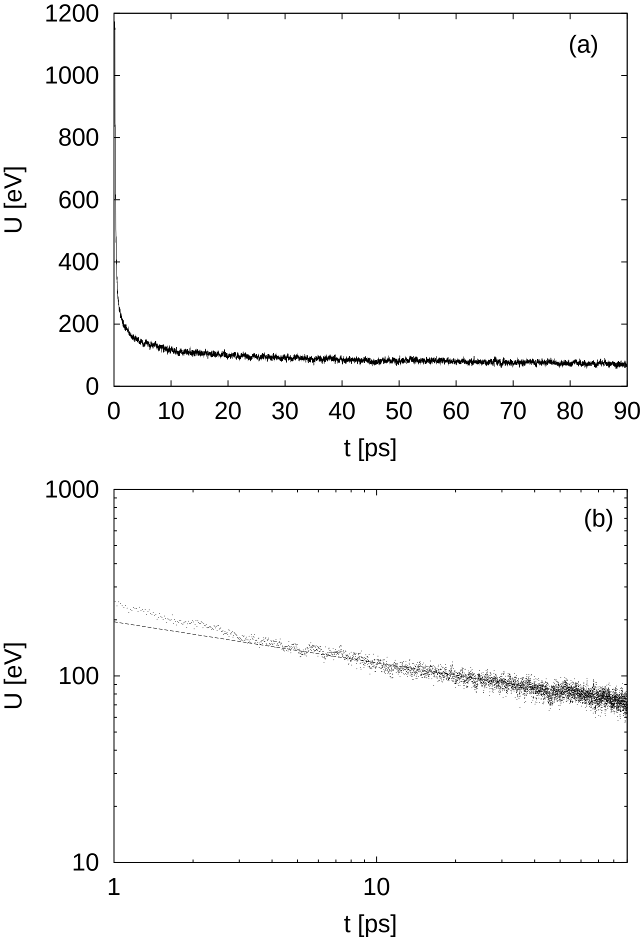
Each of the resulting configurations was then used for measurement runs at 2 700, 3 000 and 3 200 K: at $t = 0$, the system was brought to the final temperature by rescaling the velocities, and the temperature was controlled throughout the run by repeating this every 50 time steps. After waiting 0, 10, 100, 500, 1 000, 3 000, 10 000 and 30 000 steps, respectively, measurements of the potential energy and the generalized scattering function were started and performed every ten steps; the scattering function was calculated by averaging over fifty randomly chosen wave vectors of absolute value 1.7 Å^{-1}, the first sharp maximum of the structure factor for silica.[4] These runs were executed on eight processors of a Cray T3E with a time limit of four hours per run, which allowed between 60 000 and 75 000 time steps; with the chosen step size, this corresponds to 96–120 ps (10^{-12}sec.) in reality.

§3. Results

3.1 Potential energy

The potential energy shows a fast decay only for a short time after the quench; after that it appears to remain constant at a first glance in a linear plot (an example is shown in figure 1a), but a closer examination by means of a logarithmic plot (figure 1b) reveals that it still decays slowly.

Fig. 1. Potential energy of the system (shifted by 13 900 eV) as a function of the time after the quench from 7 000 to 3 000 K, plotted (a) linearly and (b, dotted) logarithmically. The dashed line in (b) shows the approximation for long times using a power-law dependence with an exponent of –0.22.



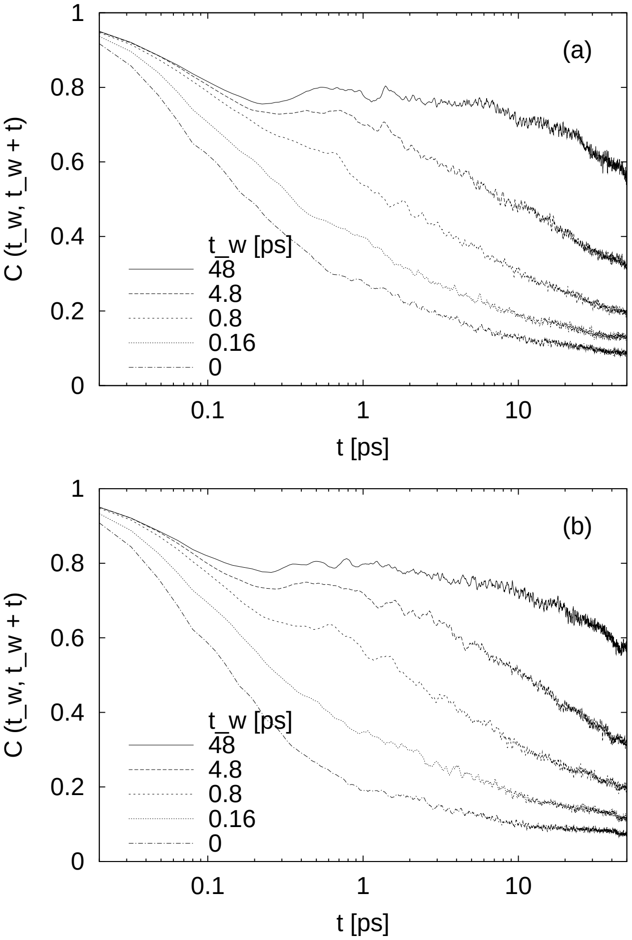
It is possible to approximate the decay for long times by a power law. The exponents for this approximation are listed in table III; the average value for all quenches is –0.20.

Table III. Estimated exponents for the time dependence of the potential energy for the various combinations of initial (rows) and final (columns) temperatures.

	2 700 K	3 000 K	3 200 K
6 000 K	–0.22	–0.18	–0.15
7 000 K	–0.26	–0.22	–0.18
8 000 K	–0.28	–0.18	–0.16

Next we compare these results to those obtained in analogous simulations for a binary Lennard-Jones (LJ) system. This model glass consists of a binary mixture of spheres which interact via an LJ potential with a strong r^{12} repulsive and a weak r^6 attracting part (van der Waals force); the spheres have two different radii to avoid crystallization. The mixture is a so called fragile glass former that has a glass transition at around $T = 0.46$ in the appropriate LJ-units.

Fig. 2. Generalized scattering function $C(t_\mathrm{w}, t_\mathrm{w}+t)$ as a function of the time for the quenches from 7 000 K (top) and 8 000 K (bottom) to 3 000 K and various selected waiting times t_w.



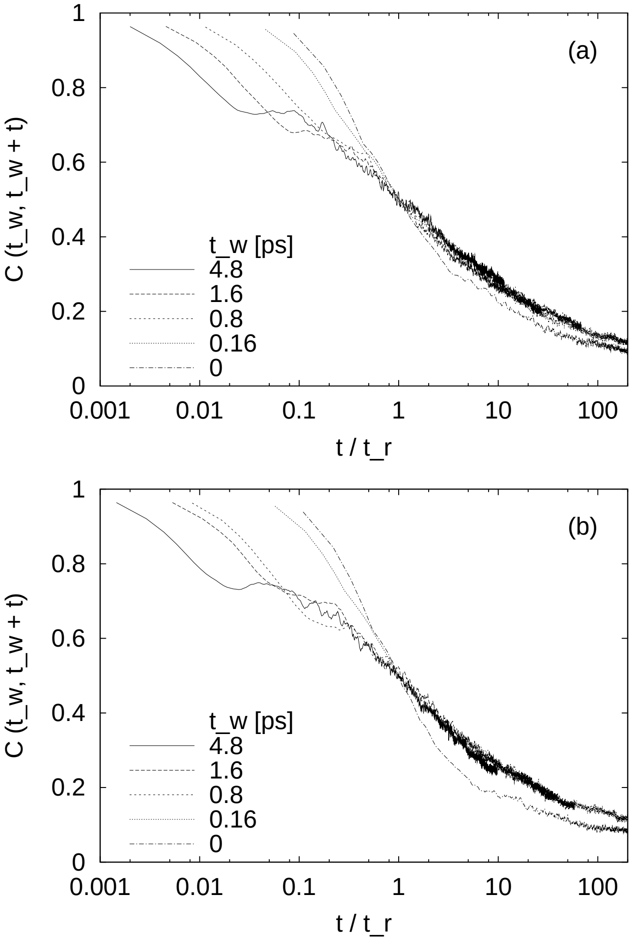
In recent simulations of this model, Kob and Barrat[5)] found a power law for the potential energy with an exponent of -0.144, which is of the same order of magnitude as our result for silica. We note, however, that in simulations for a soft sphere model,[7)] thus with a potential similar to the Lennard-Jones one, but using a Monte Carlo method instead of molecular dynamics, the different value 0.7 has been found for the exponent; Kob and Barrat mention the possibility that the disagreement is not caused mainly by the comparatively small differences of the models, but by an influence of the microscopic dynamics on the aging process. The fact that we have obtained a result similar to theirs by using the same kind of simulation, but a different potential, might be a further indication for the validity of this assumption.

3.2 *Scattering function*

Figure 2 shows two sample plots for the time development of the scattering function. A longer waiting time t_w means that the system has already had more time to relax after the quench than in the case of a short one; the speed of the decorrelation therefore decreases with growing t_w, so that the curves for larger values of t_w decay more slowly than those for short waiting times.

For short times the particles move ballistically, for long times they show a diffusive motion due to collisions with each other; particularly for low temperatures a plateau becomes visible between these two ranges, which is symptomatic for the situation that particles are trapped in "cages" formed by their neighbors and need a comparatively long time to escape from these cages. The temperatures in our simulations were not low enough to make this behavior visible very clearly, but the tendency to form a plateau is recognizable in the uppermost curves of figure 2.

Fig. 3. Data for the same quenches as in figure 2, rescaled to have all curves fall together at $C = 0.5$.



In passing we mention that the curves for longer waiting times in figure 2 also show another interesting property, a dip before the plateau or the final decay is reached, at a time of around 0.2 ps. This dip is related to the so-called boson peak, a dynamical feature at around 1 THz

(10^{12} sec^{-1}) in the spectra of many strong glass formers; several theoretical approaches have been proposed to explain this peak, but until now no consensus has been reached.

A natural scaling ansatz for two-time correlation functions is

$$C(t_\mathrm{w}, t_\mathrm{w}+t) = f_\mathrm{stat}(t) + g_\mathrm{age}(t/t_\mathrm{r}) \ ,$$

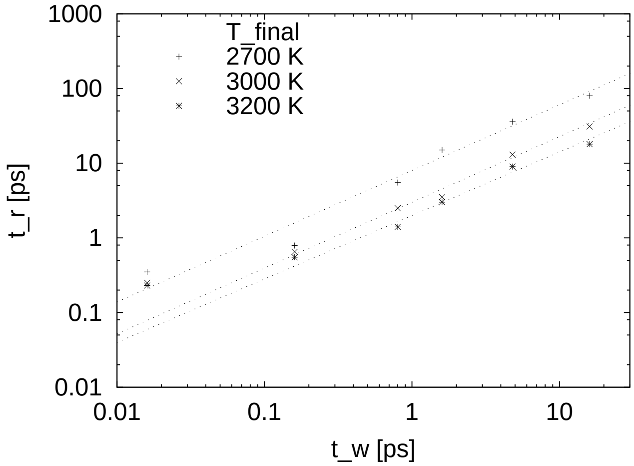
where the first term is the stationary part

$$f_\mathrm{stat}(t) = \lim_{t_\mathrm{w}\to\infty} C(t_\mathrm{w}, t_\mathrm{w}+t)$$

and $g_\mathrm{age}(x)$ is a scaling function for the aging part, which depends only on the ratio between the time t and an effective relaxation time t_r that varies monotonically with the waiting time t_w. In simple coarsening systems the off-equilibrium properties are governed by a single length scale, the domain size or correlation length ξ that grows with the waiting time as $\xi \propto t_\mathrm{w}^\beta$, and t_r is simply proportional to t_w. However, in aging experiments on glassy systems like polymer glasses$^{9)}$ and various spin glasses$^{13)}$ it was found that $t_\mathrm{r} \propto t_\mathrm{w}^\alpha$ describes the data reasonably well when the exponent α is used as a fit parameter (usually α is close to but significantly different from 1).

To examine whether a similar statement can be made for silica, we defined the relaxation time t_r of the scattering function as the time necessary to reach the value $C = 0.5$ and checked the scaling ansatz by plotting C over t/t_r. Figure 3 shows the results for two of the simulated quenches: except for the case of small waiting times, the curves fall together well for $t/t_\mathrm{r} \geq 1$, confirming the ansatz.

Fig. 4. Relaxation time t_r as a function of the waiting time t_w for the quenches with initial temperature 6 000 K. The dotted lines represent the approximation by a power law for long waiting times (from 0.8 ps upwards) with the exponent α as given in table IV.



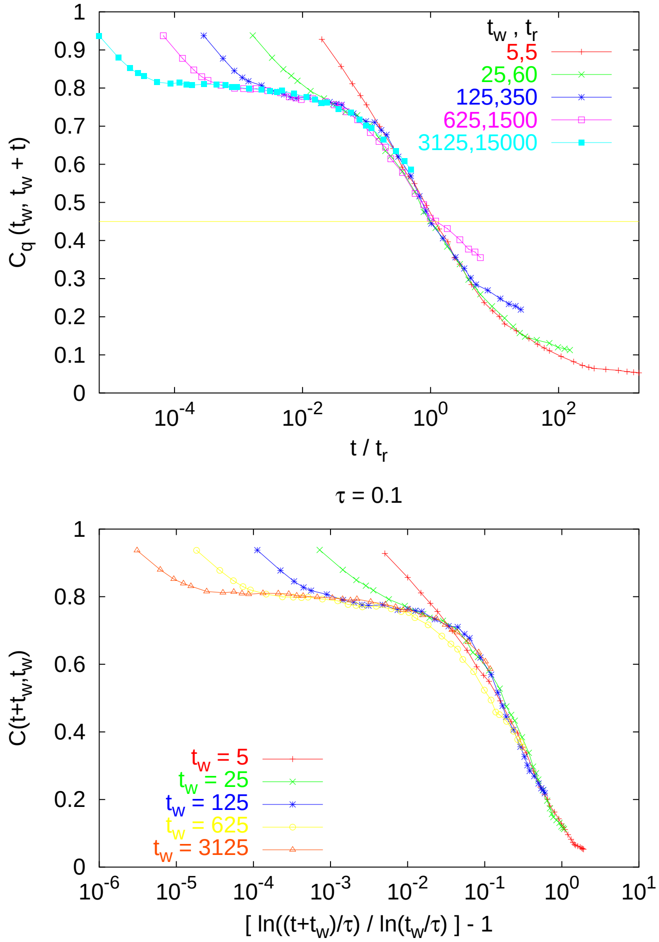
Plotting the relaxation time as a function of the waiting time reveals that, again with the exception of small waiting times, they can be approximated by a power law as well, as figure 4 demonstrates for the quenches with an initial temperature of 6 000 K. The exponents are listed in table IV; the average value turns out to be $\alpha = 0.89$.

Table IV. Estimated exponents α for the waiting time dependence of the relaxation time for the various combinations of initial (rows) and final (columns) temperatures. (Due to an error when the simulations were run, not enough data could be gathered to give reliable results for the quench from 8 000 to 3 200 K.)

	2 700 K	3 000 K	3 200 K
6 000 K	0.88	0.88	0.85
7 000 K	0.86	0.95	0.77
8 000 K	0.97	0.96	—

Again we compare our data to the one obtained in simulations of the LJ model. Recent results there$^{5,6)}$ present a somewhat controversial picture of the behavior of the scattering function, which we summarize in figure 5.

Fig. 5. Scaling plot of the scattering function (for $q = 7.2$) for a Lennard-Jones system with 8000 particles quenched from $T = 5$ to $T = 0.35$ (glass transition at $T = 0.46$). **Top**: The data are scaled according to a t/t_r aging scenario, as in figure 3 for the silica system. The data collapse is not very good. **Bottom**: The data are scaled according to a $\ln((t+t_\mathrm{w})/\tau)/\ln(t_w/\tau)$ aging scenario,$^{6)}$ the data collapse appears to be better.



Here the data collapse is slightly better when using an *activated dynamics* ansatz$^{6)}$

$$C(t_\mathrm{w}, t_\mathrm{w}+t) = f_\mathrm{stat}(t) + g_\mathrm{age}\left(\frac{\ln((t+t_\mathrm{w})/\tau)}{\ln(t_\mathrm{w}/\tau)}\right) ,$$

although for higher temperatures the t/t_r scaling scenario also works fine with $t_\mathrm{r} \sim t_\mathrm{w}^\alpha$ and $\alpha \approx 0.88$,$^{5)}$ surprisingly similar to our result for silica reported above.

To conclude we reported results of molecular dynamics simulations of a model for a strong glass former, amorphous silica, and showed 1) that the system is clearly aging on time scales of pico-seconds and 2) that the off-equilibrium or aging part of the generalized structure function obeys a t/t_r scaling scenario with the effective relaxation time (or effective age) obeying $t_\mathrm{r} \propto t_\mathrm{w}^\alpha$ with $\alpha \approx 0.88$. These results are in good agreement with those reported recently for a fragile glass former, a binary Lennard-Jones mixture.

Acknowledgement

We thank Uwe Müssel for providing us with the data for figure 5 and Barbara Coluzzi for many stimulating discussions. H.R. is grateful to the German research foundation for financial support within a JSPS-DFG binational cooperation.

---

[1] B. W. H. van Beest, G. J. Kramer and R. A. van Santen, Phys. Rev. Lett. **64**, 1955 (1990).

[2] J.-P. Bouchaud, L.F. Cugliandolo, J. Kurchan and M. Mézard in *Spin Glasses and Random Fields*, ed. A. P. Young, World Scientific, 1998.

[3] K.-U. Hess, D. B. Dingwell and E. Rössler, Chem. Geol. **128**, 155 (1996).

[4] J. Horbach and W. Kob, Phys. Rev. B **60**, 3169 (1999).

[5] W. Kob and J.-L. Barrat, Phys. Rev. Lett. **78**, 4581 (1997).

[6] U. Müssel and H. Rieger, Phys. Rev. Lett. **81**, 930 (1998).

[7] G. Parisi, preprints cond-mat/9701015, 9701100 and 9703219.

[8] D. C. Rapaport, *The Art of Molecular Dynamics Simulation*, Cambridge University Press, Cambridge, 1995.

[9] L. C. E. Struik, *Physical Aging in Amorphous Polymers and other materials*, Elsevier, North-Holland, 1978.

[10] e.g., J. S. Tse, D. D. Klug and Y. Le Page, Phys. Rev. B **46**, 5933 (1992).

[11] K. Vollmayr, W. Kob and K. Binder, Phys. Rev. B **54**, 15808 (1996).

[12] H. Wahlen, diploma thesis, University of Cologne (1999).

[13] E. Vincent, J. Hammann and M. Ocio in *Recent Progress in Random Magnets*, World Scientific, Singapore, 1992.