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Relaxation dynamics of a viscous silica melt: The intermediate scattering functions

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We use molecular dynamics computer simulations to study the relaxation dynamics of a viscous melt of silica. The coherent and incoherent intermediate scattering functions, $F(q,t)$ and $F_s(q,t)$, show a crossover from a nearly exponential decay at high temperatures to a two-step relaxation at low temperatures. Close to the critical temperature of mode-coupling theory (MCT) the correlators obey in the α regime the time temperature superposition principle (TTSP) and show a weak stretching. We determine the wave-vector dependence of the stretching parameter and find that for $F(q,t)$ it shows oscillations that are in phase with the static structure factor. The temperature dependence of the α-relaxation times τ shows a crossover from an Arrhenius law at low temperatures to a weaker T dependence at intermediate and high temperatures. At the latter temperatures the T dependence is described well by the power law proposed by MCT with the same critical temperature that has previously been found for the diffusion constant D and the viscosity. We find that the exponent γ of the power law for τ are significantly larger than the one for D. The wave-vector dependence of the α-relaxation times for $F(q,t)$ oscillates around $\tau(q)$ for $F_s(q,t)$ and is in phase with the structure factor. Due to the strong vibrational component of the dynamics at short times the TTSP is not valid in the β-relaxation regime. We show, however, that in this time window the shape of the curves is independent of the correlator and is given by a functional form proposed by MCT. We find that the value of the von Schweidler exponent and the value of γ for finite q are compatible with the expression proposed by MCT. Finally we discuss the q dependence of the critical amplitude and the correction term and find that they are qualitatively similar to the ones for simple liquids and the prediction of MCT. We conclude that, in the temperature regime where the relaxation times are mesoscopic, many aspects of the dynamics of this strong glass former can be rationalized very well by MCT.

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I. INTRODUCTION

If a glass forming liquid is cooled from high to low temperatures one finds that its relaxation time τ, or its viscosity η, increases rapidly by many decades [1]. If $\eta(T)$ is plotted in an Arrhenius plot, i.e., $\log(\eta)$ vs $1/T$, one finds that the shape of the curves is not universal but depends on the material. For two extreme cases of the shape, Angell has coined the terms ‘‘strong’’ and ‘‘fragile’’ glass formers [2]. Strong glass formers are liquids whose $\eta(T)$ curve shows an Arrhenius law in the whole accessible temperature range. In contrast to this, fragile liquids show a pronounced crossover at intermediate temperatures from an Arrhenius-like law at high temperatures to an Arrhenius-like law at low temperatures with a *higher* activation energy. It is one of the merits of the so-called mode-coupling theory (MCT) of the glass transition [3,4] to offer an explanation for the existence of this crossover in terms of nonlinear dynamical feedback effects and to make detailed predictions for the dynamics of the glass forming liquids close to this crossover temperature T_c, the critical temperature of MCT. In the past years there have been a large number of attempts to check the validity of these predictions and the result of these efforts was that the theory is indeed able to give a surprisingly good description of the dynamics in this temperature range [4]. It has to be emphasized that some of these tests concerned not only the predictions of the theory on a *qualitative* level, but also on a *quantitative* one, and that also the outcome of these tests were often in very good agreement with the theoretical prediction. Thus one can say that the theory is able to describe in the vicinity of T_c the dynamics of fragile liquids on a qualitative as well as a quantitative level.

Things are much less clear for the case of *strong* glass formers since by definition they do not show a crossover between two temperature dependences in $\eta(T)$, or only a very mild one. Hence it is *a priori* not clear at all whether these types of systems have a crossover temperature T_c and hence whether there is a temperature regime in which MCT can be used to describe their dynamics. It was therefore a bit surprising when it was found that glycerol, a glass former that is a rather strong glass forming liquid, shows a dynamics that can be described well by means of this theory [5,6]. Very recently a computer simulation study of liquid SiO_2, the paradigm of a strong glass former, showed that the dynamics of this system at high temperatures shows features that are very reminiscent of the dynamics of fragile systems around their T_c [7]. In particular it was shown that also in silica a critical temperature T_c can be identified, with a value around $T_c = 3330$ K, i.e., a temperature that is presently outside the reach of experimental investigations. It is of interest to note, however, that for this material an extrapolation of experimental data to higher temperatures gives evidence that around 3220 K a bend in the viscosity would indeed be observed [8], thus supporting the results from the simulation. Very recently it has also been demonstrated that MCT can be used to understand the dynamics of liquid silica not only on

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*Author to whom correspondence should be addressed. Permanent address: Laboratoire des Verres, Université Montpellier II, 34095 Montpellier, France. Email address: kob@ldv.univ-montp2.fr a qualitative level, but also on a quantitative one. For example, it was shown that the theory is able to predict with good accuracy quantities like the wave-vector dependence of the Debye-Waller factor [9]. The only input in that calculation were static quantities, i.e., the partial structure factors and static three-point correlation functions, which were determined directly from simulations. Also for water, another network forming liquid, it was found that MCT predicts the wave-vector dependence of the Debye-Waller factor with a very good accuracy [10]. Thus these studies give evidence that MCT is also able to give a correct description of the dynamics of strong liquids in the temperature region where the dynamics starts to slow down significantly, hence expanding the range of applicability of the theory considerably.

From the point of view of the theory this possibility is perhaps not that surprising. When the theory was developed originally, some terms in the equations of motion were dropped in order to simplify the equations and because it was argued that they are not very relevant to understand the main predictions of the theory [11]. This ‘‘ideal version’’ of the theory has subsequently been tested extensively in experiments and computer simulations [3,4]. A bit later it was recognized, however, that close to the critical temperature T_c the terms that were dropped will change some of the predictions of the theory considerably [12,13], since they are needed to describe processes, today called ‘‘hopping processes,’’ that become relevant at low temperatures. If these hopping processes are very small, the predicted temperature dependence of the relaxation times shows a strong bend in an Arrhenius plot, reminiscent of the one seen in fragile glass formers [13]. If these processes are very pronounced this temperature dependence shows only a weak bending around T_c, thus a similar behavior as the one found in strong glass formers. Thus it seems that *a priori* the theory is indeed able to describe also strong glass formers.

However, it is presently not clear whether the extended form of the theory, i.e., the version of the theory that tries to include hopping effects, is really reliable also beyond a phenomenological description. Therefore it is important to check to what extent the theoretical predictions survive in the case where one deals with a real material or a realistic microscopic model in which hopping effects are expected to be important. Such investigations might also give an idea how the theory can be improved or extended in order to describe the dynamics of realistic glass forming liquids. The present paper is hence a contribution to this issue. For this we use molecular dynamics computer simulations to investigate the dynamics of liquid silica in great detail. In particular we will study to what extent the behavior predicted by the theory can be found in this dynamics, i.e., we test in a stringent way to what extent MCT is able to give a reliable description of the relaxation dynamics of strong glass formers at high temperatures.

The rest of the paper is organized as follows. In the next section we give the details on the model we use and the simulations. Section II is devoted to the presentation of the results, which are summarized and discussed in Section IV.

II. MODEL AND DETAILS OF THE SIMULATION

In this section we present the model we used to describe the interaction of silica and give some of the details of the simulation. Further information on the latter can be found in Ref. [14].

In order to obtain a realistic description of the structural and dynamical properties of a given material by means of classical simulations, it is necessary to have a potential at hand that describes the interactions between the different ions realistically. Due to the importance of silica in applied as well as fundamental science it is nowadays possible to find a multitude of different potentials in the literature, most of them having certain advantages and disadvantages. Various simulations have shown that one of the most reliable of these potentials is the one proposed by van Beest, Kramer, and van Santen (BKS) that was obtained by determining the energy surface of a SiO_4H_4 tetrahedron by means of *ab initio* calculations, parametrizing this surface with a simple analytical expression and subsequently doing some lattice dynamics calculations with it to improve the fit parameters [15].

The functional form of the BKS potential is

$$\phi_{\alpha\beta}(r)=\frac{q_\alpha q_\beta e^2}{r}+A_{\alpha\beta}\exp(-B_{\alpha\beta}r)-\frac{C_{\alpha\beta}}{r^6},\qquad \alpha,\beta\in[\mathrm{Si},\mathrm{O}], \tag{1}$$

where r is the distance between the ions of type α and β. The values of the constants q_α, q_β, $A_{\alpha\beta}$, $B_{\alpha\beta}$, and $C_{\alpha\beta}$ can be found in Ref. [15]. For the sake of computational efficiency the short range part of the potential was truncated and shifted at 5.5 Å. This truncation has also the benefit of improving the agreement between the density of the amorphous glass at low temperatures as determined from the simulation with the experimental value. Previous simulations have shown that this potential is able to reproduce a variety of properties of real amorphous silica, such as the density anomaly, the static structure factor, the specific heat, the viscosity, and the thermal conductivity [16]. Thus it can be expected that it is also sufficiently accurate to give a reliable description of the time dependence of the intermediate scattering function, the central quantity discussed in the present paper.

The system investigated has 8016 ions in a cubic box with fixed size $L=48.37$ Å. This size is sufficiently large to avoid the finite size effects found in the dynamics of such systems [17,18]. The equations of motion have been integrated by means of the velocity form of the Verlet algorithm, using a time step of 1.6 fs. The Coulombic part of the potential has been evaluated by means of the Ewald sum using a constant $\alpha L=12.82$. Before the microcanonical production runs were started the system was equilibrated by coupling it to a stochastic heat bath. The duration of this equilibration was significantly longer than the typical relaxation times of the system. Therefore we are sure that all the results presented below reflect the relaxation dynamics *in equilibrium*, i.e., that they are not affected by aging phenomena. The temperatures investigated were 6100, 5200, 4700, 4300, 4000, 3760, 3580, 3400, 3250, 3100, 3000, 2900, and 2750 K. In order to improve the statistics of the results we averaged at each temperature over two independent runs.

Note that all these temperatures are *above* the melting temperature of real silica, which is around 2000 K [19], a temperature that the BKS potential is able to reproduce reasonably well [20]. Thus none of our simulations probe the dynamics of the system in its supercooled state. Nevertheless we will see below that even at these relatively high temperatures the dynamics of the system is very slow. Thus this shows that in order to have a slow relaxation dynamics it is not necessary to be in a supercooled state.

III. RESULTS

In this section we will present the results. In the first part we will discuss the relaxation dynamics of the system at long times, i.e., the α-relaxation regime. In the second part we will focus on intermediate times, i.e., the β-relaxation regime, and compare these results with the predictions of MCT.

The quantity of main interest that will be studied in the present paper is the intermediate scattering function $F(q,t)$ and its self-part, $F_s(q,t)$ [21]. These two space-time correlation functions can be defined most easily in terms of the density fluctuations for the particles of type α,

$$\delta\rho_\alpha(\mathbf{q},t)=\sum_{j=1}^{N_\alpha}\exp[i\mathbf{q}\cdot\mathbf{r}_j(t)], \tag{2}$$

where $\mathbf{q}$ is the wave vector. The intermediate scattering function is then defined as

$$F^{\alpha\beta}(q,t)=\frac{1}{N_{\mathrm{Si}}+N_{\mathrm{O}}}\langle\delta\rho_\alpha(\mathbf{q},t)\delta\rho_\beta^*(\mathbf{q},0)\rangle. \tag{3}$$

Here $\langle\cdot\rangle$ stands for the thermal average and we have assumed that the system is isotropic and hence $F^{\alpha\beta}(q,t)$ depends only on the modulus $q=|\mathbf{q}|$. From $F^{\alpha\beta}(q,t)$ a self-part F_s^α can be extracted that corresponds to the diagonal elements in the double sum of $F^{\alpha\beta}$,

$$F_s^\alpha(q,t)=\frac{1}{N_\alpha}\sum_{j=1}^{N_\alpha}\langle\exp\{i\mathbf{q}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}\rangle. \tag{4}$$

Note that $F(q,t)$ and $F_s(q,t)$ are the space-Fourier transforms of the van Hove correlation function and its self-part, respectively [21], thus quantities that are often studied in computer simulations of liquids. However, since in scattering experiments the latter functions are not directly accessible, in contrast to $F_s(q,t)$ and $F(q,t)$, and since also from a theoretical point of view the scattering functions are more interesting than the van Hove functions, it is appropriate to determine also them in simulations. We emphasize that to obtain the results of the present work we have not used the connection between the van Hove functions and the intermediate scattering functions, but calculated the latter functions directly from their definitions given in Eqs. (3) and (4). For this we averaged over all $\mathbf{q}$ vectors that had the same modulus and that were compatible with the size of the simulation box.

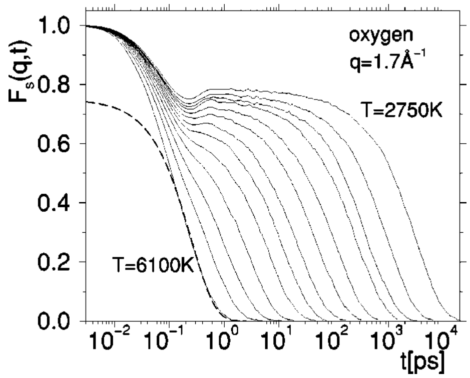

FIG. 1. Time dependence of the incoherent intermediate scattering function for the oxygen atoms for all temperatures investigated. The wave vector q is 1.7 Å^{-1}, the location of the first peak in the structure factor. The dashed line is a fit to the curve for 6100 K with an exponential function (see text for details).

In Fig. 1 we show the time dependence of $F_s(q,t)$ for the oxygen atoms for all temperatures investigated. The wave vector is $q=1.7\,\text{Å}^{-1}$, the location of the first sharp diffraction peak in the structure factor, i.e., the length scale that corresponds to the typical distance between two adjacent tetrahedra in the network [7]. (We mention that for other wave vectors the curves look qualitatively very similar.) From this graph we see that at high temperatures the curves show at very short times a crossover from a ballistic regime to a relaxation behavior that is basically exponential and that the correlation function decays to zero within 1 ps, i.e., very rapidly. To illustrate this exponential decay we have included in Fig. 1 an exponential function $f(t)=0.75\exp(-t/0.25\,\mathrm{ps})$ (dashed line), which essentially coincides with the simulation curve at $T=6100$ K for $t>0.1$ ps. (We emphasize that due to the complex vibrational dynamics of the system at short times [18], one has to use an amplitude significantly smaller than 1.0.) For intermediate and low temperatures one observes two additional regimes: Immediately after the ballistic regime, which last just up to ≈ 0.02 ps, the motion of the ions shows a vibrational character, as can be inferred from the presence of a dip in the correlator at around 0.2 ps. This type of dynamics is the dominant one for temperatures below the glass transition, but from the figure we recognize that it can be seen even at temperatures as high as 3580 K. From a microscopic point of view this dynamics corresponds to the rattling motion of the ions in the cage formed by their surrounding neighbors and the network. (Note that this cage is not rigid at all, since the particles that form the ''walls'' of this cage move themselves also.) Although every liquid will show some sort of vibrational dynamics, the one for $\mathrm{SiO_2}$ is special in that it has also important contributions at quite low frequencies (1–2 THz) the origin of which has in recent years been the matter of a strong debate [18,22]. For times that are somewhat longer than the ones for the vibrations, i.e., $t\geqslant 0.2$ ps, this type of motion is damped out and the particles slowly start to leave

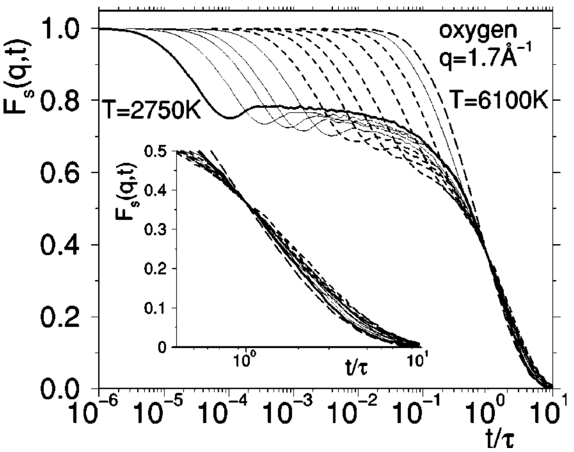

FIG. 2. Incoherent intermediate scattering function for oxygen vs $t/\tau(T)$, where τ is the α-relaxation time at temperature T. Inset: Enlargement of the curves at long rescaled time. See text for the meaning of the different line styles.

the mentioned cage. This dynamics, in the following called the β process [3,4], is thus the beginning of the α process, i.e., the time regime in which the ions leave the cage completely and lead to the structural relaxation of the system. In the correlation functions it is seen as a plateau at intermediate times, the length of which rapidly increases with decreasing temperature thus pushing the α relaxation to large times (see Fig. 1). MCT makes detailed predictions on the dynamics of the system on the time scale of the β relaxation and in the following we will check the validity of these in detail.

From Fig. 1 one gets the impression that the shape of the curves *in the α-relaxation regime* does not depend on temperature, i.e., that the correlators obey the so-called time temperature superposition principle (TTSP). This means that a correlator $\phi(t,T)$ can be expressed by

$$\phi(t,T)=\hat{\phi}(t/\tau(T)), \tag{5}$$

where $\tau(T)$ is the typical time scale for the decay of the correlation function, i.e., the α-relaxation time, and $\hat{\phi}$ is a master function. MCT predicts that there exists a so-called critical temperature T_c in the vicinity of which the TTSP is valid. Since this is one of the main predictions of the theory it is of interest to check whether or not it is valid for the present system. For this we have defined an α-relaxation time τ by requiring that at time τ the correlator has decayed to e^{-1} of its initial value. If the TTSP holds, a plot of the correlators at different temperatures versus $t/\tau(T)$ should give a master curve. In Fig. 2 we show this type of plot and we recognize that apparently the scaling does not work very satisfactorily. To show this we have plotted in the inset of the figure an enlargement of the main figure at long rescaled times. From this inset we recognize that the fact that the TTSP is not fulfilled is not due to the noise in the data but rather due to a systematic trend in the curves. We have also made sure that this violation of the TTSP is not due to the way we have defined τ, since a different definition gave qualitatively the same results [14]. Recall, however, that the TTSP is predicted to hold only slightly above T_c, which for the present system is around 3330 K [7]. In fact, if the curves for the different temperatures are inspected carefully one finds that the ones in the temperature range 4700 K$\geqslant T \geqslant$3400 K (short dashed lines in Fig. 2) do indeed fall onto a master curve whereas the ones for high ($T=6100$ K) and low ($T\leqslant 3000$ K) temperatures decay faster. Hence the curve at $T=2750$ K (bold line in Fig. 2) is already very close to the exponentially decaying one at $T=6100$ K (long dashed line in Fig. 2). Hence we see that slightly above T_c the correlation functions do indeed obey the TTSP, whereas it is violated if the temperature is too far below T_c. This behavior is in qualitative agreement with the theory, since it is predicted that far above and far below T_c the relaxation is of Debye type [3,13].

We also mention that according to MCT the TTSP is supposed to hold also in the β-relaxation regime, i.e., in the time window in which the correlation functions are close to the plateau. From the graph we see, however, that in this time regime the curves do not collapse at all. The reason for this is likely the fact that in this system the microscopic dynamics, i.e., the above-mentioned low-frequency vibrations, are so pronounced that they completely obscure the TTSP in this time window [23], in contrast to simple liquids whose vibrational dynamics does not have strong contributions at very low frequencies, i.e., around 1–2 THz. Below we will see, however, that certain predictions of MCT concerning the dynamics in the β-relaxation regime are still valid, despite the presence of the strong vibrational dynamics.

The results presented so far concerned the incoherent part of the intermediate scattering function of the oxygen atoms. For the case of the silicon atoms the time and temperature dependence is qualitatively similar, although for this species the TTSP at long times is fulfilled a bit better [14]. Since $F_s(q,t)$ measures essentially the dynamics of a tagged particle within its cage and how it escapes this cage at long times, not much can be learned from this correlation function on the *relative* motion of the particles. Therefore it is of interest to study also the coherent intermediate scattering function $F(q,t)$ that is defined in Eq. (3). In Fig. 3 we show the time dependence of the three partial $F^{\alpha\beta}(q,t)$ for all temperatures investigated. The wave vector is again 1.7 Å^{-1}, i.e., the location of the first sharp diffraction peak. Although from a qualitative point of view these correlation functions are similar to the incoherent ones, a closer inspection does show interesting differences. For example, the coherent curves show the effects of the complex vibrational dynamics of the system much more pronounced in that, e.g., several maxima and minima can be seen between 0.02 ps and 1 ps, whereas the incoherent curves show only one local minimum (see Fig. 1). We also mention that the modulus of the incoherent functions as well as F^{SiSi} and F^{OO} are always smaller than 1.0 since they are (normalized) autocorrelation functions. This is in contrast to F^{SiO} which, being not an autocorrelation function, can become larger than 1.0. A closer inspection of the curves for this correlator does indeed show that for times around 0.03 ps the curves are larger than 1.0, which is the reason why this correlator is very flat at short times.

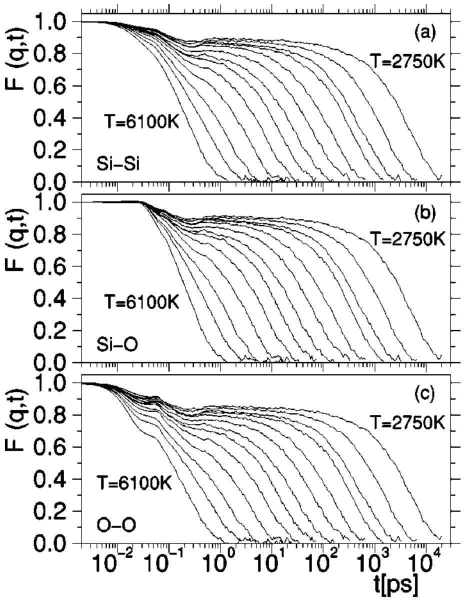

FIG. 3. Time dependence of the coherent intermediate scattering function for all temperatures investigated. The wave vector is 1.7 Å^{-1}, the location of the first peak in the structure factor. (a) Si-Si, (b) Si-O, (c) O-O.

From Fig. 3 one sees that in the α-relaxation regime the shape of the curves depends only weakly on temperature, i.e., that the TTSP is valid. That this is essentially the case is demonstrated in Fig. 4, where we plot the coherent correlation functions for the case of O-O versus the rescaled time t/τ. We see that within the noise of the data the curves basically collapse onto one master curve. However, also in this case small systematic deviations from the TTSP, as discussed for the incoherent functions, can be found upon closer inspection of the curves. Thus this shows that also for these types of correlation functions the TTSP holds only for temperatures relatively close to T_c.

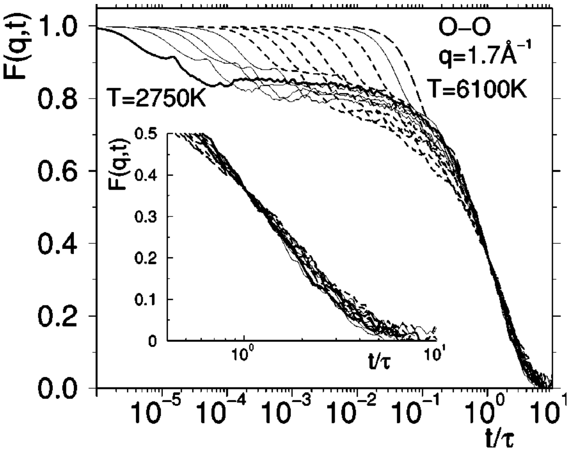

FIG. 4. Coherent intermediate scattering function for the oxygen-oxygen correlation vs $t/\tau(T)$, where τ is the α-relaxation time at temperature T. Inset: Enlargement of the curves at long rescaled time. See Fig. 2 for meaning of the dashed curves.

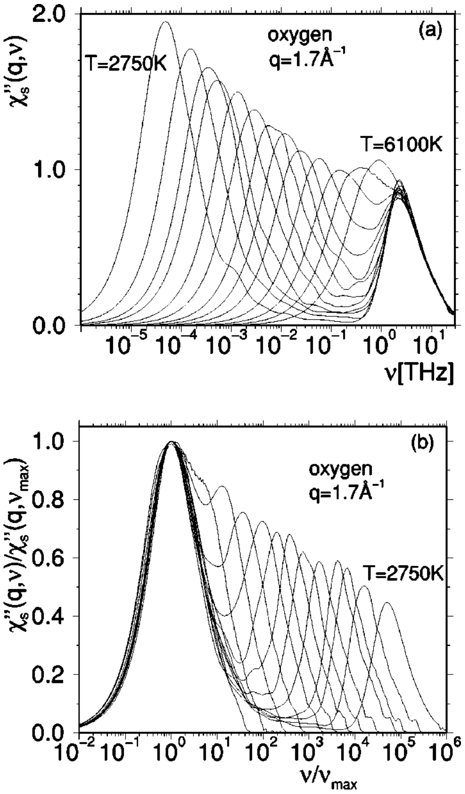

FIG. 5. Frequency dependence of the imaginary part of the dynamic susceptibility $\chi_s''(q,\nu)$ for the oxygen atoms for all temperatures investigated. (a) $\chi_s''(q,\nu)$ vs frequency ν. (b) $\chi_s''(q,\nu)/\chi_s''(q,\nu_{\max})$ vs $\nu/\nu_{\max}$, where $\nu_{\max}$ is the location of the α peak in χ_s''.

The intermediate scattering functions discussed so far can be directly measured in spin echo experiments or photon correlation experiments. However, in neutron or dynamic light scattering experiments only the time-Fourier transforms of these correlation functions are accessible. Therefore it is of interest to calculate these functions also, in order to see to what extent the various regimes seen in the time domain can be found in the frequency domain. Since the intermediate scattering functions have been measured over more than seven decades in time, the calculation of their Fourier transform is not a trivial matter. In order to do this we have approximated each curve with a spline under tension and calculated the Fourier transform of the spline by means of the Filon formula [24]. Thus we obtained the dynamic scattering functions $S(q,\omega)$ and $S_s(q,\nu)$. Since in the experiments one often measures the imaginary part of the susceptibility, $\chi''(q,\omega)$, we have multiplied these functions with ω/T to obtain $\chi''(q,\omega)$ and $\chi_s''(q,\omega)$, respectively.

In Fig. 5(a) we show χ_s'' as a function of $\nu=2\pi\omega$ for all temperatures investigated. We see that at 6100 K χ_s'' shows only a single broad peak. The width of this peak at half maximum is approximately 1.5 decades, which shows that it is not Debye-like, since this would correspond to a width of 1.14 decades. This increase is simply due to the fact that the broad peak at $T=6100$ K is a sum of a microscopic and a relaxation peak, where the relaxation peak should be of Debye type in agreement with the exponential decay of the corresponding curve for $F_s(q,t)$ in Fig. 1 for $t>0.1$ ps.

If the temperature is lowered the single peak splits up into two, i.e., into a microscopic peak at high frequencies and an α peak at lower frequencies. With decreasing temperature the amplitude of the microscopic peak decreases but its location is independent of T. In contrast to this the α peak quickly moves to lower frequencies and also its height increases slightly. However, the shape of the peak seems to be essentially independent of T. At low temperatures we find a well-defined plateau between the α peak and the microscopic peak. A plot of $\log(\chi_s'')$ vs $\log(\nu)$ shows that at these low temperatures the whole spectrum can be described very well by a sum of a peak at microscopic frequencies and an α peak with a high-frequency wing that scales like ν^{-y}, where the exponent y is ≈ 0.6 and independent of T. Thus this result is in agreement with the von Schweidler law discussed below in the context of Fig. 12 that gives an exponent 0.62. It is remarkable that this type of a plot shows that for temperatures around 3250 K, i.e., around T_c, the susceptibility seems *not* to be just the sum of an α peak and a microscopic peak, but that near the minimum between the two peaks $\chi_s''(\nu)$ is enhanced. This means that there is an additional process in this frequency regime, the β process of MCT. We emphasize that this enhancement is only seen close to T_c, in agreement with the prediction of the theory.

That the shape of the α-peak does indeed not depend on temperature, is demonstrated in Fig. 5(b). Here we show $\chi_s''(q,\nu)/\chi_s''(q,\nu_{\max})$ as a function of $\nu/\nu_{\max}$, where $\nu_{\max}$ is the location of the maximum of the α peak. From this plot we clearly see that within the accuracy of our data the curves for low temperatures fall on top of each other. Finally we mention that qualitatively the same results have been obtained for the case of the silicon atoms.

Since the TTSP is valid to a high degree, we can determine the shape of the master curves as a function of the observable. We have done this for the case of the coherent and incoherent intermediate scattering function for several values of q. To determine this shape we proceeded as follows: For each correlator $\phi(t)$ we determined an α-relaxation time τ' at 2750 K by requiring that $\phi(t)=0.1$ [25]. We then fitted $\phi(t)$ with a Kohlrausch-Williams-Watts function

$$\phi(t)=A\exp[-(t/\tau')^{\beta}], \tag{6}$$

where the amplitude A and the stretching parameter β are free fit parameters. This fit was done in the interval $0.02 \leqslant t/\tau' \leqslant 2$ that for typical values of β corresponds to about 90% of the height of the α relaxation (see Fig. 2). We made sure that choosing a different interval does not affect the results significantly and we estimate the systematic error bar of β due to this choice being usually smaller than 0.03 [14]. In Fig. 6 we show the wave-vector dependence of β for the two incoherent functions as well as for two coherent ones. We see that for small and intermediate q the value of β is relatively large, in agreement with the observation that strong glass-formers do not show much stretching [26]. However, for the large values of q, β is significantly smaller than 1.0 since the curves for F_s decrease progressively with increasing q. This trend can be rationalized with the prediction of MCT [27] that with increasing q the value of β should approach the value of the von Schweidler exponent b, discussed in more detail below, which for our system is around 0.62, i.e., significantly smaller than 1.0. At $q=4$ Å^{-1} the value for $\beta(q)$ as determined from F_s for silicon and oxygen is around 0.77, i.e., higher than the value predicted by the theory for large q. However, it has to be realized that $q=4$ Å^{-1} cannot be considered yet as ‘‘large’’ since at this wave vector the static structure factor shows still significant oscillations [7]. In a MCT calculation for a hard sphere system it has been found that only at very large wave vectors the value of β becomes close to the von Schweidler exponent, i.e., at q at which the static structure factor is essentially 1.0 [28]. In view of this result it is hence not surprising that the value of our β at the largest q is still significantly above b.

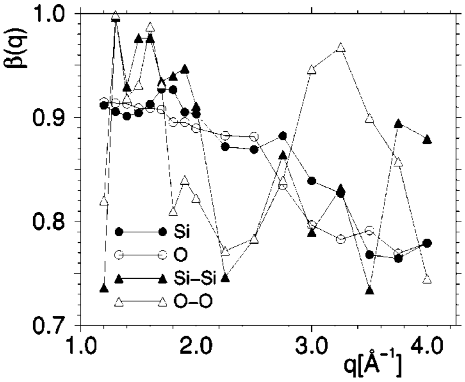

FIG. 6. Wave-vector dependence of the Kohlrausch-Williams-Watts stretching parameter for the silicon and oxygen incoherent intermediate scattering functions and the silicon-silicon and oxygen-oxygen coherent intermediate scattering functions. $T=2750$ K.

The curves for the coherent functions oscillate around the ones for the incoherent ones. This oscillation is in phase with the partial static structure factor with peaks that correspond to the maxima in $S_{\alpha\alpha}(q)$. Note that for large q the coherent functions are approximated well by the corresponding incoherent ones [21] and thus it is expected that the values of β become identical also. However, in the range of q for which we can reliably determine the value of β this is not yet the case. This supports our argument given above that none of the $\beta(q)$ curves has yet converged to its asymptotic value for $q\to\infty$. Note that qualitatively the same behavior for $\beta(q)$ has also recently been observed for water, where it was found that $\beta(q)$ converges to the von Schweidler exponent b for large q and that it shows oscillation in phase with the static structure for its coherent part [29].

We now address the temperature dependence of the α-relaxation time τ. Since SiO_2 is a strong glass former [2] one expects that τ follows an Arrhenius law. In Ref. [7] we have shown, however, that for the diffusion constant as well as the viscosity this law is found only at relatively low temperatures. For intermediate and high temperatures a significant deviation was found in that the temperature dependence was weaker than the one expected from an Arrhenius law. That this is the case for $\tau'(T)$ as well is demonstrated in Fig.

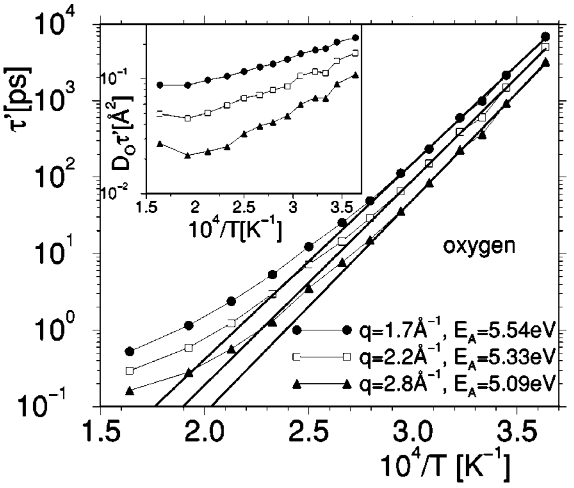

FIG. 7. Temperature dependence of the α-relaxation time τ' as determined from $F_s(q,t)$ for oxygen for various values of q. The solid straight lines are fits to the data at low temperature with an Arrhenius law with the activation energies given in the figure. Inset: Temperature dependence of the product $D_{\rm O}\tau'$, where $D_{\rm O}$ is the diffusion constant for the oxygen atoms.

7 where we show the α-relaxation time for $F_s(q,t)$ for the oxygen atoms (the curves for the silicon atoms look qualitatively the same). The three curves that are shown correspond to q values at the first sharp diffraction peak ($q=1.7\,\text{Å}^{-1}$), the location of the first minimum in the structure factor ($q=2.2\,\text{Å}^{-1}$), and the location of the main peak in $S(q)$ ($q=2.8\,\text{Å}^{-1}$). We see that, apart from a q-dependent prefactor, the temperature dependence of the three relaxation times is very similar in that we find at low T an Arrhenius law and at intermediate and at high temperatures a crossover to a weaker temperature dependence. The activation energies found at low T are between 5 and 5.5 eV, which compares well with the experimental values for the diffusion constant and the viscosity (4.7 eV and 5.33 eV, respectively [30,31]). Thus we conclude that also with regard to this quantity the BKS model is quite reliable.

In Ref. [7] we showed that the deviations from the Arrhenius law at intermediate and high temperatures are related to a change of the transport mechanism of the ions in that at low T the atoms make independent hops whereas for high T the motion is much smoother and flow like. Such a change in mechanism is predicted by MCT around the critical temperature T_c [3,4], which for our system has been estimated to be around 3330 K [7]. The theory predicts that for temperatures a bit above T_c the typical relaxation times increase like a power law,

$$\tau(T) \propto (T-T_c)^{-\gamma}, \qquad (7)$$

with an exponent γ that is universal for the system, i.e., is independent of the observable (Si or O, value of q, etc.). Thus the bending of the curves in Fig. 7 can be rationalized by the crossover from the power-law behavior given by Eq. (7) to an Arrhenius behavior at low temperatures.

MCT predicts that the exponent γ is independent of the observable and that the diffusion constant D should be proportional to $1/\tau$. In order to check the validity of this prediction we have calculated the product $D_{\rm O}\tau$ and plot it in the inset of Fig. 7 as a function of $1/T$ for the three relaxation times shown in the main figure. We see that although the product is basically constant at high temperatures, it increases continuously at intermediate and low temperatures. Since in this log-lin plot the curves at low T become a straight line we conclude that the activation energies for the diffusion constant and the relaxation times are not the same, a conclusion that is confirmed if one measures these energies directly (see below). Thus we conclude that the proportionality $D\propto\tau^{-1}$ does not hold around T_c or lower temperatures. One reason for $D\not\propto\tau^{-1}$ might be the presence of dynamical heterogeneities [32], i.e., that the cage that each particle sees changes significantly from particle to particle which has the effect that also the time to escape this cage depends strongly on the particle. It is then easy to see that in this case the (average) diffusion constant is not inversely proportional to the (average) relaxation time [33]. The observation that D is not strictly proportional to τ^{-1} has in the past already been made in other systems for which the predictions of MCT hold extremely well not only on a qualitative but also on a quantitative level [34]. Thus, since the prediction of MCT that $D\propto\tau^{-1}$ is only the result of a leading order calculation of the theory, the fact that the product $D\tau$ is not completely constant should not be taken as strong evidence that for the present system the theory is not applicable.

Since for the present system the temperature dependence of the diffusion constant is not described so well by MCT, we investigate now the T dependence of the relaxation times directly. In Ref. [7] we determined the value of T_c to be around 3330 K. Therefore we plot in Fig. 8 the α-relaxation time as a function of $T-T_c$, for those temperatures that are higher than T_c. From this plot we see that the data at high

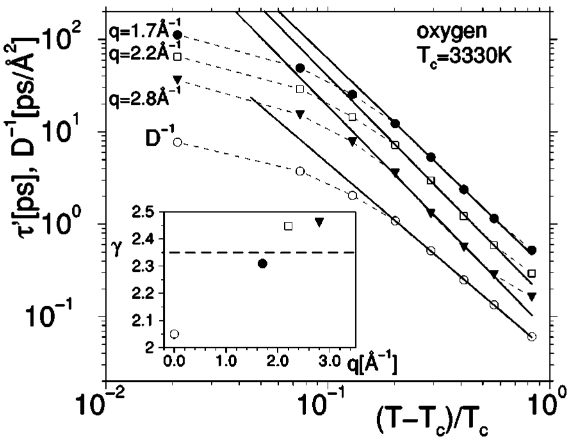

FIG. 8. The α-relaxation time τ', as determined from $F_s(q,t)$ for oxygen, as a function of $(T-T_c)/T_c$, where $T_c=3330$ K is the critical temperature from MCT as determined in Ref. [7]. Also included is the inverse of the diffusion constant as determined in Ref. [7]. The solid straight lines are fits with power laws of the form given by Eq. (7). Inset: Value of the exponent γ. The point at $q=0$ corresponds to the exponent for the diffusion constant. The horizontal dashed line is the value of γ as determined from the dynamics in the β-relaxation regime.

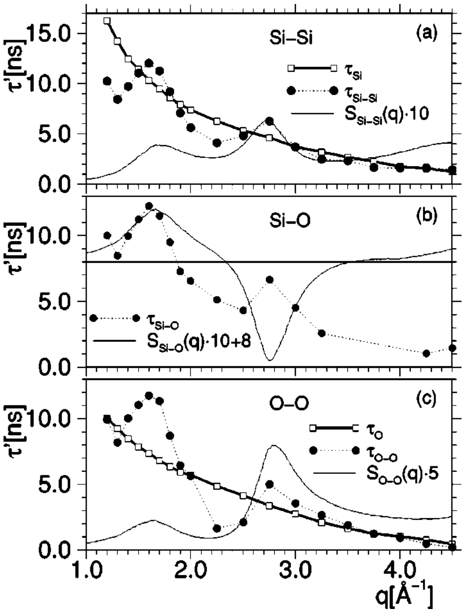

FIG. 9. Wave-vector dependence of the α-relaxation time τ' at $T=2750$ K as determined from the incoherent and coherent intermediate scattering functions (curves with symbols). Also included are the partial structure factors from Ref. [7] (curves with no symbols).

temperatures can indeed be described well with a power law (bold straight lines), in agreement with the prediction of the theory [see Eq. (7)]. The same conclusion holds for the diffusion constant of the oxygen atoms, as can be seen from the open circles in Fig. 8. Similar results have also been obtained for the relaxation time of $F_s(q,t)$ for silicon as well as the various coherent intermediate scattering functions [14]. It should be noted, however, that this power law can be observed only in a temperature range in which τ changes by about 1 decade. This is significantly less than the range that has been observed for simple liquids [34–36], water [29], molecular glass formers [37,38], or polymeric systems [39]. Thus we conclude that for this system the corrections to the idealized version of the theory due to the hopping processes make the observation of the power law rather difficult.

As mentioned above, the value of the exponent γ should be independent of the observable. In the inset of Fig. 8 we plot the value of γ for the three different wave vectors as well as the diffusion constant (point at $q=0$). We see that whereas the value of γ for intermediate values of q is around 2.4, the one for the diffusion constant is significantly smaller, $\gamma=2.05$. Thus again we find that this quantity behaves somewhat anomalous with respect to the ones at large q, and the reason for this is likely the one discussed above. Also included in the inset, horizontal dashed line, is the value of γ as determined from a completely different approach, namely, the analysis of the β-relaxation regime (discussed below). We see that this estimate of γ is in very good agreement with the values from the α-relaxation times, thus supporting the prediction of the theory that the exponent is not just a fit parameter but a quantity with a fundamental theoretical meaning.

We now discuss the wave-vector dependence of the α-relaxation times in more detail. Since we have seen, see Fig. 7, that in the whole temperature range investigated the temperature dependence of τ is basically independent of q, it is sufficient to consider the q dependence at only one temperature. This is done in Fig. 9 where we show the q dependence of τ' for the two incoherent as well as the three coherent functions. (Note, that for the reasons discussed in the context of Fig. 6, we show the q dependence of τ' instead of the one of τ.) From the figure we see that the relaxation time for the incoherent functions, panel (a) and (c), decrease with increasing q. For a diffusive process, and hence also for small q, this decrease is given by $1/q^2$ [21]. However, for the q range considered here, i.e., $q \geqslant 1.1\,\text{Å}^{-1}$, one would expect that the behavior of τ is affected by the local structure. That this indeed is the case is shown in Fig. 10 where we plot $\tau' q^2$ vs q. The product $\tau' q^2$ can be interpreted as an inverse q-dependent diffusion constant. Thus, generally speaking, for q values that correspond to length scales of nearest-neighbor distances, $\tau' q^2$ should be relatively large because then diffusion processes should be relatively slow due to the local order. As we see in Fig. 10 $\tau' q^2$ exhibits a maximum around $2.7\,\text{Å}^{-1}$ for silicon as well as for oxygen, which is close to the position of the main peak in the static structure factor corresponding to the length scale of a Si-O bond. It is of course remarkable that no such feature is found at the position of the first sharp diffraction peak, at $q=1.7\,\text{Å}^{-1}$, although such a feature is probably buried under the broad peak around $q=2.7\,\text{Å}^{-1}$ (see Fig. 10). We can rationalize this q dependence from our previous observation [7] that the elementary diffusion step for the oxygen atoms is due to the breaking of a Si-O bond (and a slightly more complicated process for the silicon atoms) which shows that this length scale is of particular importance for the dynamics. We note that a similar behavior is found also in the MCT calculation for a hard sphere system [40]. In this case one obtains a peak in τq^2 at a position that is close to the first peak in the static structure factor.

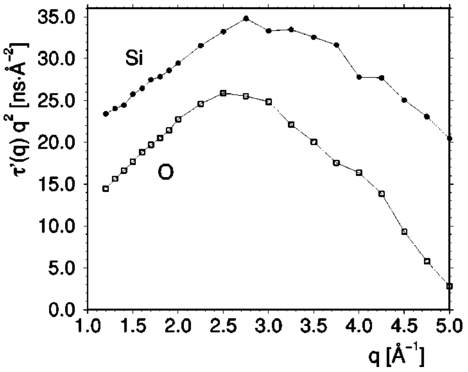

FIG. 10. The product $\tau'(q)q^2$ as determined from the incoherent intermediate scattering functions as a function of q at $T=2750$ K.

In contrast to the monotonic decrease of the relaxation time for the incoherent functions, the one for the coherent functions shows an oscillatory behavior around the incoherent one, see Fig. 9. These oscillations are in phase with the partial static structure factors, which have been included in

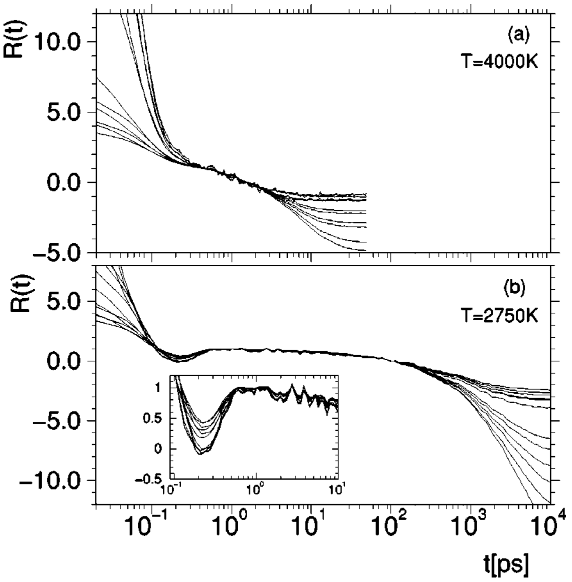

FIG. 11. Time dependence of the ratio $R(t)$, as defined in Eq. (9), for various correlators. (a) $F_s(q,t)$ for silicon and oxygen at $q=1.7$, 2.2, 2.8, 4.43, 5.02, and 5.31 Å^{-1}. $T=4000$ K; (b) the same set of correlators as in (a) but now at $T=2750$ K.

the figures as well. Whenever the modulus of $S_{\alpha\beta}(q)$ is large, the corresponding $\tau(q)$ is large also, a phenomenon that is very similar to the so-called de Gennes narrowing [21]. [Note, however, that, strictly speaking, the de Gennes narrowing is a phenomenon related to the dynamics at *short* times [21] and thus cannot be used to explain the $\tau(q)$ dependence on the time scale of the α relaxation.] Finally we mention that this type of dependence has also been found in a MCT calculation for a hard sphere system [28] and recently in a neutron scattering experiment of toluene and *m*-toluidine [41]. This shows that our findings can also be seen in real experiments and that MCT is able to rationalize them at least qualitatively.

Having discussed so far mainly the α relaxation, we now turn our attention to the β-relaxation, i.e., the time window in which the correlators are close to the plateau. MCT makes several interesting predictions about this relaxation regime and therefore we will check in the following to what extent they are valid for the present system. The first prediction of the theory is the so-called ''factorization property,'' which says that close to the plateau every time correlation function $\phi_A(t)$ of an observable A is given by

$$\phi_A(t)=\phi_A^c+h_A G(t), \tag{8}$$

where ϕ_A^c is the height of the plateau, h_A is a constant, and the whole time and temperature dependence is given by the function $G(t)$, *which does not depend on the observable A*. If the factorization property holds one can see immediately that the ratio

$$R_A=\frac{\phi_A(t)-\phi_A(t')}{\phi_A(t'')-\phi_A(t')} \tag{9}$$

is independent of A if the times t, t', and t'' are in the β-relaxation regime, i.e., where Eq. (8) holds. Note that this prediction of the theory does not only hold for the idealized version of the theory but also for the extended one, i.e., if the hopping processes mentioned in the Introduction are taken into account. Therefore it is reasonable to check the validity of Eq. (8) not just above T_c, but also below. This is done in Fig. 11 where we plot the ratio $R(t)$ for a temperature above T_c, 4000 K in panel (a), and below T_c, 2750 K in panel (b). The correlation functions shown are $F_s(q,T)$ for silicon and oxygen at $q=1.7$, 2.2, 2.8, 4.43, 5.02, and 5.31 Å^{-1}. The times t'' and t' are 0.4 ps and 1.6 ps for $T=4000$ K and 11 ps and 106 ps for $T=2750$ K, respectively.

From Fig. 11(a) we see that all the various curves collapse nicely onto a master curve at intermediate times, i.e., in the β-relaxation regime. That this collapse is by no means trivial is seen at short and long times since there we find no collapse at all, thus showing that in general the shape of the correlation function does depend on the observable. Only in the β regime the correlators show a system universal time dependence, in agreement with the theory.

The theory also predicts that with decreasing temperature the time window over which the β relaxation is observed should expand. That this is indeed the case is demonstrated in Fig. 11(b), where we show the same correlation functions as in panel (a), but now at a lower temperature. From the figure we see that now the range over which the correlators fall onto a master function has indeed increased considerably, in agreement with the theory. Also included in this panel is an enlargement of $R(t)$ at times where the correlator shows a dip, due to the boson peak mentioned above. From this inset we see that on this time scale the factorization property no longer holds since there the correlation functions are dominated by the vibrational dynamics for which Eq. (8) is not valid.

We have considered here only the incoherent intermediate scattering functions. But recently we have shown that the factorization property holds also for other time correlation functions [42]. In Fig. 6 of Ref. [42] we plot, for $T=2750$ K, the time dependence of $R(t)$ for $F_s(q,t)$ for oxygen at $q=2.8$ Å^{-1}, for $F(q,t)$ for Si-Si at $q=1.7$ Å^{-1} and the functions $a_0^{\rm Si}(t)$ and $a_0^{\rm SiO}(t)$ that have been proposed by Roux *et al.* [35] and which are defined as

$$a_0^{\rm Si}(t)=\int_0^{r_0^{\rm Si}} 4\pi r^2 G_s^{\rm Si}(r,t)dr \tag{10}$$

and

$$a_0^{\rm SiO}(t)=\int_0^{r_0^{\rm SiO}} 4\pi r^2[G_d^{\rm SiO}(r,t)-1][G_d^{\rm SiO}(r,0)-1]dr. \tag{11}$$

Here $G_s^{\rm Si}(r,t)$ and $G_d^{\rm SiO}(r,t)$ are, respectively, the self and distinct parts of the van Hove correlation functions [21] that have been calculated and discussed in Ref. [7]. The values of $r_0^{\rm Si}$ and $r_0^{\rm SiO}$ are 0.4 Å and 2.35 Å, respectively. Thus we see that the four time correlation functions considered are of very different nature and their overall relaxation behavior is

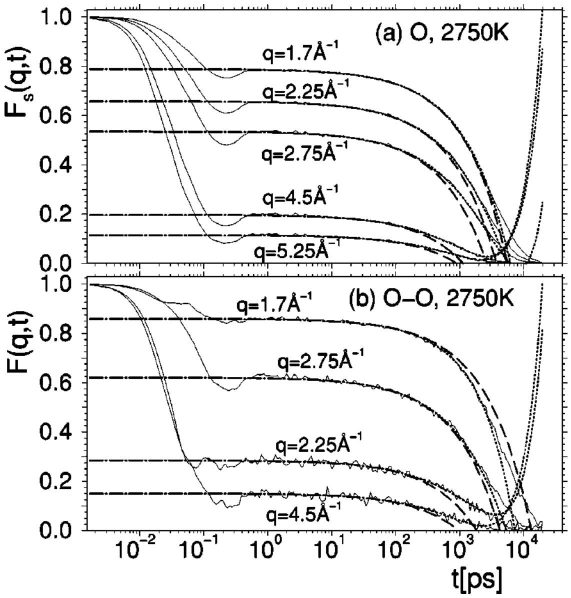

FIG. 12. Time dependence of $F_s(q,t)$ for oxygen, panel (a), and $F(q,t)$ for the oxygen-oxygen correlation, panel (b), for various wave vectors (solid lines). The dotted lines are fits the functional form given by Eq. (12). The dashed lines are fits with the functional form given by Eq. (12) without the last term.

certainly not the same. In Fig. 6 of Ref. [42], however, in the β-relaxation regime the four functions fall as nicely onto a master curve as the incoherent intermediate scattering functions shown in Fig. 11(b). Therefore we find that also for these correlators Eq. (8) holds, which is hence strong evidence that for the present system the factorization property is a general property of a very large class of time correlation functions.

Having shown now that in the β-relaxation regime the shape of a time correlation function $\phi_A(t)$ is independent of the observable A considered, we continue now to study this shape in more detail. For this we make use of a further prediction of MCT, namely, that the time dependence of $\phi_A(t)$ at long times is not arbitrary, but given by a sum of power laws of the form

$$\phi_A(t)=\phi_A^c-h_A t^b+h_A^{(2)}t^{2b}+\cdots. \tag{12}$$

Here ϕ_A^c is the height of the plateau, often also called the nonergodicity parameter, and h_A (also called critical amplitude) and $h_A^{(2)}$ are constants. According to MCT the value of the exponent b, also called von Schweidler exponent, is *independent* of A, i.e., it is a system-universal quantity. The first two terms on the right-hand side are the so-called von Schweidler law. Note that Eq. (12) is an expansion of the correlator in terms of t^b, i.e., it is assumed that the third term is smaller than the second one. However, it has been suggested by the theory [43] that in order to determine reliably the coefficient h_A it is usually necessary to take into account this correction as well. In order to check whether the ansatz (12) gives a good description of our correlation functions we have fitted them in the β-relaxation regime with this functional form. The temperature we used was 2750 K, since this gives us the longest plateau and hence allows us to determine the fit parameters with the highest precision. The result of these fits are shown in Fig. 12 for the case of the incoherent function for the oxygen atoms, panel (a), and the coherent function for the O-O correlation, panel (b). For each correlator (solid lines) two fits are shown: The one in which all three terms in Eq. (12) were used (dotted lines) and the one in which the third term was neglected (dashed lines). The difference between these two fits are seen at long times where the fits with the correction terms are able to describe the correlator for about one decade more than if these terms are not taken into account. That the quality of the fits improves significantly by considering the correction term $\propto t^{2b}$ was first shown by Sciortino *et al.* for the case of water [29]. We emphasize that for these fits the value of b was kept fixed for all the different correlators, i.e., it was a global fit parameter. The value we obtained for b was 0.62 ± 0.02. It can be seen from the figure that, if the correction terms are taken into account, the resulting fits are very good and describe the data over more than three decades. Therefore we conclude that this prediction of the theory, i.e., Eq. (12), holds for the present system.

A further interesting prediction of MCT is that there exists a one-to-one correspondence between the value of the von Schweidler exponent b from Eq. (12) and the exponent γ of the α-relaxation time in Eq. (7) [3,4]. According to the theory one can start with b and determine from

$$\frac{\Gamma^2(1+b)}{\Gamma(1+2b)}=\frac{\Gamma^2(1-a)}{\Gamma(1-2a)} \tag{13}$$

the value of the parameter a and then use the relation

$$\gamma=\frac{1}{2a}+\frac{1}{2b} \tag{14}$$

to calculate γ. [Here $\Gamma(x)$ is the Γ function.] If this is done for our value $b=0.62$, one obtains $\gamma=2.35$. Since we have determined the value of γ, as defined by Eq. (7) also directly from the temperature dependence of the α-relaxation time, we can compare it now to this theoretical value. This is done in the inset of Fig. 8 and, as discussed already above, the theoretical value agrees well with the ones from $\tau(T)$ for finite values of q. Thus we conclude that also this highly nontrivial prediction of the theory is satisfied quite accurately.

In the last part of this section we discuss the wave-vector dependence of the parameters that where obtained from the fits of the correlators in the β regime to the functional form given by Eq. (12). For this we have made fits to the two incoherent and the three coherent intermediate scattering functions at $T=2750$ K for a wide range of wave vectors. The dependence of the nonergodicity parameters is shown in Fig. 13. For the case of the incoherent function $f_s^c(q)$, we see that the q dependence is Gaussian-like. A fit with the functional form $\exp(-q^2r_s^2)$ gives a very good description of the data (see solid lines in panels (a) and (c)]. For the localization length r_s, i.e., the size of the cage, we obtain for silicon

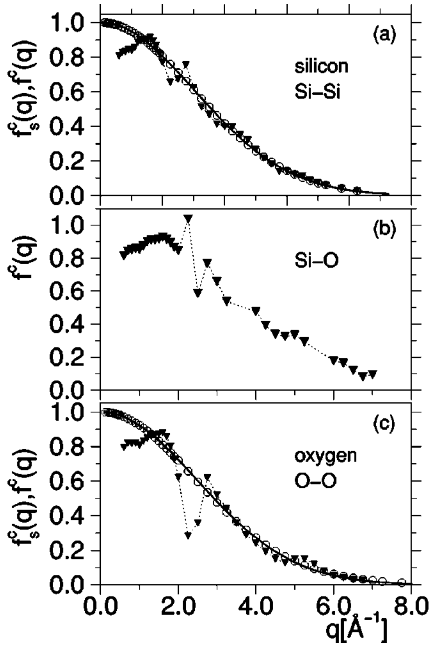

FIG. 13. Wave-vector dependence of the nonergodicity parameters. (a) $f_s^c(q)$ from $F_s(q,t)$ for silicon and $f^c(q)$ from $F(q,t)$ for the silicon-silicon correlation; (b) $f^c(q)$ from $F(q,t)$ for the silicon-oxygen correlation; (c) $f_s^c(q)$ from $F_s(q,t)$ for oxygen and $f^c(q)$ from $F(q,t)$ for the oxygen-oxygen correlation. The solid lines in (a) and (b) are a fit with a Gaussian to the incoherent data.

and oxygen the values 0.23Å and 0.29Å, respectively. This has to be compared with the typical nearest-neighbor distance between silicon and oxygen, which is $d = 1.6$ Å [7,44]. Thus we find that r_s is around $0.14d$ and $0.18d$ for silicon and oxygen, respectively. This size is somewhat larger than the one found in most solids which, in agreement with the Lindemann criterion [45], have usually $r_s \approx 0.1d - 0.14d$. The reason for this difference might lie in the fact that SiO_2 is a very open network and thus the atoms can vibrate with a relatively large amplitude without approaching each other too much.

The wave-vector dependence of the nonergodicity parameter for the coherent functions shows oscillations that are in phase with the corresponding partial structure factor. For the case of Si-Si and O-O they oscillate around the corresponding f_s^c and become basically indistinguishable from them at large q. These results are in qualitative agreement with the ones obtained for other systems [29,34,37–39] which shows that from this point of view the present open network system does not behave differently as a simple liquid or a polymer. As already mentioned in the Introduction, it has recently been shown that the q dependence of the nonergodicity parameters $f^c(q)$ shown here can be calculated also reliably with the theory *without any fit parameter*. Since the agreement was also good at large wave vectors, and since we see now that the coherent function oscillates around the incoherent one, we expect that the theory is indeed able to give a reliable estimate of the size of the cage for this network forming system.

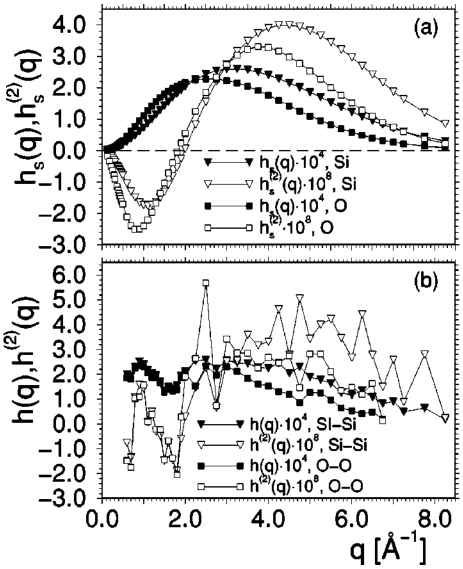

FIG. 14. Wave-vector dependence of the critical amplitude $h(q)$ and the first correction term $h^{(2)}(q)$. (a) Incoherent functions for silicon and oxygen; (b) coherent functions for the silicon-silicon and the oxygen-oxygen correlations.

The wave-vector dependencies of the remaining parameters are shown in Fig. 14. In panel (a) we show the critical amplitude h_s and the first correction $h_s^{(2)}$ for the two incoherent functions. From this figure we recognize that from a qualitative point of view the curves are very similar to the ones calculated within the MCT for a system of hard spheres [28]. In particular we find that at small wave vectors $h_s^{(2)}$ shows a negative minimum and subsequently a positive maximum at significantly larger q. In between it becomes zero at $q = 1.98$ Å^{-1} and 1.82 Å^{-1} for the case of silicon and oxygen, respectively. This is close to the first peak in the structure factor, in agreement with the results for the hard sphere system [28]. This result shows that from this point of view the theoretical calculation is qualitatively correct. Note that the fact that $h_s^{(2)}(q) = 0$ means that for this wave vector the von Schweidler law, i.e., the second term in Eq. (12) can be seen over the broadest possible time-window, since the first correction to this law is zero.

Also the q dependence of $h(q)$ and $h^{(2)}(q)$ for the collective quantities, Fig. 14(b), is in qualitative agreement with the MCT results for a hard sphere system [28]. For example, at the location of the first peak $h^{(2)}(q)$ shows a minimum and its value is negative. Thus we see that the theory is able to rationalize the behavior of this function, at least in a qualitative way. Of course it would be a more stringent test to do the MCT calculation directly for the silica system rather than for hard spheres. However, this type of calculation is currently still very demanding and thus has to be left as a future project.

IV. SUMMARY AND DISCUSSION

In this paper we have presented the results of molecular dynamics computer simulations of a model for silica, the archetype of a strong glass former. The goal of this study was twofold: On the one hand, to investigate in detail the relaxation dynamics of this system in the temperature regime where this dynamics is slow. On the other hand, we wanted to check to what extent the mode-coupling theory of the glass transition is able to describe this dynamics at low temperatures. In these investigations we mainly focused on the time and temperature dependence of the various intermediate scattering functions for different wave vectors. We found that these functions show nicely the slowing down of the system upon cooling in that they change their shape from a single exponential at high temperatures to a two-step relaxation at low temperatures. We emphasize that this two-step relaxation is already seen at temperatures that are about 70% above the melting temperature of the system, which shows that in order to show a slow dynamics the system does not have to be supercooled.

In a previous paper it was demonstrated that this system shows a crossover of the dynamics from a flowlike motion at intermediate and high temperatures to a hoppinglike motion at low temperatures [7]. The temperature of this crossover can be identified with the critical temperature of MCT and is around 3330 K. We now find that the time-temperature superposition principle holds for temperatures around T_c and that time correlation functions are stretched. For significantly higher and lower temperatures, the TTSP is violated in that the correlators become more exponential-like. This observation is also in accord with the existence of the above-mentioned crossover from a flowlike dynamics (i.e., collective motion that leads to a stretched exponential relaxation) to a dynamics in which hopping dominates (i.e., single particle dynamics that leads to an exponential relaxation). These results are in qualitative agreement with the prediction of the theory [13].

The temperature dependence of the α-relaxation times are qualitatively similar to the one of the diffusion constant in that also they show a crossover from an Arrhenius law at low temperatures to a weaker temperature dependence at higher T. In this latter temperature range the T dependence of τ can be fitted well with a power law with the same critical temperature as found in Ref. [7]. However, the exponent γ of this power law that we find for the intermediate scattering function is significantly higher than the one for the diffusion constant, in contradiction with the leading order prediction of the theory. Similar to the findings in simple liquids, the reason for this discrepancy might be the existence of dynamical heterogeneities, i.e., due to the fact that the temperature dependence of the diffusion constant is weaker than expected.

According to the theory the time-temperature superposition principle should hold also in the β-relaxation regime. We find that a plot of the correlation functions versus rescaled time does not lead to a collapse of the curves onto a master function in this time window. The reason for this is likely the presence of a very pronounced vibrational dynamics, related to the boson peak, that extends to relatively low frequency, i.e., influences the dynamics also at relatively long times. It has been shown before that the presence of a pronounced microscopic dynamics may disturb the β-relaxation dynamics predicted by MCT so strongly that the asymptotic results cannot be observed anymore [23]. Therefore it is not surprising that for the present system the TTSP does not hold in the β regime. (Note, that the reason that the TTSP is nevertheless observed in the α regime is likely the fact that the latter regime is much less affected by the microscopic vibrations than the former since on the time scale of the α-relaxation the vibrations have finally been damped out.) However, by calculating the function $R(t)$ from Eq. (9) we can show that the time dependence of a wide class of correlation functions is the same for times in the β-relaxation regime. In agreement with the theory this dependence is a sum of fractal power laws. We also find that the value of the von Schweidler exponent b in these laws obeys the connection proposed by MCT between b and the exponent γ of the α-relaxation time, if one uses the γ as determined from $\tau(T)$ from the intermediate scattering function at *finite* wave vectors. This result shows that neither γ nor b is a mere fit parameter but instead that they have a more fundamental theoretical meaning.

By fitting the coherent and incoherent intermediate scattering functions in the β-relaxation regime with the functional form proposed by MCT we have determined the wave-vector dependence of the various nonergodicity parameters, the critical amplitudes, and the correction terms. From a qualitative point of view these dependences look very similar to the ones found in simple liquids or simple molecules [29,34,37,38]. Since the latter systems are all fragile glass formers we thus conclude that for these quantities there is no qualitative difference between fragile and strong glass formers. Furthermore it has to be mentioned that these dependences are also in qualitative agreement with the ones predicted by MCT *for the simpler systems*, thus giving evidence that the theory is indeed able to describe them correctly.

However, an important difference between fragile and strong glass formers is that the typical activation energies appearing in the relaxation dynamics at low temperatures are often connected to the breaking of a covalent bond [1]. Indeed, for SiO_2 we have recently shown that the energy to break a Si-O bond is equal to the activation energy of the Arrhenius law for the oxygen diffusion constant at low temperatures, i.e., 4.7 eV [7]. This is in contrast to the case of fragile glass formers where it does not seem to be possible to relate activation energies to simple elementary events like the breaking of a bond.

In summary, we can say that MCT allows to understand many aspects of the dynamics of this strong glass former. Note that the glassy dynamics studied in this paper is seen at temperatures that are all significantly above the experimental glass transition temperature T_g, which is around 1450 K, and even above the melting point of the material, which is around 2000 K. Hence this shows that in order to have a slow dynamics it is not necessary to be in a supercooled state.

Finally we mention that in Ref. [9] it was shown that the q dependence of the Debye-Waller factor is predicted well by MCT. To what extent this is true also for the other observables studied in the present paper is not yet known and it is certainly important to check this in the future. It is of interest that we find that some of the predictions of the theory, such as the factorization property, hold also below

T_c, i.e., in a temperature regime where the hopping processes are important. For the present system we find, however, that in the β-relaxation regime the time-temperature superposition principle does not hold. Whether this is a real failure of the theory for strong glass formers or whether this is just a side effect of the strong vibrational dynamics at short times, can unfortunately not be decided. Hence it would be of great interest to investigate this question for a strong glass former that does not show such a pronounced vibrational dynamics.

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