Two-Step Relaxation Decay in a Strong Glass Former

D. Sidebottom, R. Bergman, L. Börjesson, and L. M. Torell
Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

(Received 10 May 1993)

The dynamics around the liquid-glass transition in B_2O_3 have been investigated by photon correlation spectroscopy. A two-step relaxation is for the first time observed in a "strong" network forming glass. The behavior is similar to the fast β and slower α relaxations observed for "fragile" glasses and proposed in mode coupling theory (MCT) for simple glass forming systems. We find that the time decays of the two processes obey power laws consistent with MCT. It seems that a two-step relaxation is a more general relaxation pattern than has been discussed so far.

PACS numbers: 64.70.Pf, 05.40.+j, 78.35.+c

The transition from a liquid to a glass is characterized by an enormous increase of the viscosity and the related structural relaxation time. As the glass transition is approached from the liquid state the viscosity changes by some 15 orders of magnitude and the relaxation time rises from picoseconds to some hundreds of seconds at which the system appears solid for most experimental time scales. Such enormous changes of the structural dynamics put extreme requirements on the experimental techniques for investigation of the phenomenon. The recent attention to the liquid-glass transition, triggered by the development of new theoretical models [1-3], is to a large extent due to improvements of experimental methods which make it possible to cover previously inaccessible time and/or frequency ranges [4-10]. In the present study of an oxide glass, B_2O_3, we make use of a photon correlation (PC) technique with a time window of 8 decades which allows the investigation of the so far widest range of glass formation in this system.

The temperature dependence of the structural relaxation time τ of glass forming liquids can generally be well represented by the empirical expression

$$\tau = \tau_0 \exp\{DT_0/(T-T_0)\}\,. \tag{1}$$

The parameter D is a measure of the structural "strength" of the system. The largest D values characterize those liquids which are most resistant towards temperature induced changes. These liquids display a nearly Arrhenius behavior and are referred to as "strong" [11]. To this group belong covalently bonded network glass formers like SiO_2 ($D \approx 100$) [11] and B_2O_3 ($D \approx 35$) [12], the latter being the focus of the present work. At the other extreme, those systems with the smallest D values (~ 3) demonstrate the most rapid changes of τ in the supercooled region. Here one finds weakly interacting (ionic and van der Waals) systems in which the association is readily disrupted as temperature increases. Hence they are referred to as "fragile" glasses [11]. T_0 of Eq. (1) is some temperature below the calorimetrically determined glass transition temperature T_g. For the fragile systems the dramatic change of τ in the transition range implies that T_0 is close to T_g ($T_g/T_0 \approx 1.2$ [11]) while for strong ones T_0 is far below ($T_g/T_0 \approx 2$ for B_2O_3 [12]) [13]. The sharp nature of the transition in the fragile glasses has led to the suggestion that there exists a true thermodynamic phase transition at T_0 underlying the glass formation. It is then to be noted that T_0 is close to the Kauzmann temperature, T_K, at which the excess entropy of the supercooled liquid extrapolates to zero. Recent theories, however, claim that the glass transition is of kinetic origin [1]. This is supported by the fact that T_g is cooling rate dependent and the findings that the Prigogine-Defay ratio is always larger than 1 in real systems [14].

Another characteristic of the dynamics at the glass transitions is the nonexponential time decay of the structural relaxation function $\phi(t)$. It is commonly expressed by the stretched exponential function

$$\phi(t) = A \exp[-(t/\tau_K)^{\beta_K}]\,. \tag{2}$$

Experimental findings suggest increased stretching (decreased β_K value) the more fragile the system [15,16]. However, there are recent indications of a more complicated time decay of the relaxation function than that of Eq. (2). Investigations of various fragile glass formers show a two-step behavior including a fast process, generally in the picosecond regime, which precedes the main so called α relaxation [4,5,9,17-19]. Such a fast process has in fact been suggested by the mode coupling theory (MCT) to be a general phenomenon at glass formation, at least for simple liquids with weak interparticle interactions, and it is proposed to be linked to the α process. So far the experimental observations of the effect have been limited to fragile systems. It is the aim of the present study to investigate whether short time processes are universal for glasses by investigating the relaxation function of a strong glass former such as B_2O_3.

The B_2O_3 sample was prepared as described in Ref. [20]. The 488 nm line of an Ar laser was used as a light source and the VV component of 90° scattered light was detected. The intensity-intensity correlation function, obtained at temperatures ranging from 506 to 771 K, was recorded over a time window of almost 8 decades by a correlator (ALV 3000). The correlation function is relat-

0031-9007/93/71(14)/2260(4)$06.00

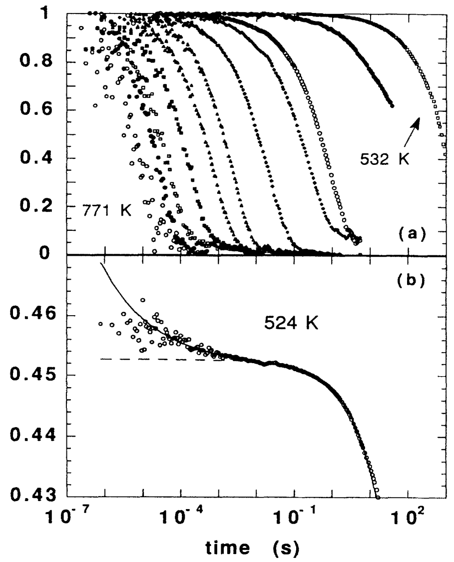

FIG. 1. (a) Relaxation functions $\phi(t)/A$ for a range of temperatures (532, 559, 592, 600, 627, 654, 672, 696, 728, 745, and 771 K) above T_g showing the main α relaxation. (b) Representative relaxation function for a temperature just below T_g ($T=524$ K) showing the long time tail of a fast process and the initial decay of the slower α relaxation. Dashed curve represents a fit of a stretched exponential [Eq. (2)] to the decay at long times. Solid curve represents a fit to $\phi(t)=\phi_\alpha+\phi_\beta$ [see Eqs. (3) and (4)].

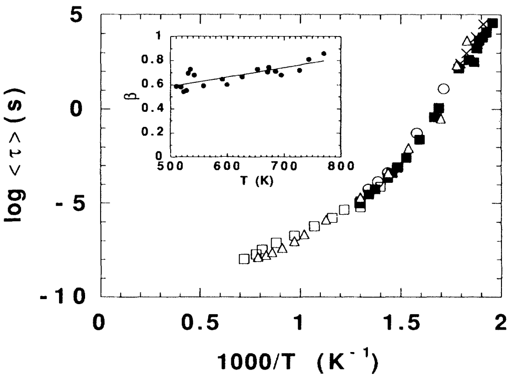

FIG. 2. Arrhenius plot of the average structural relaxation time; (■) present results as obtained from fits of Eq. (2) to the data, (○) photon correlation results [21], (×) pressure jump volume relaxation data [21], (△) hypersonic [12] and (□) ultrasonic [22] results scaled as described in Ref. [22]. Inset shows the temperature variation of the stretching parameter β resulting from fits of Eq. (2) to the data in Fig. 1(a). Solid lines represents the best linear fit to the data.

ed to the relaxation function $\phi(t)$ by $\sigma\phi^2(t)=\langle I(0)I(t)\rangle/\langle I\rangle^2-1$, where σ represents the spatial coherence factor and $\langle I\rangle$ is the time averaged intensity. The coherence factor was determined to be ~ 0.9 from a reference measurement on polystyrene microspheres.

Typical results for the relaxation function obtained above T_g (≈ 532 K) are shown in Fig. 1(a). For most temperatures the complete relaxation pattern is contained within the 8 decade time window of the correlator. The spectra are well represented by Eq. (2) and have been normalized in Fig. 1(a) by the preexponent A. In Fig. 2 we present the average relaxation times $\langle\tau_K\rangle=\tau_K/\beta_K\Gamma(1/\beta_K)$ obtained from the fits. Also presented in Fig. 2 are literature data for the relaxation times of the main α process [12,21,22] and they closely follow the present results. The stretching parameter obtained in the fits is found to slightly increase with temperature; see inset in Fig. 2. This is also in accordance with previous measurements of the α process in B_2O_3 for which β_K is reported to rise smoothly from ~ 0.5 close to T_g to about 0.8 at 800 K [21-23].

Below T_g, the rapidly increasing time scale of the α relaxation makes it impossible to obtain its complete form; see a typical spectrum in Fig. 1(b). Even though the spectra below T_g only display the initial part of the α process and the final decay towards the base line is not observed, they are well fitted to a stretched exponential in the limited range $10^{-2}<t<10^2$ s and with a stretching parameter similar to that found above T_g. More interesting is that the short time part of the spectrum ($<10^{-2}$ s) deviates from the functional form of Eq. (2). This implies the presence of another relaxation process which

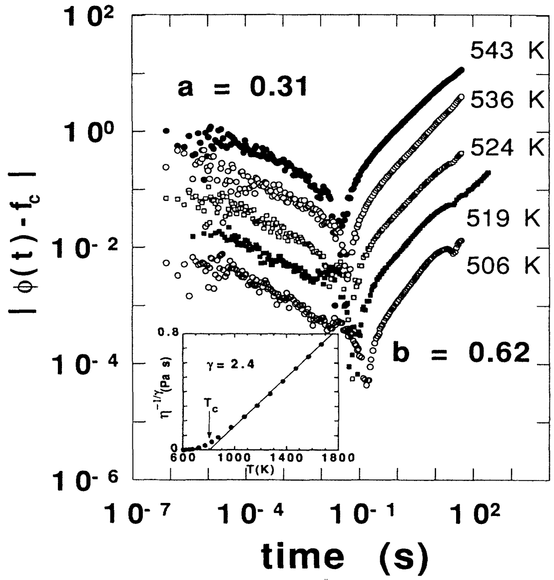

FIG. 3. Log-log plot of the absolute value of $\phi(t)-f_c$ for a range of temperatures around T_g (532 K). Subsequent spectra are upshifted by half a decade for clarity. The data display a short time linear region with a slope of $a=0.31\pm0.05$ and a long time linear region with a slope $b=0.62\pm0.03$. f_c was chosen as described in the text. Inset shows the temperature variation of the viscosity in a $\eta^{-1/\gamma}$ vs T representation ($\gamma=1/2a+1/2b=2.4$; see text).

occurs at considerably shorter times than the α relaxation. It is also to be noted that the initial and main part of the correlation function decays at shorter times than our experimental time window; see Fig. 1(b). Therefore, we can only record the tail of the fast process, which mainly relaxes at times $\ll 10^{-7}$ s. Within the experimental accuracy, no temperature dependence is noted for the short time process in the temperature range 506–543 K in which we observe it; see Fig. 3 and discussion below.

It is well known that many glass forming systems show two different relaxation processes. The commonly accepted explanation for the fastest one, often referred to as a β, secondary, or Johari-Goldstein relaxation, is that it is related to the molecular details of the glass former. Others have suggested that it may be a general dynamical feature of dense disordered systems rather than being specific to the glass under investigation [1,24]. β processes have been detected by dielectric relaxation in the time range 10^{-7}–10^{-2} s for several systems including both low and high molecular weight glass formers [24]. Faster processes ($\sim 10^{-12}$ s), likewise referred to as β relaxations, have recently been observed by neutron and light scattering techniques [5,9,16–18]. It is not clear whether the "slow" β processes are in some way related to these "fast" relaxations [25,26]. The presence of two distinct relaxation processes has theoretically been demonstrated using the mode coupling approach for simple weakly bonded glass forming liquids [1]; the slower process (α) is responsible for the diffusive motion and the faster one (β) is attributed to strongly anharmonic motions of a limited number of molecules trapped in cages formed by their neighbors. This model has been used to explain the picosecond processes reported in the light and neutron scattering studies. In the following we analyze our data using the predictions of MCT [1]. The β process is then given by

$$\phi\beta(t) = f_c + C_\beta (t/t_0)^{-a}, \quad 0 < a \le \tfrac{1}{2}\,, \tag{3}$$

where f_c is the nonergodicity level, t_0 is the microscopic time, and C_β is a temperature dependent material constant. The fast process relaxes towards the nonergodic level, f_c, given by the frozen-in relaxation strength of the cage (the "caging" molecules are reasonably fixed for short times). For sufficiently long times and for temperatures above some critical temperature T_c, the system is considered to be fully ergodic and those molecules which comprise the cage can relax. This process reflects the α relaxation and its initial part, from the plateau level f_c, is in MCT described by the von Schweidler law:

$$\phi_\alpha(t) = f_c - C_\alpha (t/\tau_\alpha)^b, \quad 0 < b \le 1\,. \tag{4}$$

In Fig. 3 we plot the present observations of the α and β processes in the double logarithmic plot of $|f_c - \phi(t)|$ vs time in order to test the predicted power-law relations. f_c is chosen to coincide with the fit parameter A of the stretched exponential [see Eq. (2)] and also with the dashed line in Fig. 1(b) of the α process. Two linear regions can easily be distinguished in Fig. 3 separated by a cusplike feature. (The small structures at long times $\sim 10^2$ s are spurious effects caused by external mechanical vibrations.) Thus, away from the crossover regime the α and the β processes are well described by the power laws, Eqs. (3) and (4), predicted in MCT for their asymptotic behavior. The cusp then represents the region in which both processes contribute to the decay. From the slopes in Fig. 3 the exponents of the two power laws are obtained as $a = 0.31 \pm 0.05$ and $b = 0.62 \pm 0.03$, respectively. Using the so obtained exponents the characteristic time of the α process and the microscopic time can be generated in fits of Eqs. (3) and (4) (C_α and C_β are of the order of unity [1] and we take $C_\alpha = C_\beta = 1$). We obtain values for τ_α which are indistinguishable from the data in Fig. 2 for the α process, and values for t_0 which are in the picosecond regime as expected for microscopic times. The full relaxation function obtained from the MCT analyses is presented as a solid curve in Fig. 1(b).

The values of the scaling exponents in the MCT approach are constrained by two relations. One relation is expressed as

$$\lambda = \Gamma(1-a)^2/\Gamma(1-2a) = \Gamma(1+b)^2/\Gamma(1+2b)\,,$$

$\Gamma(x)$ being the gamma function, and we find that our set of a and b achieves the same solution, namely, $\lambda = 0.72 \pm 0.05$. The other scaling relation is closely linked to the viscosity. In MCT the viscosity behavior is predicted to follow a power law $\eta = \eta_0 (T - T_c)^{-\gamma}$; T_c is the critical temperature and γ is related to the exponents a and b through $\gamma = 1/2a + 1/2b$. From the measured exponents a and b we obtain $\gamma = 2.4 \pm 0.4$. Using the latter, we present literature data for the viscosity in the inset of Fig. 3 in a $\eta^{-1/2.4}$ vs temperature plot and, in accordance with MCT, a linear behavior is revealed for the higher temperature range. Thus both measured exponents a and b satisfy the MCT scaling laws in a consistent manner.

The critical temperature obtained from the intersection of the viscosity data with the temperature axis (see inset of Fig. 3) is about 800 K. This implies that the present α and β processes are observed at temperatures below T_c, for which the simplified MCT version predicts α to be frozen. In the recent extended theory, the α process may, however, relax below T_c through phonon assisted jump diffusion [1]. Then Eqs. (3) and (4) are still valid, and the exponents a and b should not differ above and below T_c for systems with $\lambda \le \pi/4$, as is the case for the present system. The experimentally determined T_c is sensitive to the γ value and, taking into account the present accuracy of a and b, it can take values within the range 770–820 K. Nevertheless we note that T_c is well above the calorimetrically determined glass transition temperature T_g (532 K) of B_2O_3. This has previously been reported to be the case for several fragile systems [1,8,9,11,16, 27,28]; however, the departure is larger for the strong B_2O_3 glass ($T_c/T_g \approx 1.5$) than for fragile ones ($T_c/T_g \approx 1.2$). We then recall that the transition range of a strong glass former is much more smeared out in temperature as is seen, for example, from the large T_g/T_0 ratio discussed above. We propose that the large difference between T_c and T_g in B_2O_3 is a consequence of the slow temperature variation of the viscosity in the strong glass former.

In summary, we have observed in the strong glass former B_2O_3 a short time relaxation (β process) which exhibits a time decay and a temperature dependence significantly different from the slower main α relaxation. β processes have previously been reported for some fragile (ionic, polymeric, and molecular) glasses and are also predicted in the recently much discussed mode coupling theory to occur in simple glass formers like the fragile systems. They are then attributed to some localized diffusional motion of atoms or molecules within cages frozen in during cooling. Such a picture may be relevant for the weakly interacting fragile systems, whereas it is hard to visualize fast localized diffusional motion in the glassy state of B_2O_3 with its constrained covalently bonded network structure. Rather than molecules diffusing relative to each other, it is more plausible that the rapid relaxations in B_2O_3 are the result of cooperative molecular motions of some part of the network which locally may "flow" and rearrange without any drastic changes of the relative molecular positions. It is then interesting to note the behavior of gels, another group of structurally restricted systems. In the latter, recent PC observations show a power-law decay (β relaxation) to a nonergodic background below the gel transition and a two-step relaxation in the sol phase [29]. Thus, it seems that a two-step relaxation pattern is more general than what has been discussed so far from the theoretical and experimental work of simple glass formers.

The authors gratefully thank W. Götze, A. Sjölander, and L. Sjögren for stimulating discussions. This program is supported by the Swedish Research Council for Natural Sciences.

---

[1] For a review of the mode coupling theory see W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
[2] I. A. Campbell, J-M. Flesselles, R. Jullien, and R. Botet, Phys. Rev. B **37**, 3825 (1988).
[3] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A **40**, 1045 (1989).
[4] F. Mezei, W. Knaak, and B. Farago, Phys. Rev. Lett. **58**, 571 (1987).
[5] W. Knaak, F. Mezei, and B. Farago, Europhys. Lett. **7**, 529 (1988).
[6] P. K. Dixon and S. R. Nagel, Phys. Rev. Lett. **61**, 341 (1988).
[7] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, Phys. Rev. Lett. **65**, 1108 (1990).
[8] L. Börjesson, M. Elmroth, and L. M. Torell, Chem. Phys. **149**, 209 (1990).
[9] N. J. Tao, G. Li, and H. Z. Cumminz, Phys. Rev. Lett. **66**, 1334 (1991); Phys. Rev. B **43**, 5815 (1991); C. Dreyfus, M. J. Lebon, H. Z. Cumminz, J. Tolouse, B. Bonello, and R. M. Pick, Phys. Rev. Lett. **69**, 3666 (1992).
[10] D. L. Sidebottom, R. Bergman, L. Börjesson, and L. M. Torell, Phys. Rev. Lett. **68**, 3587 (1992).
[11] C. A. Angell, Phys. Chem. Solids **49**, 863 (1988).
[12] M. Grimsditch and L. M. Torell, in *Dynamics of Disordered Materials*, edited by D. Richter (Springer, Berlin, 1989).
[13] M. Tatsuminago, B. L. Halfpap, J. L. Green, S. M. Lindsay, and C. A. Angell, Phys. Rev. Lett. **64**, 1549 (1990).
[14] See, for example, *Physics of Amorphous Materials*, edited by S. R. Elliott (Longman, New York, 1990).
[15] L. M. Torell, L. Börjesson, and M. Elmroth, J. Phys. Condens. Matter **2**, SA207 (1990).
[16] T. A. Vilgis, Phys. Rev. B **47**, 2882 (1993); P. J. Plazek and K. L. Ngai, Macromolecules **29**, 1222 (1991).
[17] W. Petry, E. Bartsch, F. Fujara, M. Kiebel, H. Sillescu, and B. Farago, Z. Phys. **83**, 175 (1991).
[18] W. Doster, S. Cusack, and W. Petry, Phys. Rev. Lett. **65**, 1080 (1990).
[19] W. Steffen, A. Patkowski, G. Meier, and E. W. Fisher, J. Chem. Phys. **96**, 4171 (1992).
[20] A. K. Hassan, L. Börjesson, L. M. Torell, and H. Doweidar, Phys. Rev. B **45**, 12797 (1992).
[21] J. A. Bucaro, H. D. Dardy, and R. D. Corsaro, J. Appl. Phys. **46**, 741 (1975).
[22] P. Macedo and T. A. Litovitz, Phys. Chem. Glasses **6**, 69 (1965); W. Capps, P. B. Macedo, B. O'Meara, and T. A. Litovitz, J. Chem. Phys. **45**, 3431 (1966).
[23] G. M. Bartenev and V. A. Lomovski, J. Non-Cryst. Solids **146**, 225 (1992).
[24] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).
[25] E. Rössler, Phys. Rev. Lett. **65**, 1595 (1990).
[26] L. Wu and S. R. Nagel, Phys. Rev. B **46**, 11198 (1992).
[27] B. Frick, B. Farago, and D. Richter, Phys. Rev. Lett. **64**, 2921 (1990).
[28] P. Taborek, R. N. Kleinman, and D. J. Bishop, Phys. Rev. B **34**, 1835 (1986).
[29] S. Z. Ren and C. M. Sorensen, Phys. Rev. Lett. **70**, 1727 (1993).