

Evidence of two structural relaxation processes near the glass transition of a strong glass former

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The dynamics of density fluctuations in arsenic trioxide has been investigated by Brillouin and photon correlation spectroscopy over the broad temperature range of 370–770 K. Over overlapping temperature ranges, a fast secondary and slow primary (α) relaxation were clearly resolved with a time separation of about ten orders in magnitude. The former observed in the GHz frequency range appears to be of a different origin from the β relaxation that is usually probed by dielectric spectroscopy in the glassy state. Conformational transitions between specific liquid structures are evoked to rationalize these fast density fluctuations in the supercooled amorphous state.

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The dynamical and structural aspects of glass forming systems and viscous liquids in general have been the focusing point of many theoretical and experimental investigations over the past few years [1]. The great interest has arisen from the fact that a variety of universal phenomena accompanying glass formation and the underlying molecular mechanisms are not yet understood. The most important features among these are the departure from the Arrhenius temperature dependence, non-Debye relaxation behavior, the onset of multiple relaxations and their merging at temperature, T , higher than the calorimetric glass transition temperature T_g . Therefore, many theoretical efforts have been mainly oriented towards the understanding of certain dynamical features of disordered systems [2].

The theoretical approaches most widely accepted are the mode coupling theory (MCT) [2(a)], the coupling scheme for relaxation [2(d)], and a recently proposed thermodynamic model distinguished by the ignorance of the T_g [2(b)]. The recent development of the MCT that deals with the microscopic time domain (10^{-14} – 10^{-9} s) has stimulated many experimental studies, mainly neutron and light scattering, but also some molecular dynamic simulations. MCT provides certain quantitative predictions such as the fast β process, the critical ergodic to nonergodic transition at some temperature T_c higher than T_g and many scaling laws. On the other hand, the coupling scheme has been formulated and based on the nonlinear nature of the intermolecular interaction potential. The model predicts the existence of a temperature independent crossover time t_c that separates two different time regimes, characterized by a Debye-like and a nonexponential behavior for $t < t_c$ and $t > t_c$, respectively [2(d)]. In the thermodynamic model [2(b)], a frustration limited microdomain structure is postulated below a temperature T^* near and above the melting temperature, T_m .

Among the different dynamical variables affected by the glass dynamics, thermal density fluctuations play a key role in these theoretical approaches. The density correlation func-

tion $C(q, t)$ at given wave vector q can be measured by coherent spin echo neutron scattering [3] and light scattering experiments [4]. In these experiments, the main information deals with the primary (α) relaxation whereas fewer data are available concerning the secondary relaxations that affect the dielectric response usually below T_g or relate to the MCT fast β occurring significantly above T_g . In this Rapid Communication, we report on dynamic light scattering from As_2O_3 in the glassy, metastable supercooled and liquid state combining Brillouin and photon correlation spectroscopic techniques. At the same temperature, the α process with very narrow distribution relaxation times and a fast secondary process with low Arrhenius activation energy and relaxation time of about 10 ps are clearly resolved.

Arsenic trioxide was purchased from Merck and has been subjected to further purification as before [5]. The optical cells were carefully cleaned quartz tubes with dimensions 10 mm o.d. and 8 mm i.d. Before measurements the samples were kept at 400 °C for many hours until the melt was homogeneous without bubbles. The glass was then made by quenching the melt from 400 °C to room temperature. According to the literature there is a nonunique determination of the As_2O_3 glass transition temperature but the most common value is $T_g \approx 160$ °C.

For the Brillouin scattering experiment, a single mode Ar^+ ion laser was used as the exciting source, operating at the 488 nm single mode with a stabilized output power of about 200 mW. The measurements were performed at a 90° scattering angle. Scattered light was analyzed by a piezoelectrically scanned single pass Fabry-Pérot interferometer. Spectra were recorded in a multichannel analyzer with a typical scan duration of 2 s; a measurement was completed after 200 repeated scans and the finesse of the system was about 70. More details for the apparatus and the optical furnace can be found elsewhere [6]. The experimental quantities, the Brillouin shift ω_B and the full width and half maxi-

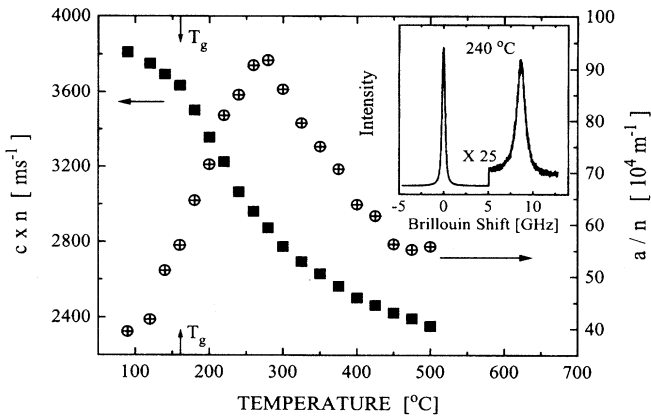


FIG. 1. Temperature evolution of the sound velocity (c) and sound attenuation coefficient (a) of As_2O_3 in the glassy up to the liquid state. At 20°C the refractive index n is about 1.8. However, its temperature dependence, albeit weak, is unknown thus precluding its substitution. Inset: Stokes side Rayleigh-Brillouin spectrum near T_{\max} , at 240°C .

imum Γ_B were obtained from the fit of the Brillouin lines with a Lorentzian line convoluted with the instrumental function and used to compute the sound velocity $c = \omega_B/q$ and attenuation $a = \pi\Gamma_B/c$. Intensity correlation functions $G(t)$ were recorded in both polarized and depolarized geometry at a 90° angle employing a digital full correlator (ALV-5000/fast) with 280 channels [7]. The desired normalized field correlation function $g(t)$ which is related to the density correlation function $C(q,t)$ (for polarized scattering) is obtained from

$$G(t) = B[1 + f|ag(t)|^2], \quad (1)$$

where B is the base line at long time, f is the coherence factor, and a is a parameter that measures the fraction of the total scattered intensity with correlation times longer than 10^{-6} s. The relatively low intensity ratio of the Rayleigh to Brillouin lines allows the use of Eq. (1) that assumes homodyne beating conditions.

Rayleigh-Brillouin spectra were recorded in the temperature interval 90 – 500°C , covering the glassy, supercooled and liquid state. A typical Rayleigh-Brillouin spectrum (Stokes side) of As_2O_3 at 240°C is shown in the inset of Fig. 1. It is well established that the Brillouin lines are a manifestation of the propagating pressure fluctuations that spontaneously occur in a liquid [8]. In viscoelastic liquids, the propagation of sound waves in the GHz range is accompanied by a decrease in their velocity and dissipation of their energy content as the temperature increases above T_g . The sound attenuation assumes its maximum value at a temperature T_{\max} at which $\omega_B\tau = O(1)$. For the few inorganic glasses examined so far $T_{\max} - T_g$ increases from about 150 K for the fragile KKN, $[\text{2Ca}(\text{NO}_3)_2 \cdot \text{3KNO}_3]$ [9] to 400 K for the intermediately strong ZnCl_2 [10] reaching approximately 1000 K for the strong B_2O_3 [11]. The relaxation time τ of this process appears to conform to the temperature dependence of the main α -structural relaxation as determined by photon correlation spectroscopy (PCS) and depolarized Rayleigh scattering near and far T_g respectively, albeit its

value can be faster by an order of magnitude [12]. The temperature T_{\max} was always found to be higher than T_m .

Figure 1 displays the temperature dependencies of the sound velocity and the sound absorption coefficient derived from our experimental measurements on the As_2O_3 . In contrast to the expected behavior the present system clearly exhibits a hypersonic dispersion near T_g in the supercooled state. Inspecting the sound absorption coefficient two important observations can be made. First, the magnitude of the dissipation is not as expected for a network type glass former; the value near the absorption maximum is lower than the corresponding value of other typical glass formers like ZnCl_2 [10] by a factor of more than 10. On the contrary, the velocity drops for the two systems are quite similar. Secondly, at high temperatures the values of a/n not only seem to approach the low- T ones but remain rather high and a second increase is discernible suggesting the presence of a second dispersion even at higher temperatures. In fact, the later would be expected based on the experience so far. Therefore, the relaxation process with $T_{\max} \approx 270^\circ\text{C}$, obtained from the absorption maximum or the sound velocity inflection point does not incorporate the usual features [7,9,10] of an α -relaxation peak mentioned above and this difference will be better clarified by the PCS data below. Furthermore, there still exists significant velocity variation, in contrast to other systems (e.g., ZnCl_2 [10] and B_2O_3 [11]) where a plateau region is reached below T_g . This striking feature calls for a special structural rearrangement that seems to persist also below T_g .

Summing up, we observe that (i) a relaxation process at low temperature (called from now on fast β relaxation) is manifested as a strong one when examining the relative decrease in the sound velocity, but seems weak when considering the sound dissipation; (ii) a second peak of the absorption maximum is probably hidden at higher temperatures; (iii) relaxation takes also place at $T < T_g$, as seen from both quantities plotted in Fig. 1.

Observation (i) forces us to consider that the molecular mechanism responsible for the onset of this relaxation process affects sound propagation in a different way than sound dissipation. Thus, certain structural rearrangements take place that produce sufficient sound wave scattering with a great amount of phonon-photon exchanged energy but a small one due to viscous dissipation. Obviously, this cannot be assigned to the network structural relaxation which would lead to a strong sound absorption characteristic of such structural rearrangements. For the latter, the relaxation strength, $R = (c_\infty/c_0)^2$ (with c_0 and c_∞ being the limiting low and high frequency sound velocities) is about 2 for KKN [9] and 3 for ZnCl_2 [10] at $T \approx T_{\max}$. Alternatively, representation of the data in Fig. 1 with a single Debye process expectedly yields significantly lower $R \approx 1.4$ at T_{\max} signifying the different nature of this relaxation process. The molecular mechanism that we assume to be responsible for this kind of behavior is shortly described as follows.

The vibrational modes of glassy, liquid, crystalline and gaseous arsenic trioxide have been studied extensively and correlated to the structural peculiarities of each phase [5,13]. Glassy and liquid arsenic trioxide form a networklike structure where pyramidal AsO_3 units are connected to each other through oxygen bridges. The pyramidal unit is rather flat

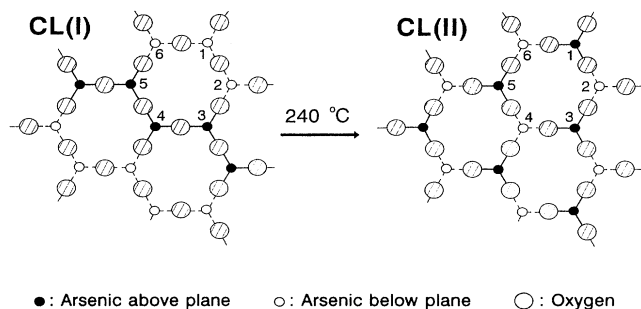


FIG. 2. The allotropic structures of crystalline As_2O_3 . The transition from claudetite I to II is at $\sim 240^\circ\text{C}$ very close to the temperature T_{max} where the maximum sound absorption occurs.

having an $\angle\text{O}-\text{As}-\text{O}$ angle of $\hat{\alpha} \approx 114^\circ$ [5]. The polarization characteristics of the Raman spectra of the amorphous phases were found to be compatible with those of the crystalline form of claudetite which forms a layerlike structure with well defined pyramidal AsO_3 units. Thermal degradation of the As_2O_3 liquid occurs at elevated temperatures ($t > 300^\circ\text{C}$) with bond breaking of oxygen bridges and generation of more “closed” cluster units in which the bond angles ($\hat{\alpha}$) are smaller [5]. The above mentioned α -relaxation process is presumably associated with this networklike thermal breaking. Two allotropic structures of claudetite are known, I and II both having a layered structure as indicated in Fig. 2. The transformation I \rightarrow II occurs at $\sim 240^\circ\text{C}$ and involves an interchange of the direction of two pyramidal units participating in the same ring (numbered as 1 and 4 in Fig. 2). Thus, by moving in claudetite I the As (1) “below” the ring “plane” and As (4) “above” the plane we obtain the “high temperature” form claudetite (II) processing a higher “ring” symmetry. The pyramidal angle $\hat{\alpha} \approx 100^\circ$ for both forms and is smaller than that in the liquid or glass [5,13(a)].

In the crystalline material the “above” to “below” change of two As atoms in the molecular (intraring) scale results in the claudetite (I) to (II) allotropic phase transformation. The exact nature of the “layer” structure of the liquid cannot be easily anticipated. It is, however, reasonable to assume that distorted ring structures similar to claudetite, which are formed [5,13] in the liquid may exhibit intraring (“above” to “below”) structural changes. The pyramidal angle of the AsO_3 unit is flatter ($\hat{\alpha} = 114^\circ$) in the liquid than in claudetite ($\hat{\alpha} \approx 100^\circ$) and the activation energy for intraring structural transformation in the liquid is smaller than in the crystals. Thus, a liquid to liquid phaselike transition may occur due to intraring layer transformations. We associate the observed β -relaxation process with this phaselike transition. It seems that in the low temperature region of Fig. 1 the claudetite I ringlike structures predominate the liquid or glass structure while increasing temperature enhances the transformation to claudetite II ringlike structures. The latter forms are predominant in the high temperature liquid where also the degradation of the network may also start (i.e., the rise of the α -relaxation process). It is noteworthy that the claudetite (I) \rightarrow (II) transition temperature at $\sim 240^\circ\text{C}$ is rather close to the $\sim 270^\circ\text{C}$ where the maximum of the sound attenuation (Fig. 1) occurs. According to this structural model the behav-

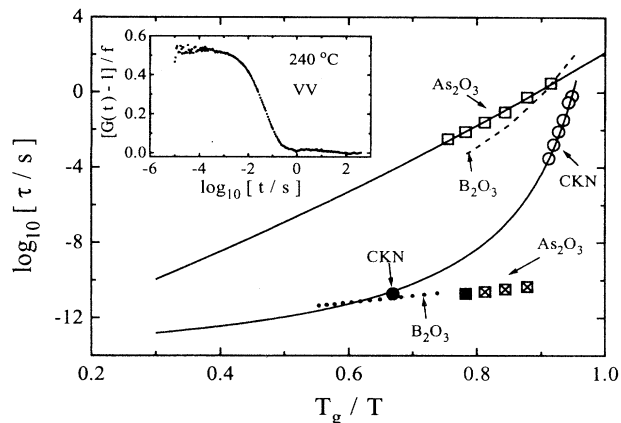


FIG. 3. Modified Arrhenius plot of the relaxation times for the following. (a) As_2O_3 : \square open squares, PCS; \blacksquare filled square, BS at maximum absorption; \boxtimes cross squares, calculated from viscoelastic theory; the hypersonic relaxation (\blacksquare) occurs at similar temperatures with the α -relaxation process of the PCS (\square) experiment. (b) CKN: \circ open circles, PCS [9]; \bullet filled circle, BS at maximum absorption [9]. (c) B_2O_3 : - - - dashed line, PCS [14]; \cdots dotted line, BS [11]. Inset: Net polarized correlation function of As_2O_3 at 240°C .

ior in Fig. 1 seems quite reasonable in the sense that density fluctuations are feasible via conformational transitions between these two liquid structures. Fast density fluctuations can then lead to hypersonic dispersion.

The α -relaxation process can be best studied by probing the dynamics of density fluctuations over a broad time range near T_g by PCS. Over the temperature range for which hypersonic dispersion is observed, PCS clearly reveals the presence of the much slower α relaxation. The inset of Fig. 3 displays a net polarized intensity correlation function [Eq. (1)] of As_2O_3 at 240°C . The density correlation function $\alpha g(t)$ [Eq. (1)] conforms to the widely accepted Kohlrausch-Williams-Watts (KWW) function [11]

$$g(t) = \exp[-(t/\tau)^{\beta_{\text{KWW}}}] \quad 0 < \beta \leq 1. \quad (2)$$

The relaxation time τ , the exponent β_{KWW} , and the amplitude α are treated as free fitting parameters. The high value of the distribution parameter $\beta_{\text{KWW}} \approx 0.8$ indicates the “strong” character (in a fragility scale) of the As_2O_3 and is similar to the values recently reported for B_2O_3 [14]. The value of α (≈ 0.7) suggests that about 30% of the total polarized dynamic light scattering intensity has correlation times shorter than 10^{-6} s in accordance with the presence of the fast β relaxation at hypersonic frequencies. In contrast, however, to the recent PCS data on B_2O_3 [14], there is no evidence of an additional relaxation mode in the time window of PCS over the examined temperature range despite the strong character of the glass. The average relaxation time $\langle \tau \rangle = (1/\beta) \Gamma(1/\beta) \tau$ [$\Gamma(1/\beta)$ is the gamma function] is plotted in a modified Arrhenius plot where the As_2O_3 data are compared with the “fragile” CKN [9], including also the relaxation time of the fast β from the Brillouin experiment. The experimental point at the highest temperature corresponds to T_{max} and differs from the α -relaxation time of the PCS experiment by about 10 orders of magnitude. It is obvious that

this point does not conform to the curve describing the much stronger temperature dependence of the α relaxation. This behavior should be contrasted with the temperature dependence of the relaxation times in the fragile CKN liquid for which a common Vogel-Fulcher-Tammann (VFT) equation [1] can describe both experiments. Thus, as argued above another relaxation process exists along with the slow α branch, but with much faster dynamics.

A similar picture emerges also for B_2O_3 [11], where a small hump in the absorption curve at $T_{\max}=770$ K was observed at a relatively low temperature near T_g , analogous to that of As_2O_3 [15] in Fig. 1. The slow α relaxation and the fast β times extracted respectively from PCS and Brillouin spectroscopy (BS) experiments on B_2O_3 are indicated as dashed and dotted lines, respectively, in Fig. 3. This finding was attributed to the thermal decomposition of the network structure which is rather surprising since these kinds of structural processes are rather associated with α relaxation and

involve significant sound dissipation. Moreover, a recent NMR study for B_2O_3 [16] showed that its network remains almost unaffected up to high temperatures. Despite this similarity between As_2O_3 and B_2O_3 these materials differ markedly because B_2O_3 lacks the sub- T_g relaxation that As_2O_3 possesses. Further, differences between these two systems arise from recent measurements [6] of the low frequency Raman spectra where the behavior of the boson peak for As_2O_3 does not follow what is expected by its very low fragility. In this context the difference between the T_{\max} values in As_2O_3 and B_2O_3 , meaning that at the same temperature the relaxation time of the former is faster, corroborates the notion that this process depends on local structure and more likely relates to the fragility index. Finally, it is clearly evident from the present investigation that two systems exist (As_2O_3 and B_2O_3) for which a fast β - and a narrow α -relaxation process are present near and above the glass transition.

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