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Temperature dependence of the density fluctuations of silica by small-angle X-ray scattering

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ABSTRACT

Low-OH-content silica samples having fictive temperatures in the interval 1000–1500°C, have been studied by small-angle X-ray scattering using

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synchrotron radiations both at room temperature and from 20 to 1500°C. The limit for zero-angle X-ray scattering intensity is analysed in term of density fluctuations. We demonstrate that density fluctuations are strongly related to structural relaxation; both depend on thermal history (i.e. the fictive temperature) of the sample, in the temperature range below T_g .

§1. INTRODUCTION

Low-OH-content silica glasses are of great interest because of their recent application in optical fibres. An important effort is devoted to reduce signal losses due to elastic scattering of light in these fibres (Sakagushi 2000). Elastic scattering originates from permittivity fluctuations assumed to be related to density fluctuations frozen in the glass.

It has been shown from the statistical mechanics that density fluctuations in a supercooled liquid or in liquid in equilibrium, are governed by the following equation:

$$\frac{\delta N^2}{\bar{N}} = \frac{(N - \bar{N})^2}{\bar{N}} = k_B T \kappa_T^0(T), \quad (1)$$

where $\kappa_T^0(T)$ is the isothermal compressibility at the temperature T and k_B is the Boltzmann constant. Moreover, the isothermal compressibility of the melt (Zarzycki 1982) can be expressed as the sum of three contributions: the difference between isothermal compressibility $\kappa_T^0(T)$ and adiabatic compressibility $\kappa_S^0(T)$, the relaxational compressibility $\kappa_S^r(T)$ and the high-frequency adiabatic compressibility $\kappa_S^\infty(T)$:

$$\kappa_T(T) = [\kappa_T^0(T) - \kappa_S^0(T)] + \kappa_S^r(T) + \kappa_S^\infty(T). \quad (2)$$

In the glassy state, equation (1) is no longer valid because of the non-equilibrium state. However, if equation (2) is followed, an expression for the mean square density fluctuations valid for a glass can be obtained (Zarzycki 1982):

$$\frac{\delta N^2}{\bar{N}} = \underbrace{k_B T_f [\kappa_T^0(T_f) - \kappa_S^0(T_f)]}_{\text{entropy fluctuations}} + \underbrace{k_B T_f \kappa_S^r(T_f)}_{\text{local variation in structure}} + \underbrace{k_B T \kappa_S^\infty(T)}_{\text{vibrations}}, \quad (3)$$

where $\kappa_T^0(T_f)$ is the isothermal compressibility at the temperature T_f , $\kappa_S^0(T_f)$ is the adiabatic compressibility at the temperature T_f , $\kappa_S^r(T_f)$ is the relaxational adiabatic compressibility at the temperature T_f , $\kappa_S^\infty(T)$ is the high-frequency adiabatic compressibility at the temperature T and k_B is the Boltzmann constant. The vibrational contribution $k_B T \kappa_S^\infty(T)$ to density fluctuations depends on the actual temperature T whereas entropic and relaxational contributions both depend on the fictive temperature T_f . Thus, density fluctuations clearly depend on the thermal history through the order parameter T_f .

Small-angle X-ray scattering (SAXS) is due to the local change in electron density. Electron density fluctuations, mass density fluctuations and molecular density fluctuations in a volume V are related by

$$\frac{V \langle \Delta \rho_e^2 \rangle}{\rho_{e0}^2} = \frac{V \langle \Delta \rho^2 \rangle}{\rho_0^2} = \frac{\delta N^2}{N}, \quad (4)$$

where N is the number of particles in a volume V , ρ is the density, ρ_e is the electron density, ρ_0 is the average density and ρ_{e0} is the average electron density. Electron density fluctuations for a microscopic volume can be obtained by extrapolating the scattering intensity at zero angle for an infinite volume; in fact

$$I(q = 0) \propto \left(\frac{\langle \Delta \rho^2 \rangle V}{\rho_0^2} \right)_{V \rightarrow \infty}$$

The aim of this work is to analyse density fluctuations as measured by SAXS for silica glasses having different fictive temperatures. These results are also compared with Rayleigh scattering data, which are also dependent on fictive temperature.

§ 2. MATERIALS AND EXPERIMENTS

Low-OH-content silica samples having fictive temperatures ranging from 1000 to 1500°C have been prepared as described by Champagnon *et al.* (2002), by long-time annealing to allow structural relaxation, followed by a quench to freeze the new structural organization.

The fictive temperatures of these samples have been evaluated by three spectroscopic methods. The first is based on the fact that the band observed by Raman scattering in silica around 440 cm⁻¹, which is due to Si–O–Si symmetrical vibration, shifts to higher frequency with increasing T_f . The second is based on the work of Galeener and Geissberger (1983) on the evolution of the intensity of the D₁ and D₂ Raman lines versus increasing fictive temperature. Finally, the third method involves a linear equation between the position of the infrared absorption band shift around 2260 cm⁻¹, and the inverse fictive temperature (Agarwal *et al.* 1995). This band is an overtone of the Si–O–Si antisymmetrical vibration.

Samples heat treated at 1100, 1200, 1300 and 1500°C are found to have respective fictive temperatures equal to 1100, 1200, 1300 and 1500°C. In addition, the fictive temperatures of two samples have been estimated by the three methods described previously: for the as-received sample the fictive temperatures were found to be equal to 1260, 1135 and 1155°C respectively. For a sample heat treated at 950°C for 10 days the fictive temperatures were estimated to 1350, 1421 and 1379°C respectively. This sample has clearly not reached its equilibrium state.

SAXS measurements have been performed on the D2AM beam line at the synchrotron at the European Synchrotron Radiation Facility (Grenoble) with an incident energy of 15 keV using a 200 s accumulation time. A high-temperature molybdenum furnace already referred to by Soldo *et al.* (1998) has been used for *in-situ* temperature measurements. Data have been collected on a charge-coupled device camera. Radial integration and corrections from background and cosmic rays have been performed on the data.

The spectra were recorded with a great accuracy from $q = 0.0019$ to $q = 1.03 \text{ \AA}^{-1}$ for room-temperature measurements and from $q = 0.0019$ to $q = 0.76 \text{ \AA}^{-1}$ for measurements in the furnace. The time necessary to raise the temperature between two accumulations is approximately a few minutes. As for light scattering, experimental conditions have been detailed by Champagnon *et al.* (2002).

§ 3. RESULTS

The amplitude of density fluctuations at zero angle can be determined by fitting data at small angles, using the following empirical law (Wiegand and Ruland 1979):

$$I(q) = I(q = 0) \exp(bq^2), \quad (5)$$

where q is the wave-vector and b is a coefficient depending on the temperature.

Figure 1 shows room-temperature measurements of $I(q = 0)$ presented as a function of the fictive temperature determined from the first of the three spectroscopic methods presented above. Except for the point at 1100°C which is an artefact, it appears clearly that electron density fluctuations increase with increasing fictive temperature. Light scattering measurements of the Landau–Placzec ratio ($R_{LP} = \text{Rayleigh intensity}/\text{Brillouin intensity}$) have been performed on the same samples (Le Parc *et al.* 2001). R_{LP} , also plotted in figure 1, increases strongly with increasing fictive temperature. Light scattering and X-ray scattering have quite similar evolutions with regard to the fictive temperature. However, the accuracy of SAXS measurements is better than the Landau–Placzec accuracy because of the very small Brillouin signal.

In situ temperature measurements have also been performed on the same samples (figure 2). Previous measurements in several organic and inorganic glasses (Golubkov and Porai Koshits 1981, Curro and Roe 1984) have shown a common behaviour: $I(q = 0)$ increases slightly or remains constant from room-temperature to glass transition temperature; then, above T_g , $I(q = 0)$ increases with the increasing actual temperature.

Low-fictive-temperature samples ($T_f < 1250^\circ\text{C}$), as shown in figure 2, actually follow this ‘usual evolution’ as T increases. Nevertheless, for high-fictive-temperature glasses, density fluctuations exhibit a different behaviour below T_g , that is between 1000 and 1250°C, with a significant decrease, related to structural relaxation, and reach the same equilibrium value at 1250°C. This merging temperature of

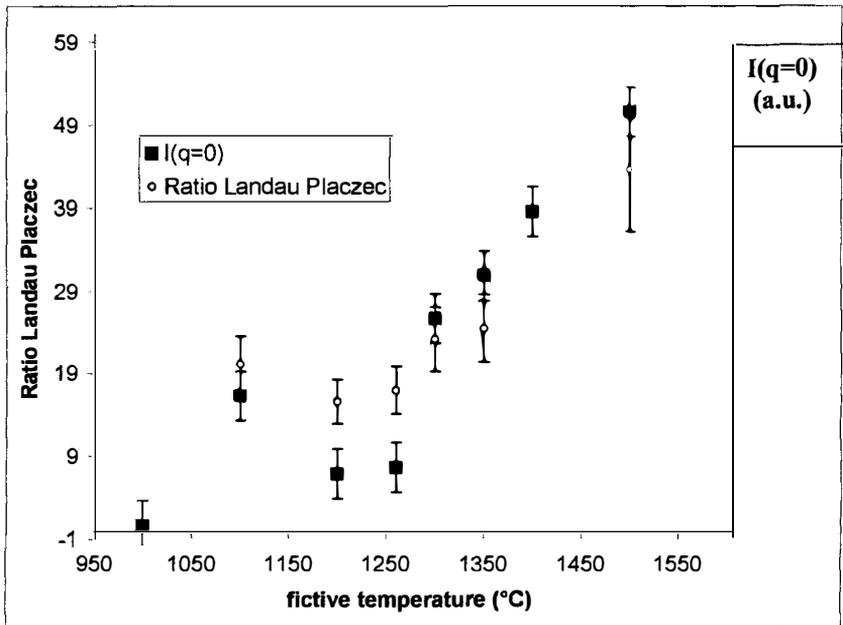


Figure 1. Zero-angle SAXS intensity and Landau–Placzec ratio versus fictive temperature at room temperature, out of the furnace.

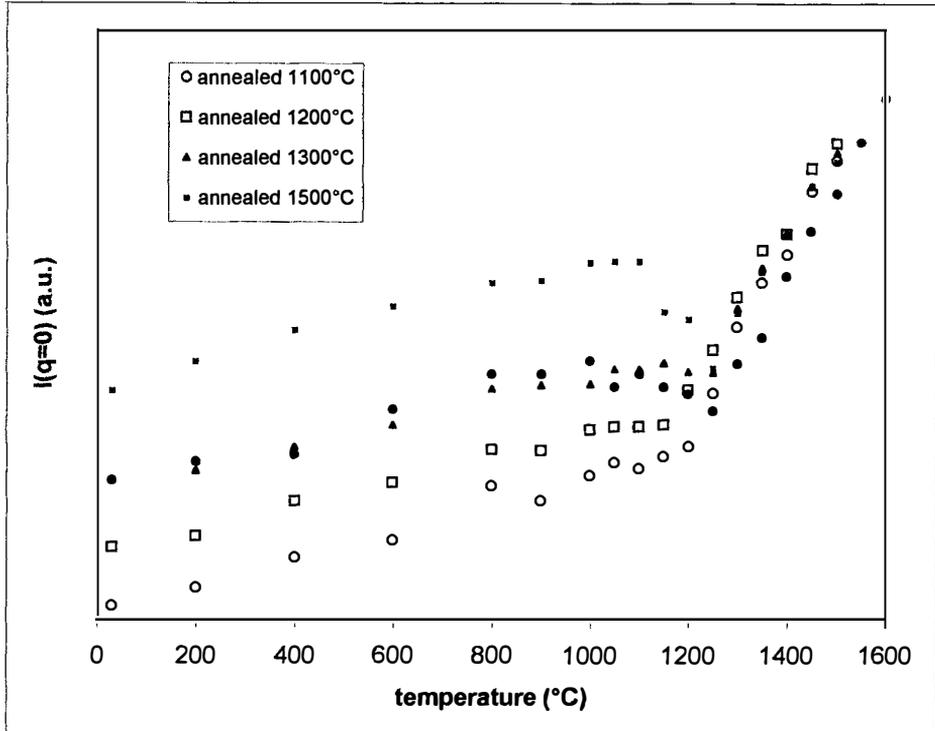


Figure 2. Zero-angle SAXS intensity temperature dependence for glasses having different fictive temperatures lower and higher than 1250°C respectively compared with as received sample (●).

1250°C depends on the heating rate and attests that all the samples have followed nearly the same heating processes.

The zero-angle scattering and hence the density fluctuations in the glassy state are strongly dependent on T_f ; at low temperatures, all curves increase with the same slopes and the level of density fluctuations increases with increasing T_f . At 1000°C, the material, still glassy, has a very high viscosity (around 10^{18} P); however, structural relaxation occurs in the high-fictive-temperature glasses; this relaxation leads to a decrease in the density fluctuations. Above 1250°C, all curves join together; this is characteristic of the metastable equilibrium state. In this supercooled liquid the main α relaxation takes place and density fluctuations increase proportionally with increasing temperature.

§4. DISCUSSION

$I(q=0)$ in SAXS contains contributions both from frozen-in density fluctuations and from vibrational density fluctuations. With reference to equation (3), frozen-in density fluctuations at a given temperature should depend on T_f and on compressibility at T_f . The vibrational contribution depends on the sample density ρ_0 and on the longitudinal high-frequency sound velocity $v_{L\infty}^2$:

$$k_B T \kappa_S^\infty = k_B T \left(\frac{1}{\rho_0 v_{L\infty}^2} \right). \quad (6)$$

To compare the ‘frozen-in’ part of the density fluctuations with the ‘non-frozen-in’ vibrational part depending on the actual temperature, we should compare the value given by equation (6) with the entropy fluctuation and the structural relaxation terms expressed in equation (3). The entropy part can be neglected compared with the relaxational part (Laberge *et al.* 1973). The relaxational term $T_f \kappa_S^r$ can be estimated using $\kappa_S = 7.3 \times 10^{-12} \text{ cm}^2 \text{ dyn}^{-1}$ or $7.3 \times 10^{-11} \text{ Pa}^{-1}$ (Laberge *et al.* 1973) or using $\kappa_S^r = 5.68 \times 10^{-12} \text{ cm}^2 \text{ dyn}^{-1}$ or $5.68 \times 10^{-11} \text{ Pa}^{-1}$ (Krols *et al.* 1986). We can use these values to compare the term $T/\rho_0 v_{L_\infty}^2$ corresponding to the vibrational part of density fluctuations with the term $T_f \kappa_T^r$, as the entropy part is negligible. All samples exhibit comparable values for κ_S^∞ , as shown by the slope of the $I(q=0)$ versus T diagram in the glassy state. In silica, the density (Bruckner 1970) and longitudinal sound velocity both increase with increasing fictive temperature in the range 1000–1450°C. For two samples having respective fictive temperatures of 1200 and 1300°C, it appears that the decrease in the vibrational part is negligible ($2.90 \times 10^{-12} \text{ K dyn cm}^{-2}$) compared with the $T_f \kappa_T^r$ increase (around $500 \times 10^{-12} \text{ K dyn cm}^{-2}$). Thus in the glassy state (at room temperature), the differences due to thermal history of the sample (T_f) can be mainly assigned to the frozen-in density fluctuations related to structural relaxation.

The most striking point of this study lies in the fact that silica is the archetype of the strong glass former (Angell 1985), with no anomaly at T_g in the Arrhenius diagram, but we show that, although the structural state and the density fluctuations depend on the thermal history of silica (effect of T_f , and *in-situ* structural relaxation), no structural dependence of viscosity is to be expected. High-fictive-temperature samples start to relax at around 1000°C. Quite a similar effect has already been noticed (Schroeder *et al.* 1995) in light scattering measurements on different glasses.

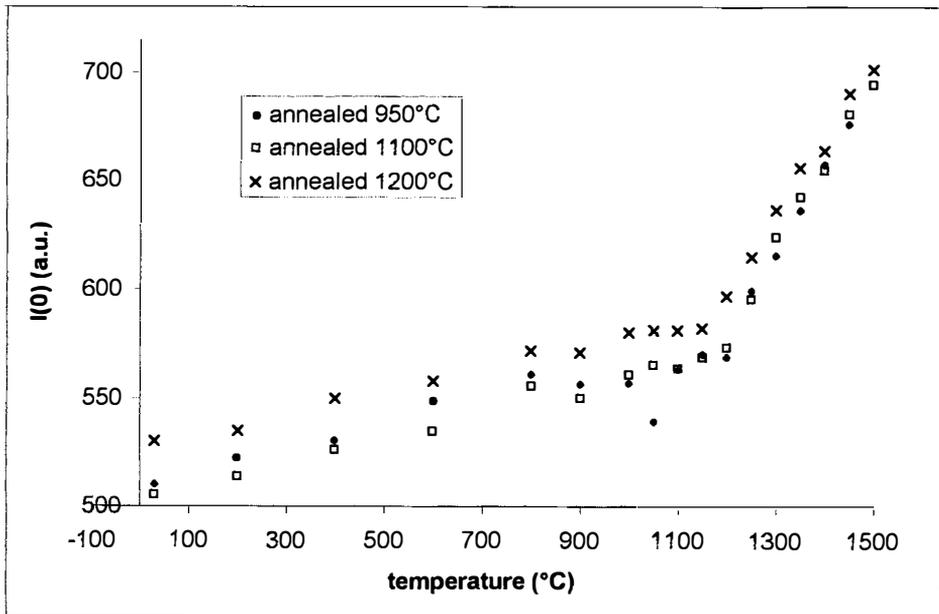


Figure 3. Zero-angle SAXS intensity temperature dependence for samples annealed at 950, 1100 and 1200°C.

These phenomena are not described by equation (3) unless a change in T_f is taken into account at a value above 1000°C.

The sample annealed at 950°C for 10 days has started to relax towards a more ordered structure but has not reached its equilibrium from the viewpoint of local structure. The fictive temperature of this sample has been estimated to be between 1135 and 1260°C by spectroscopic investigation. From SAXS results, the amplitude of the density fluctuations of a sample annealed at 950°C falls between those of samples having $T_f = 1100^\circ\text{C}$ and $T_f = 1200^\circ\text{C}$ (figure 3).

A parallel can be drawn for these subrelaxation processes and those reported by Saito and Ikushima (1998), activated by the diffusion of a very small concentration (parts per million) of impurities. More details about a diffusion model for impurities in weaker binding regions of the glass have been given by Champagnon *et al.* (2002).

§5. CONCLUSION

SAXS and light scattering investigations provide information on density fluctuations in glasses. Those two experimental methods are complementary; the SAXS contribution comes from total density fluctuations whereas Rayleigh scattering is induced only by frozen-in density fluctuations. We showed that, at room temperature, the dominant contribution to density fluctuation is the frozen-in term related to structural relaxation. Thus Rayleigh and SAXS measurements are expected to give the same results, which is in agreement with our data.

On the other hand, SAXS measurements allow us to determine high-temperature density fluctuations, as they are almost not disturbed by black-body emission. These measurements showed that structural relaxation processes already occur, on the time scale of experiment, at 1000°C in high-fictive-temperature silica samples. Moreover we confirm that reducing density fluctuations is possible by lowering the fictive temperature.

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