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LETTER TO THE EDITOR

The glass transition in confined liquids

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Abstract. Effects of confinement of the 4.0 nm pores of Vycor glass on the α relaxation associated with the glass transition were investigated for three glass-forming liquids, glycerol, propylene glycol and propylene carbonate, by dielectric relaxation spectroscopy. The relaxation shifts to lower temperatures in the isochronal (constant-frequency) measurements and to higher frequencies in the isothermal measurements for the confined liquids as compared to the bulk. Confinement induces a broadening of the relaxation and a change of its shape. The results are discussed in relation to the characteristic length of the glass transition (cooperativity length).

The dynamic and thermodynamic properties of molecular systems are known to be modified by confinement in small volumes of mesoscopic (a few nm) dimensions [1]. A fundamentally challenging question is how the glass transition in glass-forming liquids is modified by confinement in mesoscopic volumes.

Differential scanning calorimetry (DSC) and enthalpy recovery measurements on various liquids confined in glass pores of mesoscopic dimensions show a decrease of the glass transition temperature T_g and a broadening of the spectrum of retardation times as compared to bulk liquids [2–4]. On the other hand, DSC measurements on liquids confined in microemulsions [5] and hydrogels [6] show a significant broadening of the glass transition but no shift of T_g to lower temperatures as compared to bulk liquids.

Two explanations have been proposed for the observed shift of T_g to lower temperatures: the reduction of the density of the liquid in the pores [2] and the capillary effects [4]. Another way to discuss these and similar results is by using the concept of cooperativity length, the characteristic length of the cooperative process of glass transition [7]. This concept is at the centre of discussions on the glass transition [7–9] and there is growing interest in relating it to measurable physical quantities [10, 11].

According to Sappelt and Jäckle [7], confinement of glass-forming liquids in geometries of confining length comparable to the cooperativity length ξ (a few nm near T_g [7, 10, 11]) should lead to a broadening of the glass transition and a shift to higher temperatures. The reason for the shift is that with the confining length decreasing below ξ , an increasing number of molecules are permanently blocked and no longer contribute to the response of the system to external perturbations. However, from a qualitative point of view and bearing in mind that ξ increases with decreasing temperature, one might expect just the opposite: in restricted geometries of confining length D smaller than the cooperativity length ξ at T_g in the bulk (i.e. $\xi(T_g)$), ξ increases with decreasing temperature but cannot exceed D ($D < \xi(T_g)$), so that the glass transition is shifted to lower temperatures.

It seemed reasonable to us to make further experimental investigations of the changes of the glass transition of glass-forming liquids induced by geometrical confinement. We employ

dielectric relaxation spectroscopy (DRS) techniques which may provide deeper insight into the dynamics of the glass transition [12]. For the geometrical confinement we use Vycor glasses which are characterized by very narrow distributions of pore diameters [1]. Our aim is to investigate several liquids, both van der Waals and hydrogen bonded, selected on the basis of the departure from the Arrhenius behaviour at low temperatures [13] (ξ increases with this departure [11]) and molecular size and shape, by using Vycor glasses of different pore sizes. Thus we hope to estimate the cooperativity length and to contribute to a better understanding of the phenomenon of the glass transition. In this letter we report preliminary results obtained with Vycor glass of 4.0 nm pore diameter and the liquids propylene glycol, propylene carbonate and glycerol.

Reagent grade glycerol (Carlo Erba), propylene glycol (Fluka) and propylene carbonate (Fluka) were used without further treatment. Their calorimetric glass transition temperatures, T_g , are listed in table 1. Corning Vycor glass samples No 7930, with porosity 0.28, internal surface area $250 \text{ m}^2 \text{ g}^{-1}$ and an average pore diameter of 4.0 nm, were cleaned and dried according to the producer's instructions. They were of cylindrical shape with 15 nm diameter and about 1 mm thickness, which is very convenient for dielectric measurements using a parallel-plate capacitor. The Vycor glass samples were immersed in the liquids and filled to saturation.

Table 1. Summary of experimental TSDC results (many samples). T_g is the calorimetric glass transition temperature, T_m is the TSDC peak temperature and $\Delta T = T_m - T_1$, where T_1 denotes the temperature at which the current drops to half its maximum value on the low-temperature side of the peak. The errors in T_m and ΔT are $\pm 1 \text{ K}$.

Liquid	T_g (K)	T_m (K)	ΔT (K)
Propylene glycol bulk	167 [13]	174	4
Propylene glycol in Vycor glass		165	7.5
Propylene carbonate bulk	158 [13]	165	3.5
Propylene carbonate in Vycor glass		156.5	5.5

AC dielectric measurements were carried out using a Hewlett Packard HP 4192A impedance analyser combined with an Ando type TO-19 thermostatic oven and the Ando SE-70 and LE-21 dielectric cells. Thermally stimulated depolarization current (TSDC) measurements, which correspond to measurements of dielectric losses against temperature at fixed frequencies of 10^{-2} – 10^{-4} Hz [14], were carried out using equipment and procedures described elsewhere [15].

Figure 1 shows the Arrhenius plot of the dielectric α relaxation in bulk and confined glycerol. It should be noted that measurements on dry Vycor glass samples show no dielectric relaxation mechanisms in the frequency and temperature region of interest in this work. For the confined liquid we observe a shift of the frequency of maximum dielectric loss, f_{max} , to higher frequencies at constant temperature and a shift of the temperature of maximum dielectric losses to lower temperatures at constant f_{max} , i.e. a shift of the glass transition temperature T_g to lower temperatures.

At each temperature, the loss curves were found to be broader in the confined liquid than in the bulk. As an example, we show in figure 2 a normalized plot of dielectric loss in confined and in bulk glycerol at 233 K. Two theoretical curves were fitted to the experimental results, the Cole–Davidson

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{(1 + i\omega/\omega_0)^\beta}$$

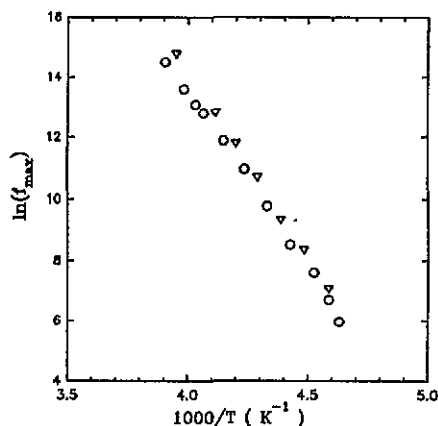


Figure 1. Arrhenius plot (natural logarithm of frequency of maximum dielectric loss against reciprocal temperature) for the α relaxation in bulk (O) and confined (∇) glycerol.

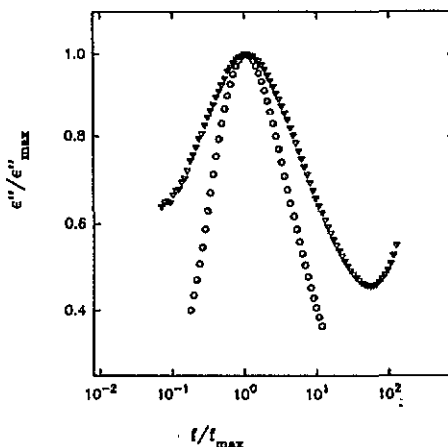


Figure 2. Normalized plot of dielectric loss ϵ'' against frequency for bulk (O) and confined (∇) glycerol at 233 K.

and the Havriliak–Negami

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{(1 + (i\omega/\omega_0)^{1-\alpha})^\gamma}$$

where $\epsilon^* = \epsilon' = i\epsilon''$ is the complex permittivity, ω the angular frequency, $\Delta\epsilon$ and ω_0 are, respectively, the intensity and the position on the frequency scale of the relaxation process, $\epsilon_\infty = \epsilon'(\omega)$ for $\omega \gg \omega_0$, and β , α and γ are the shape parameters [16]. The one-parameter Cole–Davidson expression could be fitted to the results of bulk glycerol, with $\beta = 0.63$ at 233 K, while it was impossible to obtain a satisfactory fit for confined glycerol. The two-parameter Havriliak–Negami expression could be fitted to both cases. For bulk glycerol it reduces to a one-parameter fit since it is found that $\gamma = 1.00$ and $\alpha = 0.17$ at 233 K. For confined glycerol, two parameters are needed, $\alpha = 0.32$ and $\gamma = 0.87$ at 233 K. These results indicate that the shape of the dielectric response changes significantly with confinement and suggest changes in the relaxation mechanism.

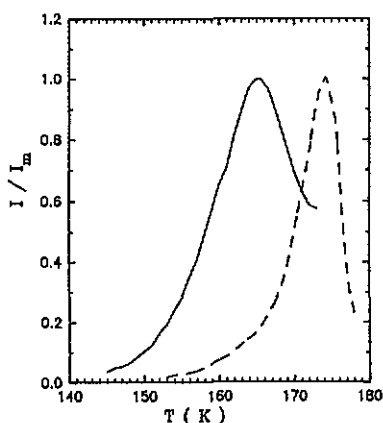


Figure 3. TSDC plots, normalized to unit height, of the α relaxation in bulk (---) and confined (—) propylene glycol.

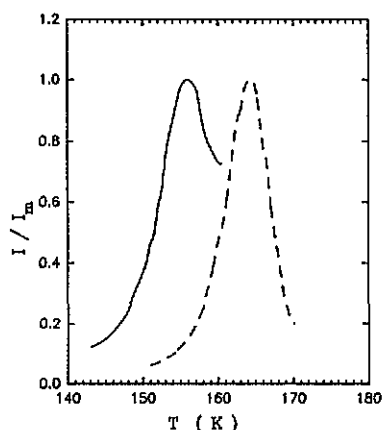


Figure 4. TSDC plots, normalized to unit height, of the α relaxation in bulk (---) and confined (—) propylene carbonate.

In figures 3 and 4 we show TSDC plots measured on bulk and confined propylene glycol and propylene carbonate respectively. The TSDC peaks are due to the α relaxation [17].

Peaks at higher temperatures due to dipolar and/or conductivity relaxations in the liquid phase have been eliminated [17]. The temperature of current maximum (peak temperature) T_m of the TSDC α peak is close to the calorimetric glass transition temperature T_g [17, 18] and therefore is a good measure of the latter's changes with confinement. The results in figures 3 and 4 and in table 1 show that T_m is reduced for the confined liquids, in agreement with the AC results (figure 1). In table 1, the quantity $\Delta T = T_m - T_1$, with T_1 the temperature at which the current drops to half its maximum value on the low-temperature side of the peak, is a measure of the broadness of the α peak. In agreement with the AC results, the α relaxation becomes broader for the confined liquids.

The decrease of T_g induced by confinement is in agreement with previous work [2–4]. In microemulsions [5] and PHEMA [6], interactions of the confined liquid with the surrounding walls may be significant and, since they are expected to reduce the molecular mobility of the liquid [1], they may compensate the reduction of T_g induced by confinement. We note in this connection the reports by Jackson and McKenna [2] that surface modification of the CPGs did not alter the results. The observed broadening of the dielectric α relaxation is in agreement with the broadening of the DSC signal observed in all relevant previous studies [2–6]. However, we have observed for the first time a modification of the shape of the dielectric response, suggesting a modification of the relaxation mechanism. This point must be studied further.

The changes in the response of confined liquids at T_g , observed in this and previous work [2–4], may be related to the cooperativity length ξ [7]. The increasing shift of T_g to lower temperatures with decreasing confining length [2, 4] is consistent with such a relation. ξ increases with the temperature decreasing towards T_g and becomes comparable to the dimensions of confinement in this and similar studies [10, 11]. Measurements at different confining lengths may be used to determine ξ . Vycor glasses are characterized by very narrow distributions of pore dimensions and are therefore very suitable for such studies. On the other hand, measurements can be made at different ξ values by suitable choice of the liquid (ξ increases with the departure from the Arrhenius behaviour at low temperatures [11]) and/or the temperature of isothermal dielectric measurements (ξ increases with decreasing temperatures [10, 11]), making use of the very broad range of frequencies available for dielectric measurements. Experiments along these lines are now in progress.

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