

## Dielectric Studies of the Glass Transition in Porous Media

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Dynamic processes in liquid propylene glycol and two of its oligomers inside the  $\approx 100$  Å pores of controlled porous glasses have been investigated as a function of temperature by dielectric spectroscopy. We find that geometrical restriction results in retardation and broadening of the inherent  $\alpha$  relaxation. This retardation is most pronounced for the monomer liquid and gives rise to an *increase* in the glass transition temperature by  $\Delta T_G = +4.5$  K. We also observe a second slower relaxation process for all liquids, ascribed to the hindered dynamics of molecules affected by the surface.

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Confinement of liquids within small pores strongly affects their physical properties as documented by a variety of experimental techniques and theoretical approaches [1–3]. Understanding the impact of geometrical constraints is relevant from both fundamental and practical perspectives. On the other hand, it facilitates differentiating among theoretical approaches to the dynamics and structure of liquids which consider finite size effects. Additionally, it is of importance for numerous technological applications of porous media, for example in chemical and petroleum industries, medicine, etc.

While it is unambiguously established that finite size effects are favorable for the depression of the first-order phase transitions, leading to a considerable shift of the freezing point to far below the appropriate solidification temperature of bulk liquids [4], the effects on the glass transition have been studied less extensively. Both experimental and theoretical developments regarding glass transitions in liquids confined to small pores with diameters in the range of several 10 Å seem to be scarce and rather contradictory. A finite size induced *decrease* of the glass transition temperature  $T_G$  is reported by Jackson and McKenna [5] for *o*-terphenyl and benzyl embedded in Vycor glasses and later by Zhang, Liu, and Jonas [6] for several organic liquids confined by the pores of silica glasses. Recently Pissis *et al.* [7] observed the same effect for propylene glycol (PG) and propylene carbonate confined to porous Vycor glass. The opposite effect, a small *increase* of  $T_G$ , has been observed by Dubochet *et al.* [8] for *o*-xylene and toluene if dispersed in glass-forming microemulsions and by Hofer, Mayer, and Johari [9] for pure ethylene glycol and solutions of LiCl in H<sub>2</sub>O in poly(2-hydroxyethyl methacrylate) hydrogels. For the experiments mentioned above, the observed shifts  $\Delta T_G = T_{G,\text{pore}} - T_{G,\text{bulk}}$  range from  $-18$  to  $+15$  K.

In this Letter we are concerned with the finite size effects on the relaxation dynamics of propylene glycol and two of its oligomers. For this purpose we use a controlled porous glass with well-defined pore diameters of  $102 \pm 5$  Å. To our knowledge these dielectric relaxation

experiments for liquids in porous glasses cover the widest frequency and temperature range reported to date. For three chemically equivalent liquids, differing only in their molecular weight, we compare the dynamics in porous glasses with the corresponding behavior in the bulk.

Reagent grade PG and two polypropylene glycols (PPGs) of  $M_w = 400$  g/mol (PPG-400) and  $M_w = 725$  g/mol (PPG-725) with  $M_w/M_n \leq 1.09$  were used as obtained from Aldrich Chemical Company. These liquids are good candidates within the aim of the present study since the temperature dependence in the range of present interest for both PG and PPGs follows the Vogel–Fulcher–Tammann (VFT) equation which promotes the detection of even small changes caused by confinement. The molecular weight  $M_w$  of PPGs was chosen to be less than 1300 g/mol to avoid a contribution of the normal mode relaxation [10].

Controlled porous glass (CPG) Bioran, purchased from Schott, FRG, was made by acid leaching of the boron-rich phase of a spinodally decomposed borosilicate glass. The material consists of 30–60  $\mu\text{m}$  porous particles with a pore volume of 0.8 cm<sup>3</sup> per g of glass and an extremely narrow distribution of pore diameters (5% standard deviation) [11]. The highly branched and connected pores are believed to be approximately cylindrical in shape. The area of the outer surface of the particles is less than 1% of the inner one. After thorough cleaning and drying under vacuum, the glass was mixed with the liquid under dry nitrogen atmosphere and gently stirred so that the pores were filled by capillary wetting for 24 h. To ensure complete filling, the liquid content of each sample exceeded the calculated pore volume by 5%. The samples were placed between the brass electrodes of a capacitor (diameter 30 mm, spacing  $\sim 100$   $\mu\text{m}$ ), tightly surrounded by a Teflon cell. Dielectric measurements in the frequency range  $10^{-2}$ – $10^6$  Hz were performed using a Solartron–Schlumberger frequency response analyzer FRA 1260 equipped with a buffer amplifier of variable gain in order to determine the dielectric loss  $\epsilon''(\omega)$  within  $\pm 3\%$ . The sample temperatures in the range 160–240 K were

controlled by a nitrogen gas stream with an instability better than  $\pm 0.1$  K. The details of sample preparation and experimental setup may be found elsewhere [12,13].

For a quantitative analysis of the complex permittivity  $\epsilon^* = \epsilon'(\omega) - i\epsilon''(\omega)$ , the empirical Havriliak–Negami (HN) [14] function in conjunction with a conductivity term was used:

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\Delta\epsilon}{[1 + (i\omega\tau)^\alpha]^\gamma} - \frac{i\sigma}{\epsilon_0\omega^s}. \quad (1)$$

The first right-hand side term describes the dielectric relaxation with a characteristic relaxation time  $\tau_{\text{HN}}$  and with a dielectric relaxation strength  $\Delta\epsilon$ .  $\alpha$  and  $\gamma$  are shape parameters ( $0 < \alpha, \gamma \leq 1$ ) characterizing asymmetrical and symmetrical broadening of the loss peaks, respectively. The Debye case is restored if  $\alpha = \gamma = 1$ . The second term quantifies the dc conductivity  $\sigma$  in terms of  $\epsilon''(\omega)$ , with fit parameter  $s \approx 1$ . From fits according to Eq. (1), we determine  $\omega_m$  (positioned at the maximum of the loss peak). Its temperature dependence can be rationalized by the VFT equation [15]

$$\tau_m = \omega_m^{-1} = A \exp[DT_0/(T - T_0)], \quad (2)$$

with prefactor  $A$ , fragility parameter  $D$  [16], and the Vogel temperature  $T_0$ .

Figure 1 shows the dielectric spectra for bulk and confined PG in a 3D-plot representation. An obvious feature related to the porous sample is the appearance of an additional relaxation process positioned within the conductivity wing, i.e., several orders of magnitude below the  $\alpha$  process with respect to frequency. Note that the dielectric strength of this slow process is of the same order of magnitude compared to that of the  $\alpha$  process. Qualitatively these features are also observed when comparing the spectra of bulk and confined PPGs. The quantitative results along the lines of Eqs. (1) and (2) are summarized in Table I and Fig. 2. These results clearly indicate that the  $\alpha$  process of confined PG is subject to longer relaxation times compared to the bulk dynamics [Fig. 2(a)]. This finite size effect increases as the temperature is lowered and thus implies a considerable retardation in molecular mobility for confined PG near  $T_G$ . For PPG-400 the effect is similar, but the onset of retardation appears at lower temperatures and is less pronounced [Fig. 2(b)], whereas for PPG-725  $T_G$  appears to be unaffected by the geometrical constraints [Fig. 2(c)]. The finite size induced increase in relaxation time of the  $\alpha$  process gives rise to a concomitant shift of the glass transition temperature for PG and for PPG-400 toward higher temperatures (Table I). Common to all three liquids is a pronounced broadening of the  $\alpha$  relaxation process and a decrease of the fragility in terms of  $D$  (Table I, Fig. 3); i.e., the  $\alpha$  peak is subject to broadening even in the absence of retardation.

As depicted in Fig. 2, the relaxation times for the additional slow relaxation process in confined PG, PPG-

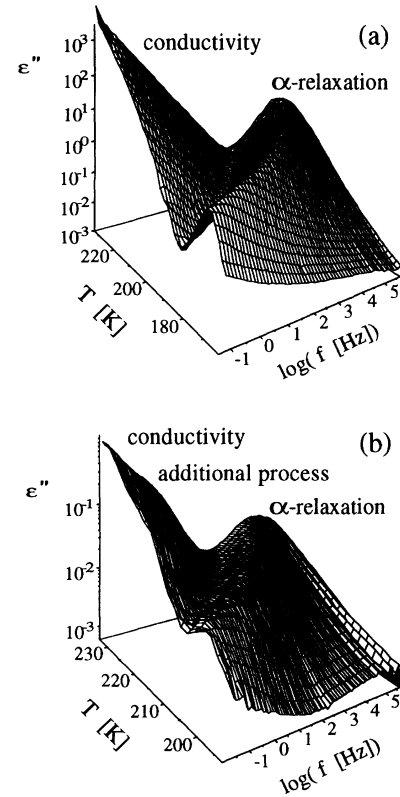


FIG. 1. Dielectric loss  $\epsilon''(\omega, T)$  of PG versus frequency  $f = \omega/2\pi$  and temperature  $T$  for the bulk liquid (a) and in pores of 102 Å diameter (b).

400, and PPG-725 are, respectively, by  $\sim 4$ , 5, and 6 orders of magnitude higher than relaxation times of the corresponding  $\alpha$  relaxation. It is interesting to note that a measurement of CPGs with a silanized pore surface and filled with PG did not reveal this additional slow process. Since the slow relaxation peak that appears upon geometrical confinement is thus correlated with the presence of active silanol groups at the pore surface, we ascribe these additional dynamics to an outer layer of the liquid whose rotational motion is strongly hindered by surface effects. In identifying a surface layer by passivation techniques we have followed the ideas of Dozier, Drake, and Klafter [17] and Awshalom *et al.* [1], and our result of hindered dynamics within the surface layer concurs well with previous observations [1,17,18]. Regarding the dipolar interactions, i.e., even in the absence of hydrogen bonding effects, there is theoretical evidence that nonmetallic interfaces tend to slow down the rotational dynamics of polar liquids [19].

The positive shift in  $T_G$  presently observed is in qualitative agreement with expectations on the ground of both entropy model and free volume concept [20,21] since one should expect the entropy and free volume of a liquid in a small pore to be reduced, which results in higher

TABLE I. Parameters of the HN (1) and VFT (2) equations regarding the  $\alpha$  relaxation in bulk and confined liquids. Glass transition temperatures  $T_G$  and their shifts  $\Delta T_G = T_{G,\text{pore}} - T_{G,\text{bulk}}$  are based on  $\tau_m(T_G) = 100$  s.  $w/w_D$  refers to the width  $w$  (FWHM) of  $\epsilon''(\omega)$  normalized to the Debye value  $w_D = 1.14$ . The results for  $\Delta T_G$  are +4.5 K (PG), +1.3 K (PPG-400), and +0.2 K (PPG-725).

	$\alpha$	$\gamma$	$w/w_D$	$A/ps$	$D$	$T_0/K$	$T_G/K$
Bulk							
PG	1.0	0.7	1.17	195	18.4	112.3	166.8
PPG-400	0.9	0.5	1.60	9	7.8	160.4	196.4
PPG-725	0.8	0.6	1.72	32	8.3	160.3	197.3
Confined							
PG	0.7	0.7	1.91	892	19.1	115.4	171.3
PPG-400	0.7	0.6	2.04	84	9.3	158.0	197.7
PPG-725	0.6	0.7	2.30	49	9.0	157.8	197.1

values of  $T_G$  compared to the bulk liquid [5]. Based on the divergence of the length scale  $\xi$  of cooperativity as  $T \rightarrow T_G$ , Sappelt and Jäckle [22] also argue in favor of both a broadening of the  $\alpha$  process and a shift of  $T_G$  to higher temperatures for confined liquids. Donth [23] as well as Fischer, Donth, and Steffen [24] have estimated the length of cooperativity to attain  $\xi \sim 20\text{--}30$  Å for  $T \approx T_G$ , i.e., below the pore diameter of  $\sim 100$  Å. This means that the inner liquid portion is not intimately linked to the dynamics of the very slow surface layer, in agreement with our observation of two distinct processes instead of a single extremely broad one. Note, however, that the inner liquid should reveal bulk behavior only in a situation where  $\xi \ll 100$  Å. The expected increase of the absolute values of  $\xi$  with the fragility parameter [24] implies that the positive shift in  $T_G$  should be most pronounced for PPG-725, just in contrast to our findings. At present, no theoretical framework is available to rationalize consistently our observations regarding the effects of geometrical constraints.

In summary, we have presented results on the dynamic behavior of liquids confined to pores of controlled porous glass. We were able to demonstrate that dielectric relaxation spectroscopy serves as a powerful tool for monitoring the dynamics of glass-forming liquids in porous media and their deviations from bulk behavior. We observe retardation and appreciable broadening of the  $\alpha$  relaxation process, a decrease in the liquids' fragility, and the appearance of an additional relaxation process which we associate with a layer of molecules adsorbed at the pore surface. The slowing down of molecular (PG) or segmental (PPG) modes of motion which govern the  $\alpha$  relaxation leads to a positive shift of the glass transition temperature for PG and PPG-400, in accord with theoretical predictions [20–22]. Unexpectedly, the extent of  $\Delta T_G$  varies with the inverse molecular weight and vanishes for PPG-725. On a spec-

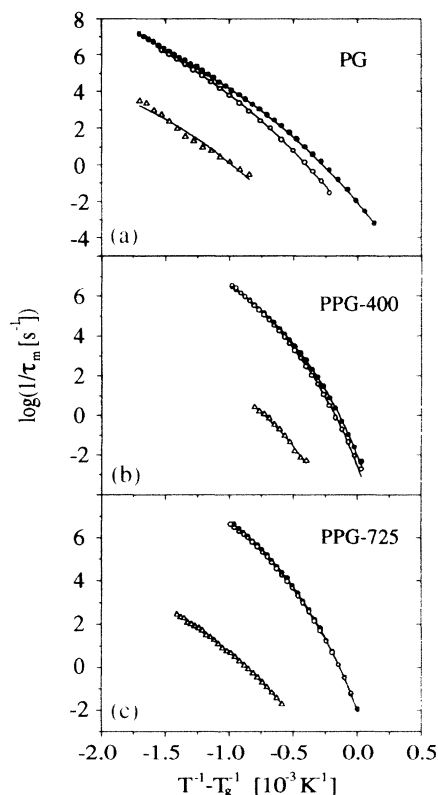


FIG. 2. Temperature dependence of reciprocal relaxation times  $\tau_m$  for the samples PG (a), PPG-400 (b), and PPG-725 (c). Different symbols denote the  $\alpha$  relaxation in the bulk ( $\bullet$ ), the  $\alpha$  relaxation in pores ( $\circ$ ), and additional relaxation in pores ( $\Delta$ ).

ulative level we relate this effect to a substantial influence of hydrogen bonding, its extent being known to decrease strongly with the degree of polymerization of PPG [25]. In order to clarify this issue, a comparative study of confinement effects for van der Waals liquids is in progress [12].

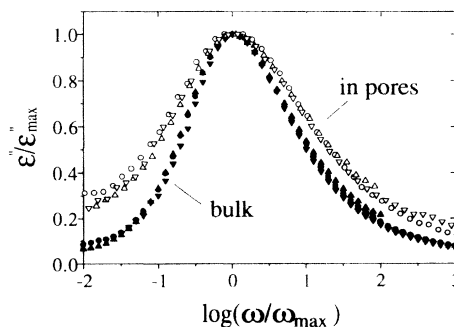


FIG. 3. Master plot of the normalized dielectric loss versus reduced frequency for bulk and confined PPG-400. Different symbols correspond to different temperatures in the range of 203–225 K (bulk) and 207–217 K (in pores).

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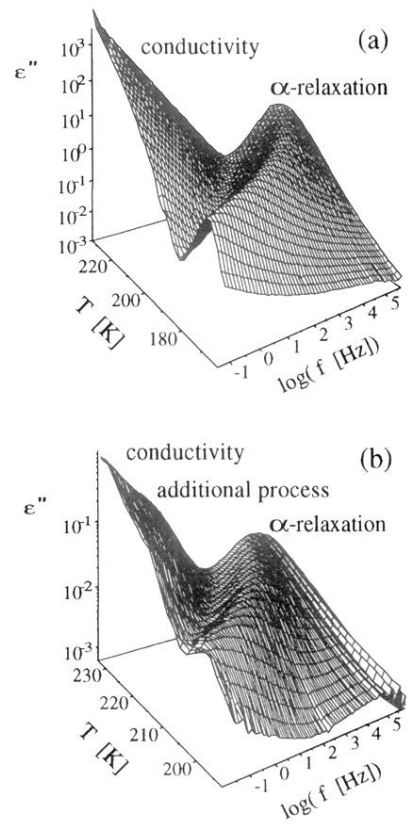


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