Dynamics of supercooled liquids confined to the pores of sol-gel glass: A dynamic light scattering study

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Dynamics of low molecular weight and polymeric glass forming liquids in confined geometries has been studied by means of depolarized dynamic light scattering: photon correlation spectroscopy and Fabry-Perot interferometry. The pore size of the glassy matrix amounted to 2.5, 5.0, and 7.5 nm. The glass transition temperature T_g of these liquids in confined geometries has been measured using differential scanning calorimetry. A systematic decrease of T_g (up to 25 K) with decreasing pore size has been observed. The relaxation times of the α process at constant temperature were decreasing with decreasing pore size (up to 6 orders of magnitude at T_g), while the width of their distribution was increasing. The change of the relaxation times can be assigned to the change of T_g in confined geometries. After correcting the activation plots for the shift of T_g a master curve was obtained for all pore sizes and the bulk material. The effect of chemical modification of the surface of the porous matrix on the dynamics of ortho-terphenyl has also been studied. These dramatic changes of the T_g and the relaxation time of confined liquids can be explained by simple thermodynamic arguments. There is no indication that they are related to the change of the correlation length of cooperative dynamics.

PACS number(s): 64.70.Pf, 78.35.+c

I. INTRODUCTION

The structural relaxation time and viscosity of super-cooled liquids change by about 14 orders of magnitude in a narrow temperature range between the melting temperature T_m and the liquid-glass transition temperature T_g. This dramatic change is usually explained by the increasing cooperativity of motion and a growing cooperativity correlation length. This notion appears in several theoretical models [1–3], however, no structural experimental evidence for this correlation length has been found. Confining a liquid to a small pore is an easy way to limit the possible correlation length of the cooperative motion, since this length cannot exceed the pore size. Thus, changing the pore size, one is able to control the maximum extent of the cooperative dynamics. Despite the many experimental and theoretical results concerning the dynamics of supercooled liquids in confined geometries, there is no clear physical explanation of the confinement effect. Moreover, some of the results are contradictive. Differential scanning calorimetry (DSC) measurements [4] usually show a strong decrease of T_g with decreasing pore size in rigid porous matrices, in analogy with the melting temperature T_m [5], while no shift of T_g was observed for droplets of supercooled liquids of comparable size, obtained in microemulsions [6–8]. In dielectric relaxation (DR) studies also a decrease of T_g was reported [9] (and literature cited therein), but recently it was found that as few as 6 molecules is enough to obtain a bulk behavior of a liquid [10]. Thus, no confinement effect is to be expected for larger pore sizes. The interpretation of the DR data is, how-

ever, not straightforward [11], and an effective medium analysis has to be used in order to remove the effect of the dielectric heterogeneity of the sample. The discrepancies between the intrinsic and measured effective properties in a DR experiment depend additionally on the topology of confinement [11]. Recent inelastic neutron scattering experiments [12,13] have shown that the density of the supercooled liquids in the pores close to T_g is slightly lower (less than 2%) than that in the bulk. An additional complication in the studies of supercooled liquids confined to nanometer size pores is the strong contribution of the interactions of these liquids with the surface of the pores of the confining matrices, which is strongly material dependent. Another interesting problem is the influence of the topology of the pores on the confinement effect. In this paper, we present depolarized dynamic light scattering (DDLS) and DSC studies on the confinement effect in low molecular weight van der Waals glass forming liquids and a polymer. The advantage of the DDLS, used here to study the dynamics of confined supercooled liquids, is that the measured correlation functions (spectra) contain only information on the dynamics of the optically anisotropic molecules of the confined liquid without any contribution from the porous matrix. Thus, no additional parasitic processes occur and no correction procedures are necessary. We also show a possibility of consistently explaining all the existing data (some of them apparently contradictive) using simple thermodynamic arguments where the cooperativity correlation length plays no role.

II. MATERIALS AND METHODS

A. Materials

Ortho-terphenyl (OTP) (Merk-Schuchardt, 99.7% pure) and phenyl salicylate (Salol) (Aldrich, 99% pure) were puri-
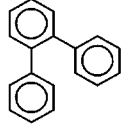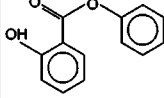

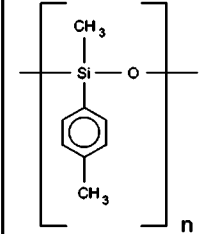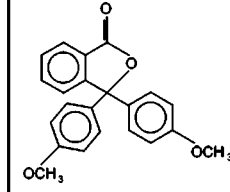*Electronic address: patkowsk@amu.edu.pl
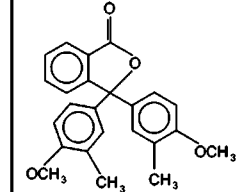
Sample	OTP	Salol	PMpTS	PDE	KDE
Formula	$C_{18}H_{14}$	$C_{13}H_{10}O_3$	$[C_8H_{10}OSi]_n$	$C_{22}H_{18}O_4$	$C_{24}H_{22}O_4$
Structure					
M [g/mol]	230	214	~3600	346	374
T_m [K]	329	316	---	376	388
T_g [K]	244	225	236	295	313

FIG. 1. Materials.

fied by multiple recrystallization from methanol. Poly(methyl-*p*-tolyl-siloxane) (PMpTS) of weight average molecular weight $M_w = 3600$ g/mol was synthesized using anionic polymerization [14]. Phenylphthalein-dimethylether (PDE) and cresolphtalein-dimethylether (KDE) were synthesized in the laboratory of Professor H. Sillescu at Johannes Gutenberg University, Mainz, Germany, and were used without further purification. The chemical structures and relevant parameters of the samples are given in Fig. 1.

B. Porous silica substrates

High purity GELSIL porous silica glasses produced by sol-gel process were purchased from GELTECH (Alachua, Florida, USA) The relevant physical parameters of these matrices are given in Table I.

C. Sample preparation

The porous glasses were purified by slow heating up to 800°C in vacuum (20 h), kept at this temperature for 6 h and then cooled down slowly to room temperature within 36 h. After this cleaning procedure the samples were transferred to a glove box filled with nitrogen and silanized. The aim of silanization was to replace the polar OH groups on the surface of the porous material by nonpolar $OSi(CH_3)_3$ groups in order to reduce the interactions of the samples with the matrix surface. Also the Pyrex light scattering cells (Willmad, USA, OD=20 mm, ID=18 mm) were silanized. The porous glass matrices in a form of a cylinder (OD=10 mm) were placed and centered in the light scattering cells using specially made teflon holders. Glass forming liquids after filtration through millipore filters (pore size 0.22μ) were either distilled under vacuum (OTP) or injected (Salol, PMpTS) into dust-free light scattering cells containing porous glasses and the cells were flame sealed under vacuum.

TABLE I. Specifications of GELSIL porous glasses.

	2.5 nm	5.0 nm	7.5 nm
Total pore volume [cm^3/g]	0.4	0.7	1
Inner pore surface [m^2/g]	610	580	525
Bulk density [g/cm^3]	1.2	0.9	0.7

All the samples were kept at temperatures above their melting temperature for several days or weeks until the porous matrices were filled uniformly. At this stage all samples were optically homogeneous and transparent.

D. Depolarized dynamic light scattering (DDLS)

1. Photon correlation spectroscopy (PCS)

The experimental setup for PCS measurements consisted of a Nd:YAG laser (Adlas, model DPY 425II) operating at $\lambda = 532$ nm with a power up to 400 mW and a home-made cryostat. The scattered light, after passing a polarizer (Glan-Thompson, extinction coefficient 10^{-7} from Halle, Berlin, Germany) was fed into a monomode optical fiber (Spindler and Hoyer) and a photomultiplier tube (PMT) (Thorn EMI, model 9863). The PMT signal after passing the amplifier and discriminator (ALV Langen, Germany) was fed into a digital correlator (ALV-5000, ALV Langen, Germany). The sample cell was placed in a home-made vacuum cryostat in order to avoid water condensation on the cell walls at low temperatures. The temperature of the sample was stabilized within 0.1 K using a liquid thermostat (Huber). The depolarized PCS time autocorrelation functions were analyzed using the Kohlrausch-Wiliams-Watts (KWW) function,

$$g^{(1)}(t) = A \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right], \qquad (1)$$

and the mean relaxation time was calculated as

$$\langle\tau\rangle = \frac{\tau_{KWW}}{\beta_{KWW}}\Gamma\left(\frac{1}{\beta_{KWW}}\right), \qquad (2)$$

where $\Gamma(x)$ is the Γ function.

2. Fabry-Perot interferometry (FPI)

The experimental setup for DDLS FPI measurements consisted of a single mode Ar-ion laser (Spectra Physics, model 2025) operating at $\lambda = 514.5$ nm with a power up to 400 mW and a 6-pass Tandem FPI (Sandercock) free spectral range (FSR) =15 GHz and was described in detail elsewhere [15]. An electrically heated oven was used for temperature control of the samples and the temperature was stabilized within 0.1
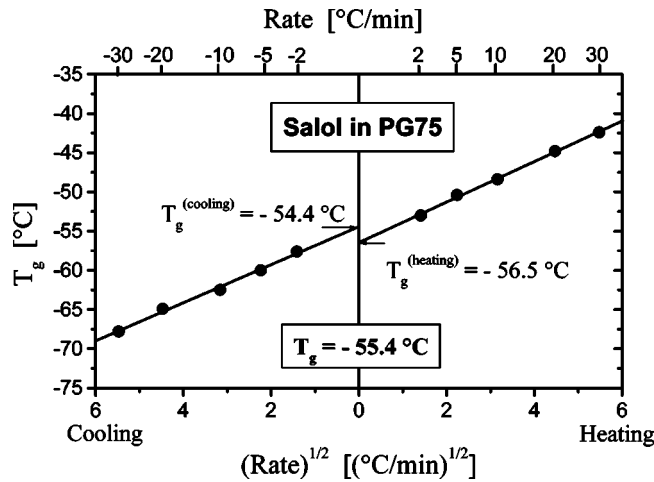
FIG. 2. Dependence of the glass transition temperature measured by means of DSC on heating or cooling rate.

K. Since the main aim of these measurements was to compare the dynamics of glass forming liquids in bulk and confined to a porous glass, we decided to make the analysis of the T-FPI spectra as simple as possible. We fitted the experimental spectra with a single Lorentzian convoluted with the experimental instrumental function. From the half width at half height Γ of this Lorentzian one can calculate the relaxation time of the process

$$\tau = \frac{1}{2\pi\Gamma}. \qquad (3)$$

Obviously, this kind of analysis results in systematic errors (small in a log scale) due to the fact that the β_{KWW} value in this temperature range is not exactly equal to 1, but is not very far from that value [16]. The high frequency contributions to the spectrum are negligible in the small FSR of this experiment [16].

E. DSC measurements

The glass transition temperatures of the glass forming liquids confined in porous glass were measured using a commercial DSC instrument (Mittler, model DSC 30).

III. RESULTS AND DISCUSSION

A. DSC measurements

In order to obtain the glass transition temperature of glass forming liquids contained in porous matrices, the DSC measurements were performed using different heating and cooling rates. It is known from the theory of the heat-flow calorimeter that the error in the measured value of melting temperature T_m is proportional to the square root of the heating or cooling rate [17]. The same holds for T_g measurements. Thus, in order to remove this instrumental deficiency, we obtained the correct values of T_g by plotting T_g versus (*heating or cooling rate*)$^{1/2}$ and extrapolating these plots to rate which is equal to 0. An example of such procedure is shown in Fig. 2.
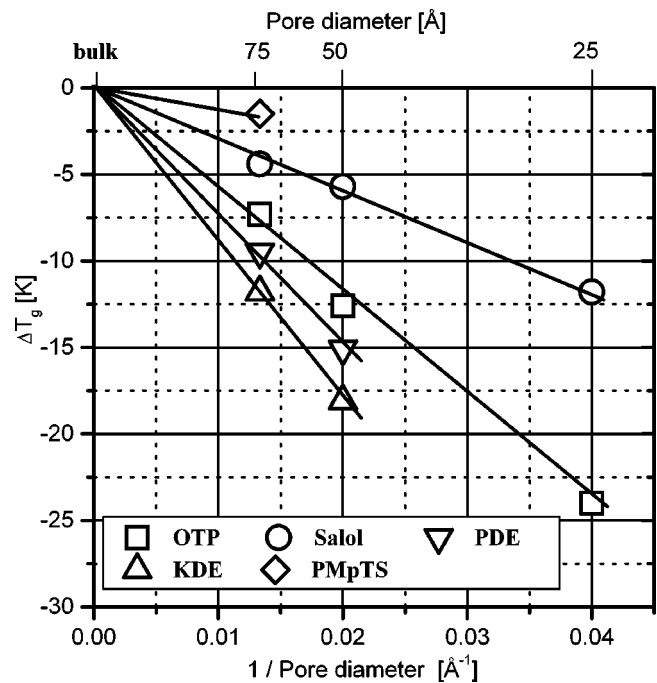

FIG. 3. Pore size dependence of the glass transition temperature shift ΔT_g—(extrapolated to zero heating or cooling rate) in silanized porous silica GELSIL glass measured by means of differential scanning calorimetry (DSC).

As one can see the square root dependence of T_g on heating or cooling rate is evident. From the values of T_g obtained in this way the difference $\Delta T_g = T_g(porous\ glass) - T_g(bulk)$ was calculated and plotted versus inverse pore size in Fig. 3.

The measured T_g values for OTP are in a good agreement with the literature OTP data [4]. As one can see the change of T_g of glass forming liquids contained in porous glass is substantial and depends on material. In all cases a linear dependence of the calorimetric T_g on inverse pore size can be observed.

B. Depolarized dynamic light scattering measurements

The mean KWW relaxation times for OTP confined to the pores of GELSIL glasses measured by means of PCS in the lower temperature range close to T_g are shown in Fig. 4.

The KWW stretching parameter β_{KWW} is also shown. As one can see, the PCS measurements for OTP were possible only in a very limited temperature range for the following reasons: The high temperature limit is defined by the time window of the experiment. At lower temperatures close to T_g the sample became turbid, making any light scattering measurements impossible. This turbidity disappeared upon heating.

Before discussing the experimental results, let us first consider the possible reasons for turbidity of the samples at low temperatures. The first possibility is that the sample crystallizes upon cooling. Actually, we have observed crystallization of the confined liquid in some samples. However, in this case the samples remain turbid also after heating them to temperatures above T_m. This behavior of the crystallized
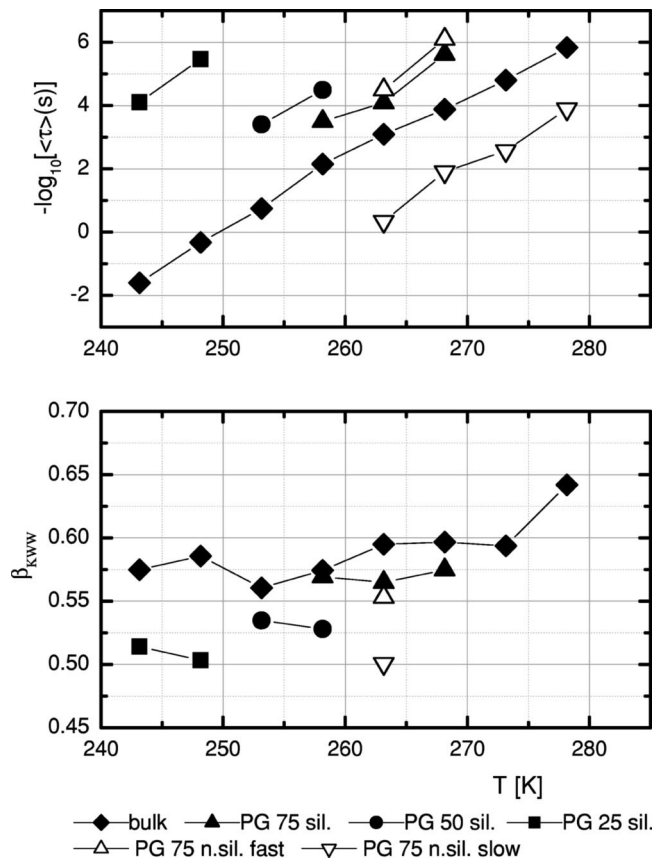
FIG. 4. Mean KWW relaxation times and β_{KWW} parameters measured for OTP in bulk and in porous glasses of indicated pore sizes by means of photon correlation spectroscopy.

samples can be explained by a breakdown of the porous glass matrix upon crystallization of the confined liquid. This led to permanent optical heterogeneity of the sample which cannot be removed by any temperature treatment. Thus, the reversible turbidity of the sample cannot be due to crystallization. Another possible explanation is that upon cooling the supercooled liquid confined to the pores contracts more than the glassy matrix and in this way voids in the pores are created. This, however, is not a good explanation of the turbidity either, since the voids would be smaller than the pore size and thus being much smaller than $\lambda/20$ would never cause the turbidity. Additionally, clean empty matrices are always perfectly transparent, although the refractive index of air is much more different from that of the glassy matrix, and a partial filling of all pores would only decrease the scattering. That means that any optical heterogeneity of the sample of the length scale comparable or shorter than the pore size cannot make the sample turbid. We will come back to the turbidity problem later in this paper after discussing the possible explanation of the confinement effect on the dynamics of supercooled liquids.

In Fig. 4 the mean relaxation times and corresponding β_{KWW} parameters are shown for OTP confined to the pores of the sizes of 2.5, 5.0, and 7.5 nm in silanized matrices. In order to see the influence of the liquid-surface interactions, experimental data for OTP in 7.5 nm pore size of not silanized porous glass are also shown. As one can see, the
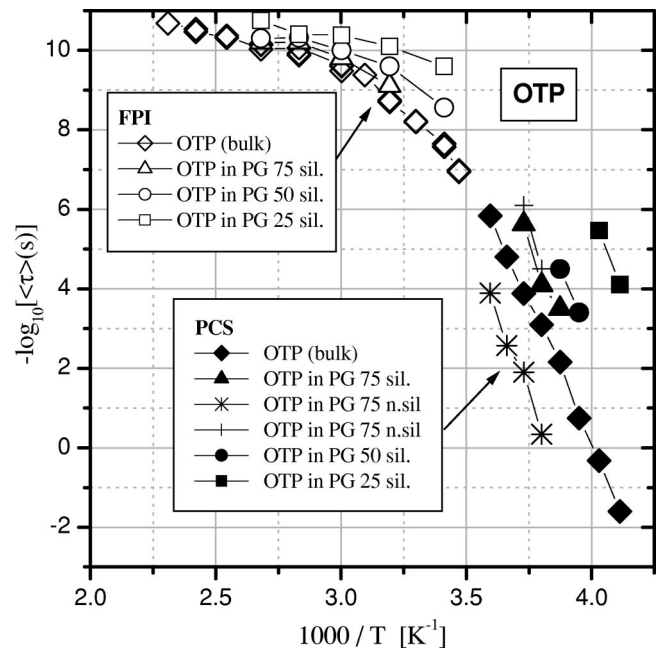

FIG. 5. Temperature dependence of the mean relaxation times measured for OTP in bulk and in porous glasses of indicated pore sizes by means of photon correlation spectroscopy and Fabry-Perot interferometry.

effect of pore size on the structural relaxation time of OTP is dramatic: with decreasing pore size the relaxation time is getting shorter, up to about 6 orders of magnitude when we compare the bulk and 2.5 nm data close to T_g. At the same time the value of the β_{KWW} parameter is decreasing with decreasing pore size. A very interesting effect of confined liquid-surface interactions can be seen when we compare the OTP relaxation times obtained in silanized and not silanized matrices of pore size of 7.5 nm. In the not silanized matrix two processes can be clearly seen: (i) a faster process, similar to that observed in silanized matrix, but slightly faster, and (ii) another process about 4 orders of magnitude slower than the fast one and slower than that in the bulk. These two processes can be assigned to the relaxation of liquid confined to the pores and to the liquid layer on the surface of the pores, respectively. The fact that the fast process in not silanized matrix is faster than that in silanized porous glass can be explained by effectively smaller pore size in the former case, due to the fact that the surface layer of OTP on the pore surface is thicker than the corresponding layer of the silan groups, in the latter case, making the pores effectively smaller. The same effect can be seen in the behavior of the β_{KWW} parameter. Actually, the slower process appears also in the correlation functions measured for OTP in silanized matrices. Its amplitude, however, is much lower than that for not silanized glasses making the analysis not reliable.

The combined activation plot obtained by means of PCS and T-FPI for OTP confined to pores of different sizes is shown in Fig. 5. As one can see, the effect of confinement on the structural relaxation times at higher temperatures is much weaker although qualitatively similar to that at low temperatures: the smaller the pore size the shorter the relaxation time.
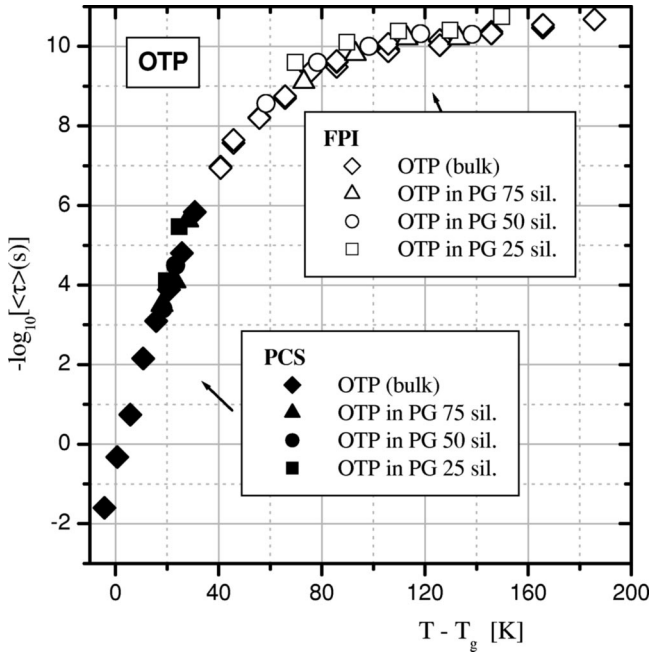
FIG. 6. Temperature dependence of the mean relaxation times of OTP in bulk and in porous materials, corrected for the shift of T_g.

As we have shown before, the glass transition temperature T_g of OTP depends strongly on the pore size. Therefore, we have corrected the activation plot for the shift of T_g plotting the relaxation times vs $T-T_g$ in Fig. 6. It is evident that this correction is sufficient to cause a collapse of all data on one master curve, i.e., the dramatic change of the relaxation times of the confined liquid can be related to the corresponding change of T_g.

Similar effect of confinement was also observed for Salol, Fig. 7, where the relaxation times obtained previously for bulk Salol by means of FPI [18] and dielectric relaxation [19] are also shown. A good agreement of the values of relaxation times obtained by us, using simplified analysis of the FPI data, with the literature values can be seen. In the case of Salol we were able to measure the dynamics of the confined liquid only at high temperatures using the T-FPI, because at low temperatures, in the PCS range, the samples were turbid. Also in this case, the correction of the activation plot for the shift of T_g results in a master curve, Fig. 8.

Measurements on PMpTS samples confined to the pores, performed at higher temperatures by means of T-FPI show much weaker influence of confinement on the structural relaxation, Fig. 9. Such an effect was to be expected from the much smaller shift of T_g in the porous matrices.

C. Possible explanations of the confinement effect

So far, there is no theory that can be used explicitly to explain the confinement effects. For qualitative considerations let us first assume that the confined liquid is at thermal equilibrium during isobaric cooling from the filling temperature to the temperature of experiment. The melting point depression for a small crystal of size d is given by the Gibbs-Thomson equation
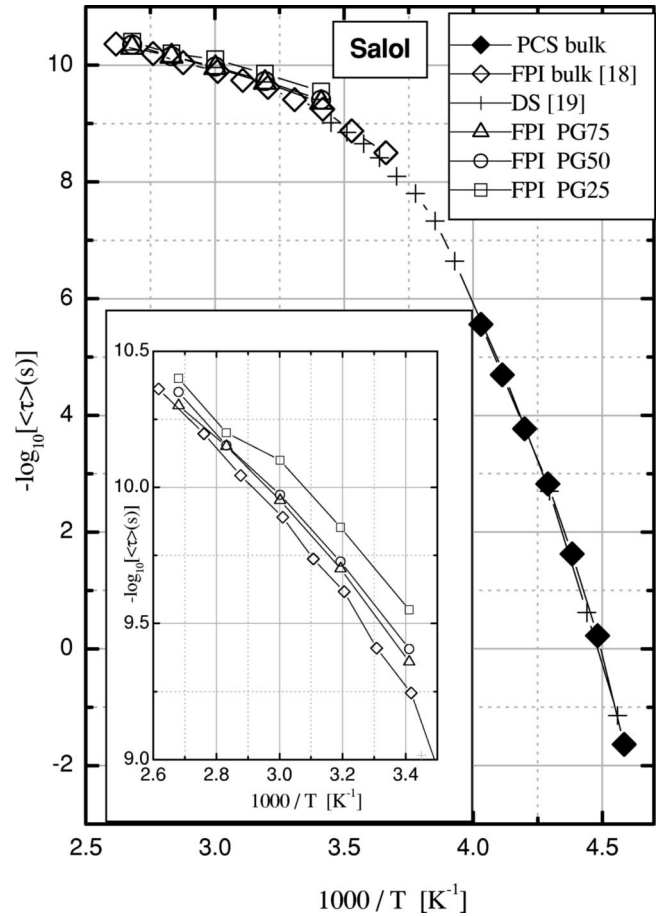

FIG. 7. Temperature dependence of the mean relaxation times measured for Salol in bulk and in silanized porous glasses (inset) of indicated pore sizes by means of Fabry-Perot interferometry. The decrease of the relaxation times with decreasing pore size is smaller than for OTP in agreement with the smaller change of T_g observed in Salol.

$$\Delta T_m = T_m - T_m(d) = \frac{4\sigma_{sl}T_m}{d\Delta H_f\rho_s}, \tag{4}$$

where σ_{sl} is the surface energy of the solid-liquid interface, T_m and $T_m(d)$ are the normal melting point and that of a crystal of size d, respectively, ΔH_f is the bulk enthalpy of fusion (per gram), and ρ_s is the density of the solid. If a similar relation holds for the glass transition temperature [4,5], then

$$\frac{\Delta T_g}{T_g} \propto \frac{\sigma_{sl}}{d}. \tag{5}$$

For a rough estimate we can replace the values of σ_{sl} by the gas-liquid interface energy σ_{gl} measured for a free liquid droplet in air, which amounts to $\sigma_{gl}=3.74\times10^{-2}$ N/m for OTP and $\sigma_{gl}=1.73\times10^{-2}$ N/m for Salol, respectively. For a constant pore size, using Eq. (5) we get

$$\frac{\Delta T_g^{OPT}}{T_g^{OPT}} \bigg/ \frac{\Delta T_g^{Salol}}{T_g^{Salol}} \cong \frac{\sigma_{gl}^{OTP}}{\sigma_{gl}^{Salol}}. \tag{6}$$
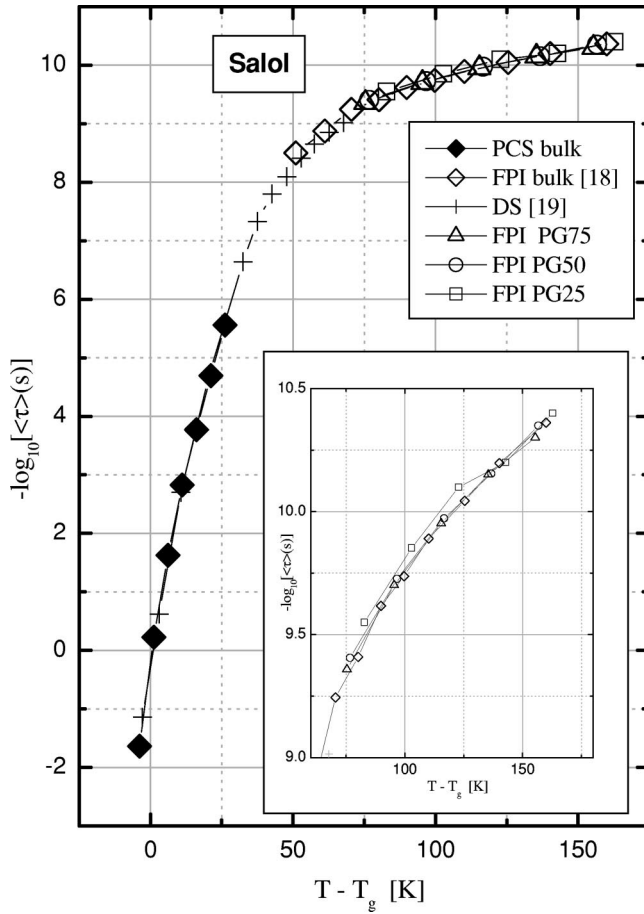
FIG. 8. Tempereture dependence of the mean relaxation times of Salol in bulk and in porous materials (inset), corrected for the shift of T_g.
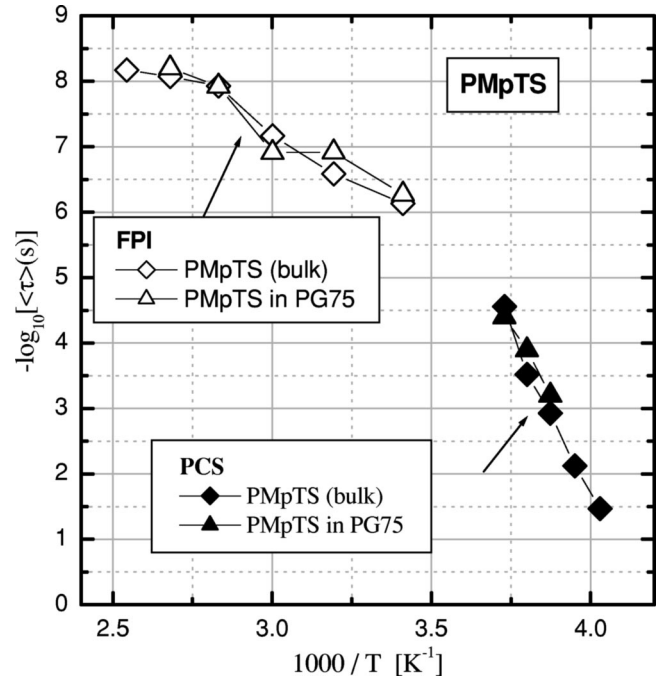

FIG. 9. Temperature dependence of the mean relaxation times measured for PMpTS in bulk and in silanized porous glasses of indicated pore sizes by means of photon correlation spectroscopy (PCS) and Fabry-Perot interferometry. The decrease of the relaxation times with decreasing pore size is very small as expected from the weak effect of the confinement on T_g.

The estimated ratio of the relative change of T_g: $\Delta T_g/T_g$ for OTP and Salol [Eq. (6)] amounts to 1.84 and is in a reasonable agreement with the corresponding ratio of the surface energies which amounts to 2.16. For both liquids T_g in porous matrix is lower than in the bulk.

For glass forming liquids confined to spherical pores of radius r the pressure reduction can be estimated by [20]

$$\Delta P = \frac{2\sigma}{r}, \qquad (7)$$

where σ is the interfacial energy of glass-liquid interface. Since the value of dT_g/dP is usually known from high pressure studies, we can estimate the corresponding decrease of T_g in the pores—ΔT_g as

$$\Delta T_g = \frac{dT_g}{dP}\Delta P = \frac{dT_g}{dP}\frac{2\sigma}{r}. \qquad (8)$$

Thus, the $1/r$ dependence of ΔT_g is obtained in agreement with our experiment and literature data [4,21]. In order to obtain a rough estimate of ΔT_g for OTP in 2.5 nm pores, we can use the corresponding gas-liquid interface energy σ_{gl} and $dT_g/dP = 0.26$ K/MPa [22,23]. In this way we obtain the pressure reduction in the pores $\Delta P = 60$ MPa and the

glass transition reduction $\Delta T_g = 16$ K, in a semiquantitative agreement with our experimental values.

Another simple possibility to explain the decrease of T_g and structural relaxation times with decreasing pore size results from the fact that the originally isobaric cooling at higher temperatures turns into quasi-isochoric cooling at lower temperatures. This is due to the difference in the thermal expansion coefficients γ of the glassy matrix and the liquid and to the very high viscosity of the liquid. The porous materials used in our studies were filled with liquids at high temperatures above T_m. Even if at equilibrium at this temperature the densities of the liquid in the bulk and in pores were equal, it will not be so at lower temperatures. For OTP we have $\gamma = 7.5 \times 10^{-4}$ K^{-1} and for Salol $\gamma = 7.49 \times 10^{-4}$ K^{-1}. Upon cooling the supercooled liquid contracts more than the glassy matrix [γ(porous glass) $= 7.5 \times 10^{-7}$ K^{-1}, [24]] and the equilibration of density through a flow of the bulk liquid into the pores is prevented due to the high liquid viscosity. Such a quasi-isochoric cooling will result in negative pressure (additional free volume). Since the OTP samples were filled at about 70°C then, when measured at 0°C, the difference in the thermal expansion coefficients leads to $\Delta V/V = [\gamma$(porous glass) $-\gamma(OTP)]\Delta T = -5 \times 10^{-2}$, i.e., -5%. Such a decrease of density and corresponding negative pressure would cause a dramatic shift of T_g and τ_α, much larger than that observed in the experiments. The estimated density change required to obtain a shift of $\Delta T_g(OTP) = -24$ K and $\Delta T_g(Salol) = -12$ K in 2.5 nm pores amounts to about 2% and 0.9%,

respectively. This discrepancy may be due to the fact that the calculation actually overestimates the effect, since flow of the confined liquid and equilibration of density might be possible even at temperatures lower than the filling temperature, making ΔT_g in the estimation smaller.

The turbidity of the samples at low temperatures may be also explained in the same way. Upon cooling some short range mobility of the liquid molecules is still possible. Thus, liquid can flow to some pores in order to increase and equilibrate the density there, decreasing in this way the density of neighboring pores even further. This may lead to the formation of regions of substantially different densities of the liquid in the porous matrix. If the size of these regions approaches the value of the wavelength of light, the sample becomes turbid. Upon reheating these filling inhomogeneities disappear making the sample transparent again. Since the viscosity of the supercooled liquid is very high, a complete filling of the porous matrix at lower temperatures by liquid from outside would take a very long time, much longer than the time of experiment.

If this simple explanation of the confinement effect is correct, then the shift of T_g would depend mainly on the thermal expansion coefficients γ of the confined liquid and the confining matrix. In fact the γ values for polymers are lower (of the order of 10^{-5} K^{-1}) than those for simple van der Waals liquids which would correspond to smaller confinement effects as observed for PMpTS.

Density of liquids confined to the pores lower than that in bulk at the same temperature has been reported for Glycerol in GELSIL matrices of the pore size of 2.5 nm [12] on the basis of inelastic neutron scattering measurements. The relative density decrease in the pores amounted to 2% which was equivalent to a temperature shift of 27 ± 7 K. Similar effect has also been observed for toluene [13].

We have presented two possible ways to explain the confinement effects in porous matrices observed in DSC and DDLS experiments, which are in a qualitative agreement with the experimental data. In the first approach, the shifts of T_g and the structural relaxation times and the corresponding density difference in the pores and in bulk at constant temperature and pressure depend only on the surface tension σ_{sl} of the liquid and the pore radius r ($d=2r$). In the second model the confinement effect depends only on the difference of the thermal expansion coefficients of the confined liquid and the porous matrix. In order to decide which mechanism prevails in real systems, more experimental data for materials of different surface tension σ_{sl} and pore radius r are needed. Angell and co-workers have measured the glass transition temperature for supercooled liquids in microemulsions [6–8]. Although the droplet size was very small (2–6 nm) and similar to the pore size of the GELSIL glasses, they observed practically no shift of T_g ($\Delta T_g < 2$ K) in comparison with the bulk material, but only a substantial broadening of the transition range. Thus, for liquids in microemulsions the size effects seem to be insignificant. This result can be easily explained by our second approach: There is no shift of T_g because there is no additional free volume, since the thermal expansion coefficients of the confined liquid and the confinement (the surfactant shell) are the same, i.e., the con-

finement volume remains equal to the liquid volume at all temperatures. In order to explain the microemulsion data using the analogy to the melting temperature depression, the surface tension of the surfactant-confined liquid surface must be at least one to two orders of magnitude lower than the surface tension of the free liquid surface, i.e., must be smaller than 10^{-4}–10^{-3} N/m.

All these considerations concern the changes of the glass transition temperature T_g and the structural relaxation time τ_α in confined geometries only in the case when the confined liquid-confining surface interaction can be neglected. If this is not the case, then the situation is more complex and the interplay of two opposite effects has to be considered: (i) the volume effect—when the confined liquid does not interact with the surface, a faster dynamics and lower T_g are observed, and (ii) the surface effect—when the confined liquid interacts with the surface, a slower dynamics and a higher T_g than in the bulk, can be seen. These two effects were observed in our studies for OTP confined to not silanized porous silica glass of the pore size of 7.5 nm (Fig. 4), where the slow process, much slower than in the bulk, results from the dynamics of the molecules interacting with the surface and corresponds to the surface effect, while the fast process, much faster than in the bulk, is the relaxation of the remaining confined liquid and corresponds to the volume effect. The amplitude of the slow process (surface effect) decreases substantially in silanized porous glass, where the liquid-surface interaction is much weaker. Similar interplay between these two effects has been observed recently for toluene [13]: For the larger pore sizes (4.7 and 8.7 nm), where the volume contribution prevails, a decrease of T_g was observed, while for the smallest pore size (2.4 nm) an increase of T_g in comparison with the bulk was seen, due to the dominance of the surface effects. The increase of the width of the glass transition range with decreasing pore size, observed in that study [13], as well as in most previous investigations, corresponds to a decrease of the β_{KWW} seen for our samples.

In our previous papers [25,26] we have shown that in glass forming liquids long range density fluctuations are observed, which result in an additional slow process in the isotropic part of the correlation function (6 to 8 orders of magnitude slower than the α process) and in an excess isotropic intensity. The correlation length of these fluctuations is of the order of 100 nm and depends on temperature. Obviously, this slow process was not observed in glass forming liquids confined to the pores, since the pore size was much smaller than the expected correlation length of the long range density fluctuations.

IV. CONCLUSIONS

The glass transition temperatures of OTP, Salol, PDE, KDE, and PMpTS confined to porous glass (GELSIL) of pore size of 2.5, 5.0, and 7.5 nm were measured by means of DSC. A strong, material dependent decrease of T_g (up to 25 K) was observed. At the same time the structural relaxation time τ_α was measured for OTP, Salol, and PMpTS by means of DDLS. This time decreased by up to 6 orders of magni-

tude close to T_g, depending on the material. The changes of T_g and τ_α are correlated and a plot of $\log_{10} \tau_\alpha$ vs $T - T_g$ for all pore sizes and the bulk material results in a master curve. The strong changes of T_g and τ_α due to confinement can be explained by the difference of densities of the confined and bulk liquids at low temperatures. The decrease of liquid density is sufficient to explain the observed shifts of T_g and τ_α due to confinement. Two simple explanations are proposed: In the first one, the density change is proportional to the liquid-pore surface tension and inversely proportional to the pore size. In the second one, the density difference results from the difference of the thermal expansion coefficients of the confined liquid and the porous matrix and the fact that the density of the confined liquid at low temperatures cannot be equilibrated, in the time scale of experiment, through a flow of the liquid from outside due to its high viscosity. Using these approaches one can explain the apparently contradictory confinement effects: the strong decrease of T_g and τ_α usually observed in rigid porous matrices and no change of T_g and τ_α reported for droplets of glass forming liquids in microemulsions of comparable size. Thus, there is no obvious indication that the dramatic effect of confinement on the dynamics of confined liquid is related to the change of correlation length of cooperative dynamics close to T_g.

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