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Cooperativity and heterogeneity of the dynamics in nano-confined liquids

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Abstract. We have measured the time resolved Stokes shift of the probe molecule quinoxaline in glass-forming solvents of different polarities under the condition of geometrical confinement, for which this solvation dynamics technique is particularly suitable. While solvation probes the local dielectric relaxation in polar liquids, it is associated with the local mechanical responses in non-polar systems. The effect of porous glasses on the relaxations of supercooled liquids is strongly dependent on the surface chemistry and can be rationalized on the basis of the cooperativity concept. We also present evidence for the heterogeneous nature of relaxation dynamics in nano-confined liquids. In a further experiment, in which the chromophores are selectively positioned at the liquid/solid interface, we observe that the relaxation in the immediate vicinity of the glass surface can be qualitatively similar to the bulk behaviour.

1. Introduction

The study of molecular dynamics under the constraints of spatial restrictions is an active area of research with the aim of understanding the confinement and interfacial effects on the behaviour of liquids, supercooled liquids and polymers [1]. Confining systems are also applied in order to seek length scales intrinsic in the molecular motion of disordered materials in the viscous regime [1–4]. As an example, the picture of cooperatively rearranging regions (CRRs) advanced by Adam and Gibbs is associated with spatial scales well above the molecular distances [5]. Porous silica glasses are attractive materials for such investigations because of their large surface area per sample volume and their availability with pore diameters in the range of several nanometres. On the other hand, the geometry of such irregularly interconnected voids is not well defined. Dielectric relaxation spectroscopy is one of the experimental approaches to geometrically confined condensed matter, with the capability of revealing the orientational dynamics over a large range of frequencies or time scales [6, 7]. Regarding the interpretation of dielectric data on porous samples, one has to account for the Maxwell–Wagner effect which states how the liquid filler and glassy matrix contribute to the measured dielectric signals of this composite material [8].

Solvation dynamics measurements have recently been shown to yield valuable insight into the relaxation behaviour of nano-confined materials [9]. In this type of experiment, the liquid under study is doped with chromophores at a low concentration level and the emission spectra of these isolated probe molecules are recorded as a function of time following electronic excitation [10, 11]. For dye molecules which display an appreciable change in the dipole moment μ upon excitation, the observed gradual shift of the emission energy reflects the dielectric polarization

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of the solvent. Therefore, this optical technique is capable of revealing the local dielectric properties near the position of the chromophores. In liquid solvents, the local character of this technique refers to spatial scales slightly exceeding the first solvent shell [12].

Usually, only the dipolar sources of solvation are considered in such experiments, in which case no Stokes shift is expected whenever the chromophore is not associated with a dipole moment change upon excitation or the solvent is non-dipolar. Instead, small Stokes shifts are observed in the absence of dipolar interactions, which can be attributed unambiguously to 'mechanical' solvation [13]. This latter effect refers to the probe molecule changing its nearest neighbour interaction potential upon electronic excitation, with the consequence that the surrounding solvent is required to undergo a density relaxation in order to establish steady state conditions. For dipolar chromophores in a sufficiently polar solvent these mechanical effects remain small compared with the effects of dielectric polarization.

In the first solvation dynamics study of supercooled liquids confined to nano-pores, we focused on the dipolar probe molecule quinoxaline dissolved in the polar glass-forming solvent 2-methyltetrahydrofuran [9]. As confining geometries, porous silica glasses with nominal pore diameters between 2.5 and 7.5 nm and with the native glass surface have been employed. The results have shown that the short time orientational correlation function remained unaffected in pores relative to the bulk situation. At times longer than t_e, however, the relaxation became non-ergodic, where t_e varied systematically with the pore size and with temperature. The experimental findings were consistent with the explanation that cooperativity of a certain length scale ξ couples an increasing fraction of the liquid to the boundary conditions as time proceeds [4]. These boundary conditions at the pore wall are set by the chemical and physical surface properties, which are believed to be dominated by the silanol groups of a native (clean but otherwise untreated) glass. The pore size and temperature dependences were in accord with the assumption of a cooperative length scale ξ which increases with decreasing temperature and which attains a value of $\xi \approx 3$ nm at the glass transition temperature T_g. An immediate consequence of this scenario is the pronounced sensitivity of such an interfacial effect to the surface conditions, which can be altered easily by silanizing the porous glass.

The aim of the present work is to acquire further support for the cooperativity based rationale employed in the interpretation of solvation dynamics experiments on supercooled liquids in porous media with native glass surfaces. To this end we repeated the above mentioned measurements using silanized porous glasses, where the silanol groups present at the interface are passivated by hydrophobic methyl groups. Even for pore diameters as small as 2.5 nm, the orientational relaxation observed under these conditions shows no systematic deviation from the case of the bulk liquid. We also address the question of whether dynamic heterogeneity is preserved in nano-confined supercooled liquids and how solvation dynamics can be applied for probing local mechanical relaxations in porous materials. Finally, we assess the possibility of positioning the chromophores at the liquid/glass interface in order to measure selectively the liquid dynamics in the immediate vicinity of the glass surface.

2. Experiments

Quinoxaline (QX) has been obtained from Aldrich (96%) and was freshly distilled. The main characteristics of this dye are the ground ($\mu_G = 0.44$ D) and excited ($\mu_E = 1.75$ D) state dipole moments and the phosphorescence lifetime ($\tau_{ph} = 2.27$ s) [14]. The solvent 2-methyltetrahydrofuran (MTHF, Aldrich, 99%) was purified by distillation and filtering with Al_2O_3. The solvent 3-methylpentane (3MP, Aldrich, 98%) has also been treated with Al_2O_3 in order to remove polar contaminations. Solutions of QX in MTHF and 3MP have been prepared at concentration levels of the order 10^{-4} mol mol^{-1}. Both solvents are transparent at $\lambda = 308$ nm and are glass-forming liquids with glass transitions at $T_g = 91$ K (MTHF) and $T_g = 77$ K (3MP).

As porous glasses with sufficiently high optical quality we used Gelsil glasses (GelTech) of cylindrical shape (10 mm diameter, 5 mm thick) with nominal pore diameters $\phi = 2.5$, 5.0 and 7.5 nm made by sol/gel processes. The actual characteristics in the above order of ϕ are: pore diameters 2.6, 4.6 and 8.4 nm; pore volume fractions 0.39, 0.68 and 0.72, and surface areas 609, 594 and 342 $\mathrm{m}^2\ \mathrm{g}^{-1}$. In order to obtain clean pore surfaces, the glasses were washed with H_2O_2 and heated in vacuum to 400 °C for 24 hours. Silanized glasses have been prepared by exposing the dried porous glass to hexamethyldisilazane gas at ambient temperatures for 24 h. The glasses were filled with the liquid of interest under dry N_2 atmosphere and placed into a vacuum sealed sample cell, where they were in contact with the sapphire window.

The cell is mounted in the cold stage of a closed cycle He refrigerator (Leybold, RDK 10-320, RW 2) and temperature stability within ±30 mK can be achieved by a temperature controller (Lake Shore, LS 330) equipped with calibrated diode sensors. Samples are allowed to equilibrate for a sufficiently long time in the highly viscous regime. An excimer laser (Radiant Dyes, RD-EXC-100) operated at 308 nm with pulse energies of 120 mJ served for the electronic excitation of the chromophores. The phosphorescence is coupled via fibre optics to a triple grating monochromator (EG&G, 1235) and registered by an MCP intensified diode array camera (EG&G, 1455B-700-HQ) with controller (EG&G, 1471A), gating options (EG&G, 1304) and synchronization facilities (SRS, DG-535). The spectral resolution was 0.04 nm/channel; the wavelength scale has been calibrated with Xe and Kr lamps.

3. Results

All phosphorescence spectra $I(\nu)$ referring to the $S_0 \leftarrow T_1$ (0–0) transition have been subject to a Gaussian analysis,

$$I(\nu) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{(\nu - \langle\nu\rangle)^2}{2\sigma^2}\right) \tag{1}$$

in order to determine the average $S_0 \leftarrow T_1$ (0–0) emission energies $\langle\nu\rangle(t, T)$ and the concomitant inhomogeneous line widths $\sigma_{inh}(t, T)$ as a function of time and temperature. To focus on the dynamics of the Stokes shift at a fixed temperature, we normalize the $\langle\nu\rangle(t)$ data according to

$$C(t) = \frac{\langle\nu\rangle(t) - \langle\nu\rangle(\infty)}{\langle\nu\rangle(0) - \langle\nu\rangle(\infty)} \tag{2}$$

with $C(t)$ being the so-called Stokes-shift correlation function. Experimentally, the two limits $\langle\nu\rangle(0)$ and $\langle\nu\rangle(\infty)$ are determined by varying the temperature until time invariant plateaux are observed. Figure 1(A) presents $C(t)$ decays obtained for QX/MTHF at $T = 94$ K in silanized porous glasses of various pore diameters, also including the curve for the bulk liquid. The analogous experimental results for native pore surfaces obtained earlier [9] are shown in figure 1(B). For the silanized case, the $C(t)$ data have been fitted by a stretched exponential or Kohlrausch–Williams–Watts (KWW) function of the form

$$C(t) = \exp[-(t/\tau_{KWW})^{\beta_{KWW}}]. \tag{3}$$

The characteristic time constants $\tau_{KWW}(T)$ derived from these fits are compiled graphically in the Arrhenius type plot of figure 2.

The remaining results are given in terms of $\langle\nu\rangle(t_0, T)$ and $\sigma_{inh}(t_0, T)$, i.e., they refer to spectra recorded with a fixed time window at $t = t_0$, whose width is set to $t_0/10$. Curves

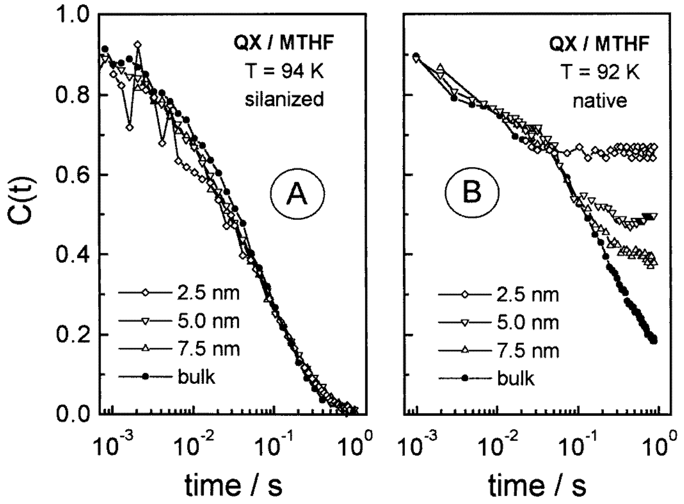

Figure 1. (A) Normalized Stokes shift $C(t)$ for QX in MTHF at $T = 94$ K confined to silanized pores of 2.5, 5.0 and 7.5 nm (open symbols) as indicated. The solid symbols refer to the bulk liquid. (B) $C(t)$ results as in frame (A) but for $T = 92$ K and with native glass surfaces [9].

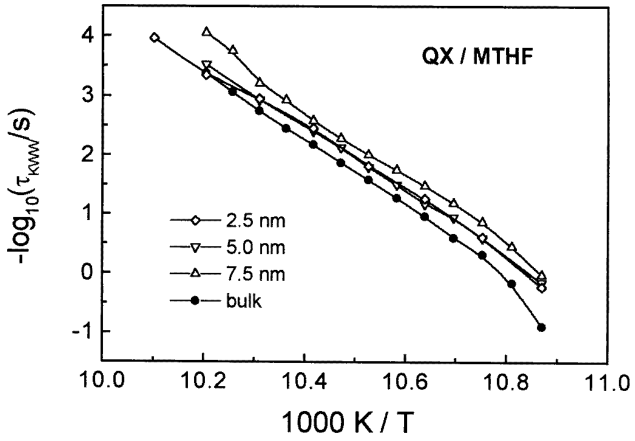

Figure 2. Activation plot of $\tau_{KWW}(T)$ derived from fits to the Stokes-shift correlation function $C(t)$ for QX in MTHF. Solid symbols refer to the bulk liquid; open symbols are for the confinement to silanized pores of various diameters as indicated. The glass transition temperature of MTHF is $T_g = 91$ K (10^3 K/$T_g = 11.0$).

of the type $\langle\nu\rangle(t_0)$ versus T indicate the extent of solvent relaxation which has developed within the time range $0 \leqslant t \leqslant t_0$ at a particular temperature. Figure 3 shows $\langle\nu\rangle(t_0, T)$ and $\sigma_{inh}(t_0, T)$ curves for a bulk QX/MTHF system, while the data in figure 4 have been obtained for QX/MTHF confined to silanized pores of 5 nm diameter.

The most pronounced difference between the bulk and confined case is observed in figure 5, which plots $\langle\nu\rangle(t_0, T)$ for QX in the non-polar solvent 3MP. In this plot, the solid symbols refer to the bulk liquid, while the open symbols are for the same liquid but imbibed into native pores of 5 nm diameter. The two curves are similar, but offset on the energy scale by as much as $\Delta\nu = 780\ \mathrm{cm}^{-1}$. The inset of figure 5 indicates the Stokes shifts relative to the respective low temperature plateau values.

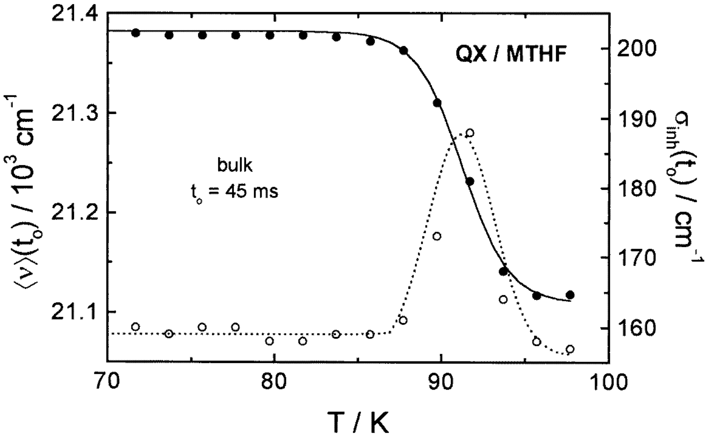

Figure 3. Average emission energy $\langle \nu \rangle$ (solid symbols) and inhomogeneous linewidth σ_{inh} (open symbols) recorded at a fixed time $t_0 = 45$ ms and as a function of temperature. The sample is QX in MTHF without geometrical confinement. The peak of $\sigma_{inh}(t_0, T)$ indicates heterogeneous dynamics.

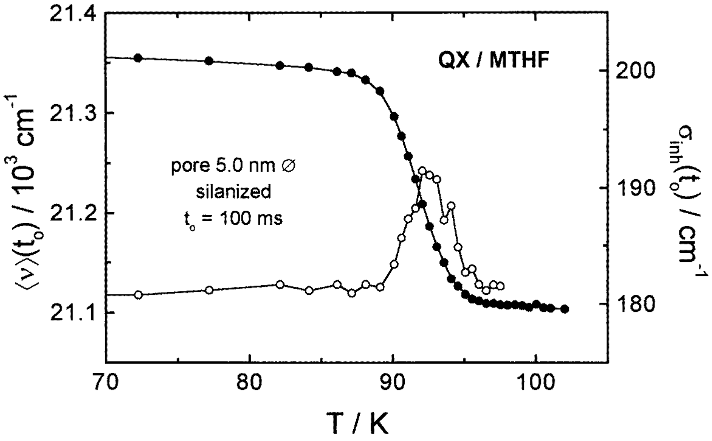

Figure 4. Average emission energy $\langle \nu \rangle$ (solid symbols) and inhomogeneous linewidth σ_{inh} (open symbols) recorded at a fixed time $t_0 = 100$ ms and as a function of temperature. The sample is QX in MTHF in a silanized porous glass with 5 nm sized pores. The peak of $\sigma_{inh}(t_0, T)$ indicates heterogeneous dynamics.

4. Discussion

From figure 1 it is obvious that silanizing the pore surfaces affects the relaxation dynamics qualitatively. Compared to figure 1(B), the new data for silanized pores in figure 1(A) are associated with a somewhat higher temperature and with an improved resolution regarding the short time regime. In the case of native pores the long time plateau increases with the degree of confinement, a feature which is similarly found in computer simulations [15]. This feature has been interpreted as the result of cooperativity which eventually couples the entire confined liquid within a pore to the motional restrictions governed by the glass surface [4]. The observation that this plateau is elevated with decreasing temperature is in accord with the

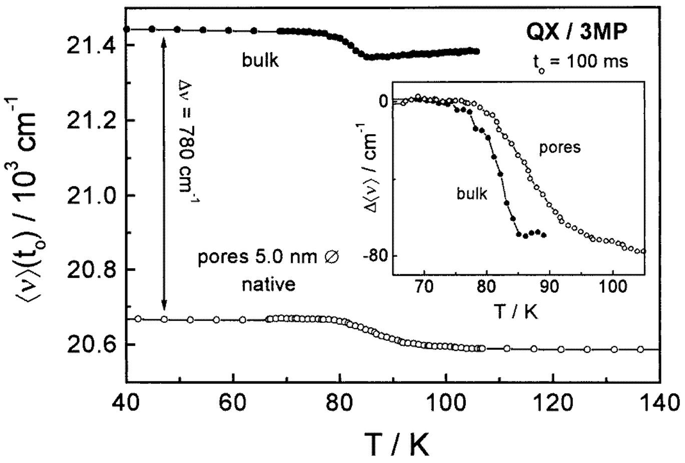

Figure 5. Average emission energy $\langle\nu\rangle$ of QX in 3MP recorded at a fixed time $t_0 = 100$ ms and as a function of temperature. The solid symbols refer to the bulk 3MP liquid; open symbols are for 3MP in a native porous glass with 5 nm sized pores. At low temperatures, $T \leqslant 70$ K, the energy values are separated by $\Delta\nu = 780$ cm^{-1}. The inset shows the relative changes of $\langle\nu\rangle(T)$ on expanded scales.

idea of an increasing length scale $\xi(T)$ of cooperativity as the temperature is lowered. It has been speculated that much of this motional restriction is due to silanol groups which populate such a native silica glass surface.

The above notions regarding cooperativity and the effect of surface chemistry are strongly supported by the present results obtained for the relaxation in silanized porous glasses. In figure 1(A), the curves for all pore sizes, 2.5, 5.0 and 7.5 nm, coincide with the bulk case. We conclude that the difference between bulk and confined relaxations for native pores in figure 1(B) is not the result of pure spatial confinement effects, which are similar for silanized samples. The effect of silanization is to passivate the –OH groups at the surface, which are capable of forming hydrogen bonds and thereby likely to hinder the orientation of those solvent molecules which are directly at the interface. We conclude that the remaining physical interactions between MTHF and the silanized glass surface are not vastly different from the bulk situation, such that cooperative coupling to the interfacial layer does not alter the overall relaxation substantially. The technique of silanization turns out to be appropriate for distinguishing between chemical and physical surface effects. The observed absence of interfacial effects for silanized glass is not considered a general rule, but rather a particular feature of the present supercooled liquid MTHF. The activation plot in figure 2 demonstrates that also the apparent activation energy of MTHF near $T_g = 91$ K is practically independent of the confinement to silanized pores.

A further important aspect of relaxations in disordered materials is the heterogeneous nature of the dynamics [16, 17]. It refers to the observation for bulk supercooled liquids and polymers that an ensemble averaged non-exponential decay is a consequence of exponential contributions with spatially varying time constants [18]. We now ask whether the heterogeneous character of relaxations is preserved in the situation of a nano-confined liquid. In a solvation experiment the signature of heterogeneous dynamics is a time dependent inhomogeneous line width $\sigma_{inh}(t)$. Consider an average emission energy with the time dependence of equation (3), a total Stokes shift $\Delta\nu$, and a steady state linewidth σ_0. If the decay intrinsic in each relaxing unit is assumed to take the stretched exponential form

$\exp[-(t/\tau)^{\beta_{intr}}]$, then the time dependence of $\sigma_{inh}(t)$ is predicted as [19]

$$\frac{\sigma_{inh}(t)}{\sigma_0} = \sqrt{1 + \frac{\Delta\nu^2}{\sigma_0^2}[C(2^{1/\beta_{intr}}t) - C(2^{1/\beta_{KWW}}t)]}. \tag{4}$$

For the extreme case of heterogeneity, in which each relaxing unit is associated with a certain exponential decay, i.e. with $\beta_{intr} = 1$, $\sigma_{inh}(t)$ has been observed to display a peak according to equation (4). Qualitatively, such a peak in $\sigma_{inh}(t)$ is a consequence of fast relaxors emitting already at lowered energies while others have not yet experienced a Stokes shift, so that the emission is broadened until steady state conditions are restored. Homogeneous dynamics would result in $\beta_{intr} = \beta_{KWW}$, which leads to $\sigma_{inh}(t) \equiv \sigma_0$. Therefore, the observation of a relative maximum in $\sigma_{inh}(t)$ or in $\sigma_{inh}(t_0, T)$ data is a clear indication of heterogeneous dynamics. Figure 3 shows such curves for unconfined QX/MTHF, a material for which the application of equation (4) with $\beta_{intr} = 1$ has been confirmed quantitatively by experiment [20]. This feature of the inhomogeneous linewidth is precisely what is seen in figure 4 for the same liquid in silanized pores of 5 nm diameter. In agreement with the bulk case in figure 3, $\sigma_{inh}(t_0, T)$ for the porous sample peaks near temperatures at which the decay of $\langle\nu\rangle(t_0, T)$ is steepest. We conclude that the molecular dynamics are heterogeneous also if the liquid is spatially confined to the 5 nm pores.

So far we have addressed only the polar glass-forming solvent MTHF, whose relaxation behaviour has been shown not to change significantly upon confinement to pores with average diameters as small as 2.5 nm. According to figure 5, the situation is apparently very different in the case of a non-polar solvent, 3MP. Each of the $\langle\nu\rangle(t_0, T)$ curves signals a gradual Stokes shift near the glass transition of 3MP with an amplitude $\Delta\nu \approx 70$ cm^{-1}, as emphasized in the inset of figure 5. However, the entire energy values for the porous sample are depressed by a temperature invariant shift of $\Delta\nu \approx 780$ cm^{-1}, a feature which is not observed for MTHF. Such a very low steady state emission energy around $\langle\nu\rangle_\infty = 20\,590$ cm^{-1} for QX is attained only in liquids of high polarity like pure alcohols. For instance, values of $\langle\nu\rangle_\infty = 20\,592$ cm^{-1} and $\langle\nu\rangle_\infty = 20\,641$ cm^{-1} have been observed for the supercooled solvents 1,3-propanediol and methanol/ethanol (mixture of 4:1 by volume), respectively [14]. From these numbers it is safe to conclude that the QX molecules are located at the pore walls, where the silanol groups are responsible for the shift of $\Delta\nu \approx 780$ cm^{-1}. Therefore, apart from the absolute energy values, the data for the native 5 nm pores in figure 5 refer to the dynamics in the immediate vicinity of the pore wall. The inset of figure 5 compares the relative changes of $\langle\nu\rangle(t_0, T)$ in the bulk 3MP liquid with the features of the interfacial layer of 3MP. The curve associated with the interfacial layer displays the amplitude $\Delta\nu \approx 70$ cm^{-1} of the bulk case, but is shifted to higher temperatures and the transition is broader. In terms of the molecular dynamics, this implies that the relaxation at the interface is a factor of ≈10 slower, its distribution of relaxation times is broader, but there appears no qualitative difference like a motionally blocked interfacial layer.

An important question regarding the QX/3MP experiment in porous glasses remains to be clarified. It concerns the cause of solvation dynamics in a non-polar solvent. Solvation dynamics are usually associated with the orientational relaxation of permanent solvent dipoles [10, 11]. It has been shown that mechanical responses dominate either if the solvent is non-polar [21] or if the solute's dipole moment change $\Delta\mu$ upon excitation vanishes, i.e. $\mu_E = \mu_G$, as in the case of naphthalene [13]. Accordingly, the solvation response of $\Delta\nu \approx 70$ cm^{-1} for 3MP is believed to be due to the local mechanical response to the excitation induced change in the pair potential,

$$\upsilon(r) = \kappa\left[\left(\frac{\sigma_{12}}{r}\right)^{12} - \left(\frac{\sigma_6}{r}\right)^{6}\right] \tag{5}$$

but it is not yet clear which of the parameters in equation (5) is involved most [22]. The chromophore naphthalene shows only the mechanical solvation effects, irrespective of the solvent polarity [13]. It is therefore an interesting candidate for assessing the mechanical relaxation phenomena in confined materials.

5. Conclusions

We have assessed the relaxations of glass-forming liquids in their highly viscous regime under the constraints of a spatial confinement to porous silica glasses using solvation dynamics experiments. The geometrical confinement of a simple liquid, 2-methyltetrahydrofuran, in silanized pores with diameters between 7.5 nm and 2.5 nm has no striking impact on the orientational dynamics of the supercooled liquid. We observe that the main characteristics of a glass-former are all preserved under nano-confined conditions: the relaxation time, the relaxation pattern, the apparent activation energy and the heterogeneous nature of the dynamics. This result differs from the effects of native glass surfaces, which tend to frustrate the molecular mobility at the liquid–glass interface. The highly local character by which solvation experiments probe the molecular dynamics allowed us to assess specifically the liquid layer in the immediate vicinity of the glass surface. For 3-methylpentane, such an experiment revealed that the interfacial layer is somewhat slower but qualitatively similar to the behaviour of the bulk liquid.

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