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Geometrical confinement and cooperativity in supercooled liquids studied by solvation dynamics

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The molecular dynamics of supercooled liquids confined to the mesopores of sol-gel glasses are interpreted in terms of the spatial competition between the average length scale of cooperativity assumed to increase with time and the geometrical confinement on scales between 2.5 and 7.5 nm. Opposed to relating the fast and slow relaxation components to spatially distinct regimes, the picture of a mesoscopically uniform but cooperative relaxation as stimulated by the theoretical work of Jäckle is proposed. It will be demonstrated that rationalizing the data along these lines leads to a consistency with the theory while relaxing some of the conceptual problems encountered in previous interpretations. The data supports the idea that the relaxation in restricting geometries proceeds like in the bulk liquid until the length scale $\xi(t)\propto\log(t)$ of cooperativity reaches the pore size leading to nonergodic behavior within the experimental time scale. For a characteristic cooperativity length ξ_c the data analysis yields $\xi_c(T)\propto T$ and $\xi_c(T_g)\approx 3$ nm. The solvation dynamics results under study are compared to analogous dielectric relaxation data. [S0163-1829(96)01246-5]

I. INTRODUCTION

The effect of geometrical confinement on the molecular dynamics has attracted much attention in recent years, both from the experimental as well as from the theoretical side.[1–6] Despite the current activity in this field, no generally accepted satisfactory coincidence between theoretical approaches and experimental observations has been achieved. Much of the experimental effort focuses on liquids and supercooled liquids in mesoporous media because of the enormous surface to volume ratio with well characterized pore sizes currently achievable.[2] The interest in studying supercooled liquids near their glass transition temperature T_g in mesopores is stimulated in part from the expectation that the spatial dimension of mesopores in the range 1–10 nm should compete with the characteristic length scale ξ of cooperative motion in such highly viscous liquids.[5] In this context the cooperativity scale outlines the average number of molecules involved in the relaxation process at a certain site and is believed to be an important factor in the extreme slowing down of motional time scales as the temperature approaches T_g.[7]

Dielectric relaxation studies regarding glass-forming liquids confined to porous glasses have facilitated the experimental access to the relaxation dynamics in a wide range of frequencies. The main features seen by this technique under geometrical confinement are alterations in the time scale and dispersion of the structural α process relative to the bulk behavior and the appearance of a further process at low frequencies.[3,4,8,9] Although the details of the interpretation are a matter of controversy, there has been only little ambiguity in assigning the fast and slow relaxation components in pores to spatially distinct regimes, with the slow process being attributed to an interfacial surface layer of the liquid whose dynamics are frustrated by physical and/or chemical interactions with the pore walls.[4,8] The problematic issue of such a picture is the necessity of explaining the faster structural relaxation in pores compared to the bulk liquid and the inherent assumption that adjacent molecules at the boundary between surface layer and inner pore liquid differ by orders of magnitude with respect to their relaxation time scale.

It is the purpose of this contribution to investigate the compatibility of experimental findings with the assumption of uniform dynamics in the pores, i.e., while refraining from any spatial localization of distinct relaxation times. An unambiguous decision towards the previous or the currently proposed alternative interpretation calls for further experimental evidence, preferentially with a technique having a mesoscopic spatial resolution. Strongly stimulated by the theoretical work of Donati and Jäckle,[5] cooperative dynamics are assumed and the slow relaxation component is understood as a signature of nonergodicity emerging from motionally blocked molecules at the pore surface. An important and immediate consequence of analyzing the experimental results in this fashion is the result that the dynamics of the confined liquid is at no time faster than its bulk counterpart. The discussion is based on the results of a solvation dynamic study, where the dielectric relaxation of the supercooled liquid of interest is locally probed by means of optical spectroscopy. The advantage over dielectric relaxation measurements are the lacking effects of dc conductivity and Maxwell-Wagner polarization which otherwise interfere with a straightforward data analysis.

II. RESULTS

The technique of solvation dynamics used previously for confined liquids employs phosphorophores as probe molecules at low concentrations, whose emission spectrum is recorded as a function of time following the excitation into the triplet state.[10,11] Electronic excitation and the subsequent change in the permanent dipole moment of the probe molecule induces a dielectric relaxation process in the immediate vicinity of the chromophore, which can be observed in terms of a time dependent redshift of the mean emission energy $\nu(t)$.[12] Analogous experiments in bulk liquids have revealed that the temporal evolution of the Stokes-shift quantitatively reflects the dielectric relaxation behavior $\varepsilon^*(\omega)$ of the

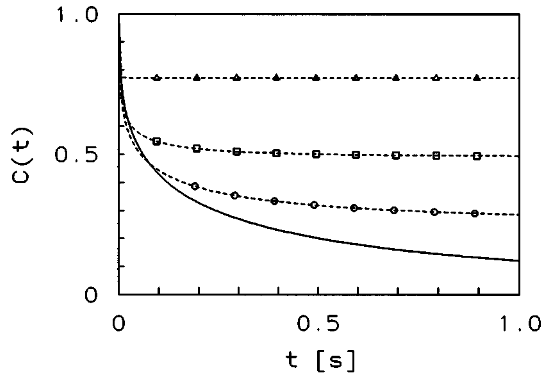

FIG. 1. Experimental results for the Stokes shift correlation function $C(t)$ for MTHF probed by QX at $T=92.5$ K$\approx T_g+2$ K. The solid curve refers to the bulk liquid. The dashed curves are the result in mesopores for the different pore sizes $\phi=7.5$ nm (—○—), 5.0 nm (—□—), and 2.5 nm (—△—). The symbols are for curve identification purposes only.

solvent.[10–13] Because the probe molecule is electrostatically coupled mainly to its first solvent shell,[14–16] solvation dynamics results are not affected by Maxwell-Wagner polarization or dc conductivity.

The data which form the basis for the present investigation and the concomittant experimental conditions have been presented in detail previously.[17] The liquid under study is the glass former 2-methyltetrahydrofuran (MTHF), optically probed by the phosphorescent solute quinoxaline (QX). The solvation dynamics of this system has been measured in the time range 1 ms–1 s in the bulk and in pores of nominal diameter $\phi=2.5$, 5.0, and 7.5 nm. As porous matrices Gelsil glasses (GelTech) being produced by sol-gel technology have been employed. In the bulk MTHF liquid the glass transition temperature is found to be $T_g=91$ K.[18] The experimental temperature window was 80 K$\leqslant T \leqslant$100 K.

The emission spectra of the electronic $S_0 \leftarrow T_1$ (0-0) transition of QX were subjected to a Gaussian profile analysis in order to obtain the mean emission energy $\nu(t,T,\phi)$ and the according Gaussian widths $\sigma(t,T,\phi)$. For focusing on the Stokes-shift dynamics it is convenient to normalize the $\nu(t)$ data to the so-called Stokes-shift correlation function $C(t)$:

$$C(t)=\frac{\nu(t)-\nu(\infty)}{\nu(0)-\nu(\infty)}. \tag{1}$$

To a first approximation, $C(t)$ is the normalized polarization of the material under the condition of a constant charge distribution and thereby strongly related to the dielectric modulus $M(t)$.[19,20] A representative set of $C(t)$ decays is portrayed in Fig. 1 for MTHF at the temperature $T=92.5$ K with the curves being parametric in the pore size. For the decay analysis the tendency of the geometrically confined cases to attain a quasistationary level well above zero is accounted for by an additional offset C_0 to the Kohlrausch-Williams-Watts[21] like structural process, so that the curves are well represented by

$$C(t)=C_0+(1-C_0)\exp[-(t/\tau)^{\beta}]. \tag{2}$$

The data representation thus reduces to $C_0(\phi,T)$, $\tau(\phi,T)$, and $\beta(\phi)$, where the bulk liquid is designated $\phi=\infty$. The qualitative features are that (i) C_0 increases with decreasing pore size and temperature, (ii) τ decreases with decreasing pore size, and (iii) β in pores is smaller than $\beta(\infty)$. Taken the present experimental time range limitation of $t \leqslant 1$ s, the offset C_0 should be understood as a contribution to $C(t)$ for which the relaxation time scale is well above 1 s so that its decay pattern remains unresolved.

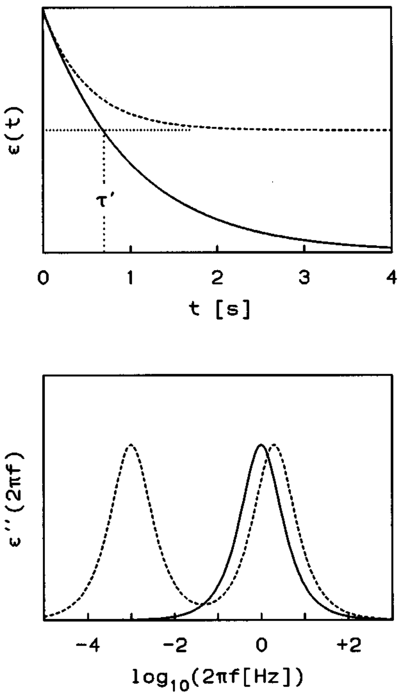

FIG. 2. Time domain [upper frame: $\varepsilon(t)$] and frequency domain [lower frame: $\varepsilon''(\omega)$] schematic representation of the comparison of dynamics in the bulk (solid lines) and in the confined state (dashed lines) of a supercooled liquid. The rate distributions underlying the $\varepsilon(t)$ and $\varepsilon''(\omega)$ plots are identical. The average rates $\langle\omega\rangle$ or $\langle\tau^{-1}\rangle$ are the same for all four curves, such that the initial slope $d\varepsilon(t)/dt$ at $t=0$ is equal for the bulk and confined case. The peak normalized $\varepsilon''(\omega)$ curves actually have identical areas.

III. DISCUSSION

The above shown existence of a slow and fast relaxation component operating on strongly separated time scales in confined liquids is unambiguously confirmed by dielectric relaxation results[3,4,8] for analogous samples. In this technique the material is characterized by the complex dielectric function $\varepsilon^*(\omega)=\varepsilon'-i\varepsilon''$, where a peak situated at $\omega=\omega_0$ within the loss spectrum $\varepsilon''(\omega)$ indicates an orientational relaxation process with a characteristic time $\tau_0=1/\omega_0$. In contrast to a single asymmetrically broadened peak for the bulk liquid, one observes in the porous samples a bulklike loss peak but shifted to higher frequencies and an additional peak at much lower frequencies.[3,4,8] A schematic comparison of typical dielectric loss spectra for the bulk and confined case is depicted in the lower frame of Fig. 2. On the basis of this phenomenology is appears natural to conclude on the acceleration of the structural process and to assign the slow component to a spatially distinct subensemble of molecules, believed to reflect a surface layer with frustrated dynamics due to interfacial effects. The upper frame of Fig. 2 outlines the identical scenario as shown in the $\varepsilon''(\omega)$ curves, but simply converted to a time domain representation. Again in terms of two distinct contributions one easily arrives at the same interpretation.

The above conclusions drawn either from $\varepsilon(t)$ or $\varepsilon''(\omega)$ data become less obvious when observing that the $\varepsilon(t)$ curve for the confined case actually contains no faster component on the absolute $\varepsilon(t)$ scale. The $\varepsilon(t)$ curves in Fig. 2 have been chosen to display identical slopes at time $t=0$ and, equivalently, the average frequencies $\langle\omega\rangle$ of the two $\varepsilon''(\omega)$ curves are identical. The main point is that only the artificial decomposition into distinct processes is responsible for concluding on an accelerated structural relaxation for the confined liquids relative to the bulk behavior. Following the idea put forward by Donati and Jäckle,[5] the following is devoted to investigating the applicability of an understanding of confinement effects assuming spatially uniform dynamics as an alternative to localizing the distinct relaxation times.

The starting point of the proposed alternative interpretation is that the obviously existing slow and fast relaxation contributions are both an inherent property in each relaxing unit. In the original experimental paper[17] it has been argued that the dynamically different domains cannot be separated on length scales of the pore size or above, i.e., the picture of some pores displaying the fast relaxation, while others are entirely filled with the motionally slow liquid does not comply with the solvation dynamic results. The basis for this notion is that a spatial heterogeneity of time scales beyond the dipolar coupling range of the probe molecule to the solvent dipoles would have led to wider emission spectra than actually observed. The recent progress in understanding this dipolar coupling range in disordered materials has revealed that mainly the first solvent shell is ''seen'' by the molecular probe.[14–16] Therefore, the observation of time-independent widths of the emission spectra within $\approx 5\%$ argues against dynamically distinct domains of considerable size.

Anticipating spatially uniform dynamics in the following, the pore-size-dependent relaxations as plotted in Fig. 1 are to be compared on the absolute $C(t)$ scale, which immediately indicates that the confined liquid displays at no time a decay pattern which is faster than the bulk curve (solid curve in Fig. 1). Note that the previous data analysis has claimed an acceleration of the α process by a factor of 10 or more, depending on pore size ϕ and temperature. More specifically, the data of Fig. 1 reveals a bulklike decay at short times $t\leqslant\tau'$ for all pore sizes. It should be emphasized that the qualitative features of Fig. 1 discussed here are paralleled by the results obtained at the other experimental temperatures.[17] The effect of the pore diameter or extent of geometrical confinement is to alter the time $\tau'(\phi)$ at which a transition from a bulklike behavior to a freezing in of the remaining relaxation occurs at the amplitude $C(t\gg\tau')=C_0$. Therefore, at short times $t<\tau'$ the structural relaxation does not sense the geometrical confinement, whereas it depends strongly on ϕ after which time τ' or after which relaxation extent $1-C_0$ the systems appears to become nonergodic on the experimental time scale $t\leqslant 1$ s.

A molecular scenario which supports the above-mentioned transition from a bulklike decay to a nonergodic appearance is schematically visualized in Fig. 3. The model underlying this scheme is that the ensemble averaged initial short-time motion of a relaxing site involves only the cooperative motion of a few neighboring molecules. Further steps towards the equilibrium situation require more and more molecules to act cooperatively, so that the number of dynamically coupled relaxors increases during the progress of equilibration. In other words, the length scale $\xi(t)$ of cooperativity is an increasing function of time, an idea which is conceptually similar to Ngai's coupling scheme.[22] If subject to geometrical confinement such a relaxation mechanism proceeds initially as in the bulk material but is expected to differ from the bulk behavior as soon as the spatial extent of cooperativity has reached the pore size. In this latter situation, the rigid pore wall is likely to block any further approach to equilibrium conditions in the entire pore because now all molecules are dynamically coupled to the interface. The transition time τ' at which this blocking of the dynamics takes effect will thus depend on pore size and on temperature. Eventually, the final equilibrium case is restored but on a much longer time scale dictated by the effectivity by which the pore boundary frustrates the molecules which reside in immediate contact with the pore wall.

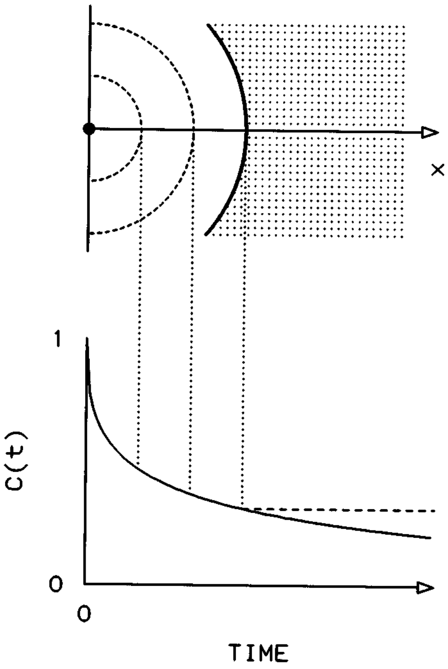

FIG. 3. Schematic illustration of the interrelation between decay pattern and temporal progress of the length scale of cooperativity. The bold solid arc is meant to represent the pore wall and the SiO_2 glass surrounding the pore is indicated by the shaded area. The temporal increase of the cooperativity length (dashed semicircles) is understood to have no effect on the relaxation relative to the bulk decay (solid decay curve) until it matches the pore size and thus induces nonergodicity on longer time scales. None of the axes are meant to be scaled.

One could conclude on the same scenario without regarding the ensemble average only. Consider a statistical distribution of the number of environmental molecules needed to move cooperatively for a certain site to relax. Those sites coupled dynamically to only a few molecules will dominate the short-time response, while sites demanding a large num-

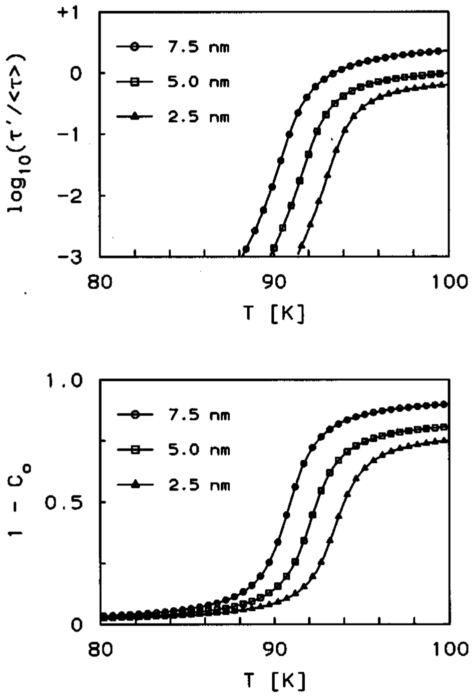

FIG. 4. Temperature and pore size dependence of the transition from bulklike relaxation to quasistationary conditions as inferred from the solvation dynamic data for MTHF in porous glasses. The upper frame indicates the time τ' of this transition relative to the average relaxation time $\langle\tau\rangle$ in the bulk in terms of $\log_{10}(\tau'/\langle\tau\rangle)$. The lower frame indicates the extent $1-C_0$ of the relaxation prior to τ'.

ber of cooperatively rearranging units will equilibrate on longer time scales. In the case of geometrical confinement, all sites associated with a few cooperative neighbors will relax as in the infinitely extenting liquid, while those which are dynamically coupled to the boundary will remain blocked for times well above the average bulk relaxation time. Within the scope of the present discussion, this idea is identical to an ensemble average length scale of cooperativity which increases with time.

In Fig. 3 the transition of the decay into the quasistationary situation is oversimplified by assuming a sharp break at τ', which in reality should be smeared out on the time scale. In order to gain access to the transition time τ' as a function of pore size ϕ and temperature T, all $C(t)$ fits following Eq. (2) are analyzed by evaluating the time τ' which satisfies the condition $C_0(\phi,T)=C(t=\tau',\phi=\infty,T)$. According to Fig. 2, this is the time at which $C(t)$ for the bulk case has decayed to the offset value $C_0=C_0(\phi,T)$. The resulting values $\tau'=\tau'(\phi,T)$, normalized to the average bulk relaxation time $\langle\tau\rangle$ for the same temperature T, are plotted in the upper part of Fig. 4 in terms of $\log_{10}(\tau'/\langle\tau\rangle)$ versus T for the different pore sizes. The lower part of Fig. 4 indicates the extent of relaxation, $1-C_0=1-C_{\mathrm{bulk}}(t=\tau')$, which is covered in the time range $0\leqslant t\leqslant\tau'$. From these results it is seen that for a certain ϕ the time τ' (in units of the average relaxation time $\langle\tau\rangle$) needed for the cooperativity to spread over the entire pore size is a strongly increasing function of temperature, in accord with the idea of the characteristic length scale ξ of cooperativity increasing significantly as the temperature is lowered towards T_g. At a certain temperature slightly above T_g it is in turn a matter of the pore size after which time the blocking of the dynamics takes effect. At sufficiently high temperatures the spatial extent of cooperativity is low such that the crossover time τ' attains values above $\langle\tau\rangle$, i.e., the confinement has practically no effect on the dynamics of the liquid. The equivalent statement can be inferred from the $1-C_0$ data which approaches $C_0=0$ only in the range $T\gg T_g$.

The more quantitative results inferred from the data in Fig. 4 are as follows: If a specific characteristic length scale ξ_c of cooperativity is (arbitrarily) identified with its length $\xi(t_c)$ at the time $t_c=0.1\langle\tau\rangle$, then the condition $\tau'=t_c$ or $\log_{10}(\tau'/\langle\tau\rangle)=-1$ marks where ξ_c is on average equal to the pore radius $\phi/2$. Reading this condition for $\xi_c=\phi/2$ from the $\log_{10}(\tau'/\langle\tau\rangle)$ curves indicates that $\xi_c(T)$ varies approximately linearly with temperature and that $\xi_c(T_g)\approx 3$ nm. At the glass transition temperature $T_g=91$ K the temporal evolution of the cooperativity length $\xi(t)$ is found to increase as $\xi(t)\propto\log(t)$. Within the above concept the competition of cooperativity lengths and mesoscopic geometrical confinement thus leads to a characterization of cooperativity scales ξ summarized by

$$\xi_c(T)\propto T,\quad \xi_c(T_g)\approx 3\ \text{nm, and}\ \ \xi(t)\propto\log(t), \tag{3}$$

where $\xi_c\equiv\xi(t_c)$ can be viewed as the length scale of cooperativity which leads to blocking almost the entire dynamics in the case of a geometrical confinement associated with this spatial scale ξ_c. The result for $\xi_c(T_g)$ is in good agreement with previous reasonings.[23]

A comparison of the present results with a Monte Carlo simulation conducted by Donati and Jäckle[5] on a geometrically confined system with inherent cooperativity appears in order. The simulated system is a lattice gas model with two-vacancy-assisted hopping where the relaxing units are associated with an orientation. It was therefore possible to calculate the orientation autocorrelation function $\phi_p(t)$ under the geometrical confinement to strips of different widths. In a case where the spatial confinement competes with the length scale of cooperativity in this system, the initial decay of $\phi_p(t)$ is only spuriously affected, while $\phi_p(t)$ attains quasistationary behavior at longer times. Qualitatively, these features are paralleled by the solvation dynamic data shown in Fig. 1. Both, the $\phi_p(t)$ simulation result and the $C(t)$ experimental evidence, can be regarded as orientational dynamics in a supercooled liquid near the glass transition and subject to geometrical constraints, so that the theoretical and experimental results are believed to reflect comparable quantities.

IV. SUMMARY AND CONCLUSIONS

The aim of the present work is to present an alternative interpretation for the effects of geometrical confinement on the dynamics of supercooled liquids which refrains from assuming a spatial localization of distinct relaxation times. The picture of uniform cooperative dynamics leads to an understanding of experimental evidence, which relaxes the previously unresolved problems of why structural relaxation becomes faster under geometrical restriction and of assuming adjacent molecules exhibiting relaxation time scales which differ by orders of magnitude. The current basic idea is that the ensemble averaged length scale ξ of cooperativity increases with time such that ξ attains values comparable to the pore size within the mean bulk relaxation time and at temperatures near T_g. The experimental test of this picture exploits solvation dynamics results obtained for the glass former MTHF in mesopores of different sizes around T_g. In accord with the model, the relaxation data for the geometrically restricted liquid decays initially like the bulk counterpart system until a transition at time τ' leads to nonergodic behavior on the relaxation time scale of the bulk material. By analyzing the temperature and pore size dependence of experimental τ' results, the cooperativity length is shown to vary as $\xi(t)\propto\log_{10}(t)$, while for a characteristic length scale of cooperativity we have $\xi_c(T)\propto T$ and $\xi_c(T_g)\approx 3$ nm. A possible application of this simple method of blocking the entire molecular dynamics slightly below T_g for long times could be the orientational arresting of solute molecules in order to introduce a permanent anisotropy. However, it is believed that further experiments capable of a spatial resolution on mesoscopic scales are necessary for unambiguously clarifying the dynamical features induced by geometrically confining a liquid.

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