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Dielectric relaxation of liquids at the surface of a porous glass

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We have measured the dielectric relaxation of the glass-forming liquid N-methyl-ε-caprolactam (as a representative of nonassociating liquids of low molecular weight) confined to the mesopores of a controlled porous glass with 102 Å pore diameter. Three distinct relaxation peaks within $\varepsilon^*(\omega)$ are found for the confined liquid: a broadened α process with slightly modified temperature dependence compared to the bulk relaxation, an intermediate peak which originates from Maxwell-Wagner polarization of the heterogeneous system, and an extremely slow process ascribed to the layer associated with the pore surface. Our assignment of the three features is supported by the results of surface modification using trimethylchlorosilane, Maxwell-Wagner-Sillars calculations, and supplementary experiments where the pores are only partially filled with the liquid under study. By analyzing $[-\partial \log_{10}(\tau_m)/\partial T]^{-1/2}$, where τ_m is the peak relaxation time, we find that the variations of τ_m with T are virtually identical for the three processes.

I. INTRODUCTION

The presence of an interface is known to have a significant impact on structure and dynamics of an adjacent liquid layer. Attractive systems to study such effects are porous glasses where pore diameters as small as ~2 nm combined with a pore fraction of ~50% leads to a surface of several hundred m^2 per g of glass.[1] An important aspect of liquids imbibed in mesopores is the mismatch in surface tension between the liquid under study and the glass, which must lead to alterations in the molecular interaction in the vicinity of the interface. Presence of the surface induces preferential molecular alignments, periodic oscillations of the density which gradually diminish with increasing distance from the wall, and strong anisotropy of molecular motions.[2,3] Additionally, chemical bonding to the glass surface might further complicate the situation.[4] On a quantitative or theoretical level only little is known about the detailed effects of a glass surface on the molecular dynamics.

Liquids for which crystallization can easily be suppressed are regarded as glass-forming materials. They retain many of their properties well below the melting temperature T_m, while the dynamics of such supercooled liquids slow down dramatically with decreasing temperature until ultimately the average relaxation times exceed the experimental time window at the glass transition temperature T_g.[5–7] In this highly viscous regime the commonly observed dispersive relaxation patterns and deviations from simple activated temperature behavior are often attributed to the cooperative nature of the structural or α process,[5–7] which is linked to the glass transition. Moreover, the length scale of cooperativity is expected to increase significantly while the temperature approaches T_g.[8] The confinement of liquids to mesoscopic pores is thus especially of interest where the pore radius competes with the spatial extent of cooperativity, which outlines the size of a liquid sphere involved in the dynamical behavior of a single molecule within this sphere.

A number of experiments has been performed in order to investigate the effect of confinement on supercooled liquids.[1,9–17] It is by now well established that the glass transition T_g of a liquid inside a porous glass is shifted by ΔT_g with respect to bulk behavior, where the sign and extent of ΔT_g turns out to be material specific.[10–16] Only recently it has been appreciated that the technique of dielectric relaxation spectroscopy serves as a powerful tool for studying the dynamics of confined liquids in detail.[14–17] The results of such studies confirm the confinement induced shift in T_g and also indicate a broadening of the relaxation time dispersion of the α process and the appearance of distinct surface dynamics which are orders of magnitudes slower than the α relaxation.[15–17] In most cases a third relaxation peak within the spectrum $\varepsilon^*(\omega)$ is observed, which is tentatively ascribed to a Maxwell-Wagner-Sillars (MWS) polarization and mainly arises from the slightly conductive liquid being enclosed in an insulating material.[18]

In the present work we discuss dielectric studies of a low molecular weight nonassociating liquid N-methyl-ε-caprolactam as a model system of small rigid molecules with predominantly van der Waals interactions. As geometrical confinement we employ controlled porous glass (CPG) with an extremely narrow distribution of pore diameters which peaks at 102 Å.[19] The dielectric data recorded in the range 10^{-2} to 10^9 Hz reveal three relaxation peaks and dc conductivity. To support the assignment of the slowest relaxation component we discuss the effect of surface modification, the expected position and strength of the MWS signal, and the results obtained after partial filling of the pores with the liquid.

II. EXPERIMENT

The glass-forming liquid N-methyl-ε-caprolactam [NMEC, 1-methyl-hexahydroazepin-2-one, μ=4.2 D (Ref. 20)] by Aldrich was passed through Al_2O_3 filters to remove polar contaminations (e.g., H_2O) directly before filling the the pores.

The controlled porous glass (CPG) Bioran (Schott, Ger-

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many) was made by acid leaching of the boron-rich phase of a spinodally decomposed borosilicate glass. The material is a powder consisting of particles 30–60 μm in diameter with an inner surface area of 225 m^2 per g of glass, a pore volume of 0.8 cm^3 per g of glass, and a mean pore diameter of 102 Å with an extremely narrow distribution of pore sizes (5% standard deviation). The approximately cylindrical voids are highly branched and connected and their native surface contains a large number of silanol groups. The outer surface area of the particles is less than 1% relative to the inner one. To remove the water adsorbed by the SiOH groups, the glass was thoroughly cleaned by boiling in acetone and drying under vacuum for 24 h at temperatures up to 350 °C. The glass was then mixed with the liquid under a dry N_2 atmosphere and gently stirred for at least 72 h so that the pores were completely filled by capillary wetting. If desired, the surface of the CPG was chemically treated using trimethylchlorosilane which replaces the polar $-$OH groups on the glass surface with the less polar trimethylsilyl groups resulting in a more hydrophobic surface.[4,21]

The imbibed CPG samples were placed between the electrodes of a capacitor (diameter 30 mm, spacing $\sim$100 μm), tightly surrounded by a Teflon cell. Dielectric measurements in the frequency range 10^{-2}–10^6 Hz were performed using a Solatron-Schlumberger frequency response analyzer FRA 1260 equipped with a buffer amplifier of variable gain in order to determine the dielectric loss $\varepsilon''(\omega)$. For the bulk NMEC measurements the frequency range was extended to 10^9 Hz using a coaxial line reflectometer HP-4191 A. The sample temperatures in the range 160–240 K were controlled by a nitrogen gas stream with a stability better than ± 0.1 K.

For a quantitative analysis of the complex permittivity $\varepsilon^* = \varepsilon'(\omega) - \varepsilon''(\omega)$, ε_∞ plus the sum of up to $N=3$ Havriliak-Negami (HN) terms $\Delta\varepsilon[1+(i\omega\tau)^\alpha]^{-\gamma}$ (Ref. 22) in conjunction with a conductivity term has been used, which for $N=1$ reads

$$\varepsilon^*(\omega) = \varepsilon_\infty + \Delta\varepsilon[1+(i\omega\tau)^\alpha]^{-\gamma} - i\sigma_{\mathrm{dc}}\varepsilon_0^{-1}\omega^{-s}. \qquad (1)$$

The first two terms on the right-hand side describe the dielectric relaxation with characteristic relaxation time τ and dielectric relaxation strength $\Delta\varepsilon$. The exponents α and γ ($0 < \alpha, \alpha\gamma \leqslant 1$) define the symmetrical and asymmetrical broadening of the loss peaks, respectively, where $\alpha = \gamma = 1$ corresponds to the Debye case. The third term quantifies the dc conductivity σ_{dc} in terms of $\varepsilon''(\omega)$, with a fit parameter s in the range $0.5 \leqslant s \leqslant 1$, where $s=1$ represents ohmic conductivity. Although expressing the spatial dependence of $\varepsilon^*(\omega)$ within the pores explicitly in terms of $\varepsilon^*(\omega, \mathbf{k})$ would be a more rigorous approach, we assume additivity of the distinct contributions in Eq. (1) since the dielectric technique contains no explicit wave-vector $\mathbf{k}$ dependence. From fits according to Eq. (1), we determined ω_m, the maximum frequency position of each loss peak. Within certain limits their temperature dependence can be described by the Vogel-Fulcher-Tammann (VFT) equation:[23]

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

where the preexponential factor A, the activation parameter B, and the Vogel temperature T_0 are temperature-independent empirical parameters.

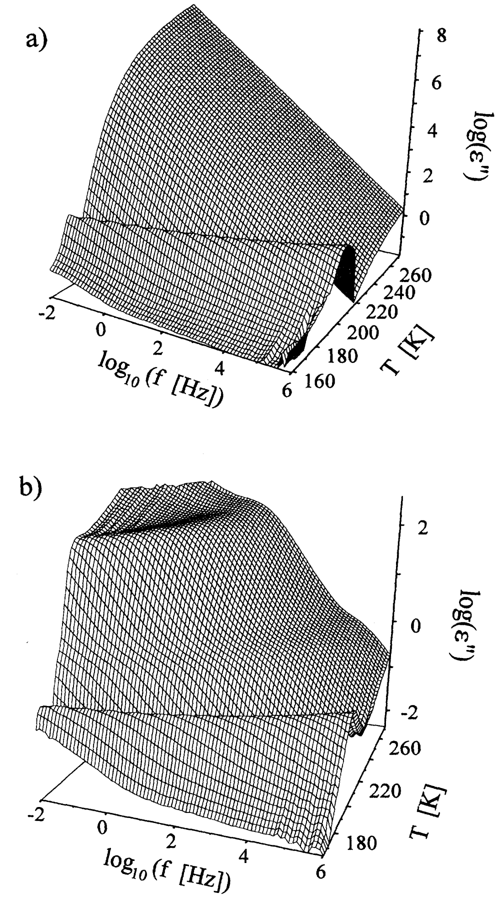

FIG. 1. Dielectric loss $\varepsilon''(\omega, T)$ of NMEC vs frequency $f = \omega/2\pi$ and temperature T for the bulk liquid [upper, (a)] and in pores of 102 Å diameter [lower part, (b)].

III. RESULTS

The dielectric loss of the CPG-NMEC sample as a function of frequency and temperature is displayed in Fig. 1(b), whereas Fig. 1(a) shows the corresponding bulk NMEC behavior for comparison. In the entire experimental temperature range the qualitative effects of the pores are a temperature-dependent broadening and frequency shift of the α relaxation (I), the occurrence of two additional loss peaks (II and III), and deviations of the dc conductivity from ohmic ($s=1$) behavior. For a single temperature Fig. 2 compares the bulk and confined NMEC dielectric relaxation in terms of the loss spectra $\varepsilon''(\omega)$. Interestingly, the dielectric strength related to peak III is $\sim$10 times larger than that of the bulk α process, i.e., much stronger even without correcting for the porosity of the CPG samples. Note that the $\Delta\varepsilon$ ratios for the different peaks are obscured in Fig. 2 due to the $\log_{10}(\varepsilon'')$ scaling. Figure 3 indicates how the frequency positions τ_m for the three peaks vary with temperature, also showing the bulk α process for comparison. Inspection of these curves shows that the α relaxation in CPG is subject to a shift in T_g towards higher temperatures relative to the bulk NMEC. Second, the two additional processes related to the CPG basically follow the same variation with T as does the α peak.

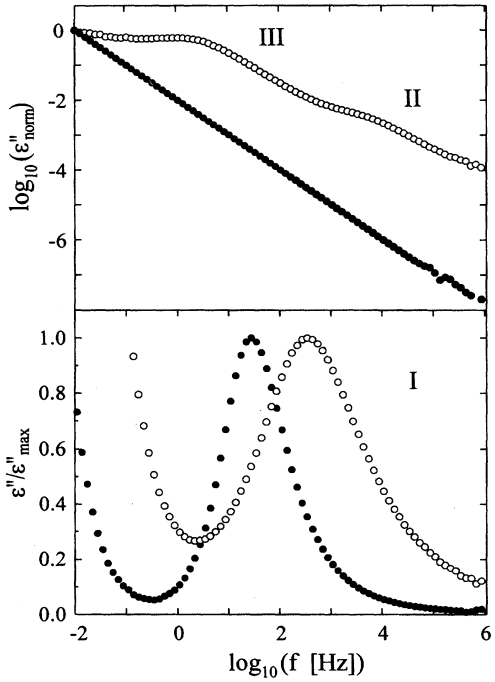

FIG. 2. Normalized dielectric loss spectra $\varepsilon''(\omega)$ of bulk (●) and confined (○) NMEC for two different temperatures. Upper panel: $T=227$ K showing peaks II and III, lower panel: $T=183$ K showing peak I.

Figure 4 shows the effect of silanizing the glass surface with trimethylchlorosilane. While the relaxation times of the fastest process I remains practically unaltered, the slowest one designated III is suppressed in intensity by this surface modification to almost below our capabilities of resolving a loss peak within the conductivity wing.

In order to unambiguously assign one of the additional slow processes to the frustrated dynamics expected for a surface layer, we have conducted a further experiment where the CPG is only partially filled with NMEC. For this purpose, the porous glass has been exposed to ~20% of the liquid's volume previously needed to completely fill the same amount of CPG. According to a crude estimate, 20% volume content corresponds to ~3 NMEC monolayers in the case of ideal surface coverage. The resulting dielectric data are displayed in Fig. 5, which reveals a reduction in the α relaxation strength by a factor of ~5 while the areas of the peaks II and III are virtually identical to the 100% filling case. For temperatures ranging from 205 to 300 K we find for relaxation I, $\Delta\varepsilon_{20\%}/\Delta\varepsilon_{100\%}=0.2\pm0.05$ and for relaxation III, $\Delta\varepsilon_{20\%}/\Delta\varepsilon_{100\%}=1.2\pm0.3$ with no strong systematic temperature variation of $\Delta\varepsilon_{20\%}/\Delta\varepsilon_{100\%}$ for both peaks. The $\tau_m(T)$ results for the partially filled case are compiled in Fig. 6, together with the data for completely imbibed CPG's.

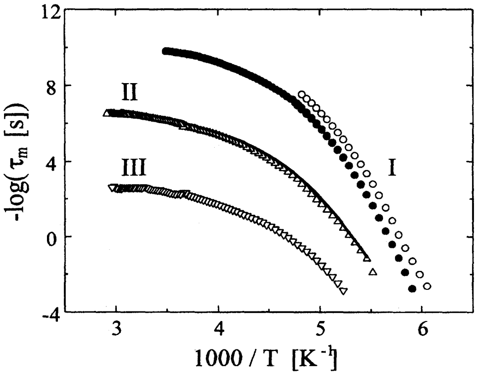

FIG. 3. Temperature dependence of the peak dielectric relaxation times τ_m for bulk (●) and confined (peak I, ○; peak II, △; peak III, ▽) NMEC. The solid line marks the calculated peak position of the Maxwell-Wagner-Sillars polarization.

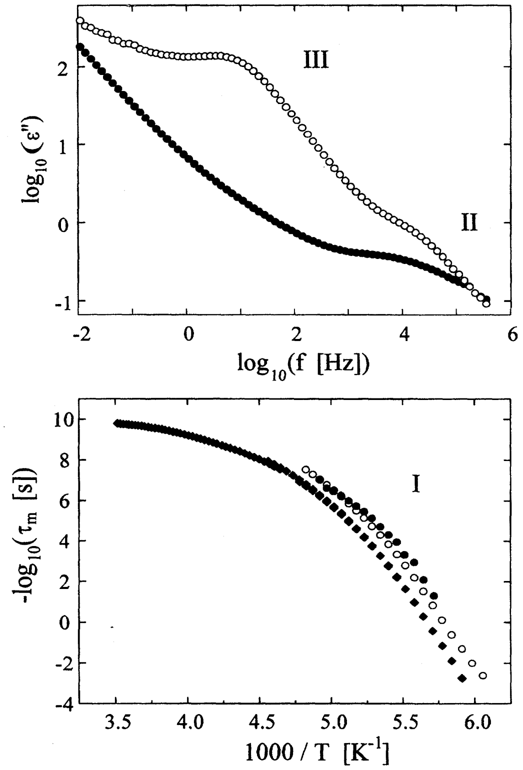

FIG. 4. Upper panel: normalized dielectric loss spectra $\varepsilon''(\omega)$ of CPG-NMEC samples at $T=239$ K with native (○) and silanized (●) pore surface showing peaks II and III. Lower panel: temperature dependence of the peak dielectric α-relaxation times τ_m (peak I) for CPG-NMEC samples with native (○) and silanized (●) pore surface and for the bulk NMEC liquid (◆).

IV. DISCUSSION

Before further analyzing the above results we wish to emphasize that we present here data of only one material as a representative for a number of other glass-forming liquids of low molecular weight. We have confirmed that the basic features shown for NMEC are paralleled by the other liquids

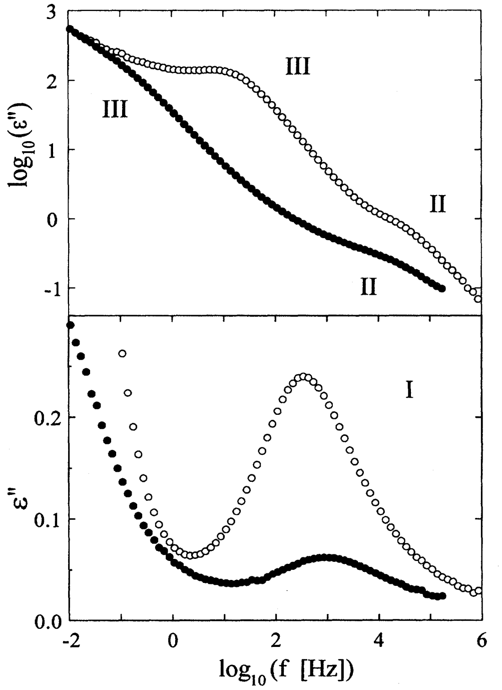

FIG. 5. Dielectric loss spectra $\varepsilon''(\omega)$ of CPG-NMEC samples with 100% (○) and 20% (●) liquid content in CPG by volume for two different temperatures. Upper panel, $T=247$ K showing peaks II and III; lower panel, $T=183$ K showing peak I.

(e.g., salol, glycerol, 1-propanol) which we address in more detail in a future paper.

The basic features of geometrically confining a liquid in terms of its molecular dynamics are readily seen in Figs. 1 and 2. In the CPG the α process (I) is only slightly modified with respect to its width of the loss peak and the temperature dependence of the peak relaxation time τ_m. More striking is the occurrence of additional peaks at lower frequencies, which are completely absent in the bulk material. The relative peak positions τ_m of the well-separated peaks are seen in Fig. 3, which also suggest that their temperature variations follow similar functional forms. In order to better compare the various $\tau_m(T)$ curves we proceed along the lines of the temperature derivative method[24] in order to obtain a data representation which is extremely sensitive to differences in the form of $\tau_m(T)$, irrespective of the offsets in the preexponential factors. For a VFT-type $\omega_m(T)$ a scaling as in Fig. 7 yields linear graphs according to the relation[24]

$$\left[\frac{\partial \log_{10}(\omega_{\mathrm{VFT}})}{\partial T}\right]^{-1/2}=B^{-1/2}(T-T_0), \tag{3}$$

where the slope and intercept correspond to B and T_0, respectively. As often found for $\omega_m(T)$ regarding the α process in nonassociated liquids of low molecular weight, the curves in Fig. 7 are well described by two distinct VFT functions, serving as data representation for the low ($185 \leqslant T \leqslant 204$ K) and high ($207 \leqslant T \leqslant 265$ K) temperature range. The departure from the low-temperature VFT, which occurs below 185 K, is a feature which is not typical for liquids which display two VFT regimes.[25] By plotting $[-\partial \log_{10}(\tau_m)/\partial T]^{-1/2}$ versus T, the upper panel of Fig. 7 indicates that within resolution the three peaks follow the same temperature dependence (i.e.,

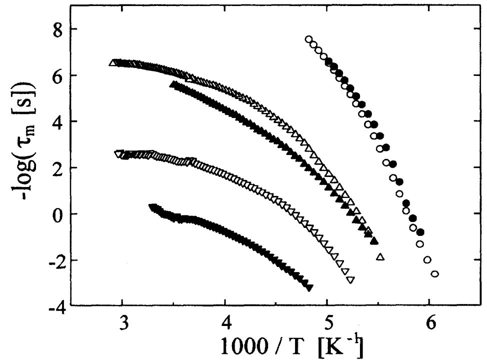

FIG. 6. Temperature dependence of the peak dielectric relaxation times τ_m for 100% (open symbols, peak I, ○; peak II, △; peak III, ▽) and 20% (solid symbols) NMEC liquid content in CPG by volume.

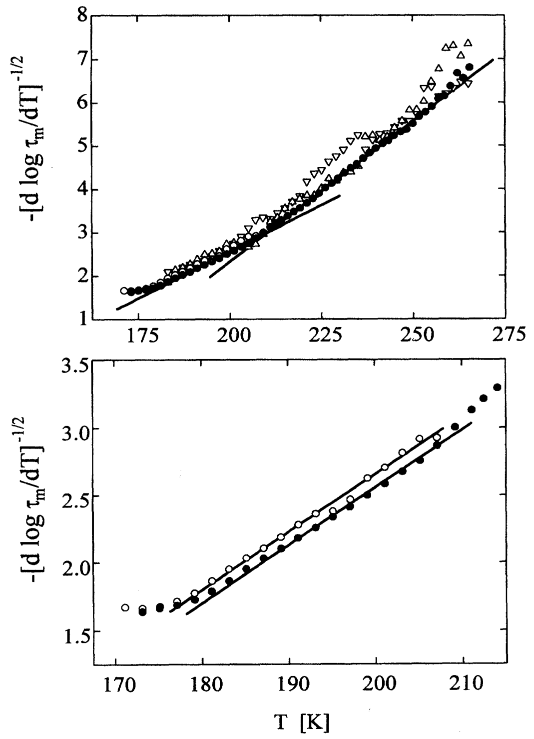

FIG. 7. Upper: temperature dependence of the peak dielectric relaxation times τ_m for bulk (●) and confined (peak I, ○; peak II, △; peak III, ▽) NMEC. Same data as in Fig. 3 but in a $[-\partial \log_{10}(\tau_m)/\partial T]^{-1/2}$ vs T representation. Solid lines show the low- and high-temperature VFT fit to the bulk relaxation times. Lower: enlarged view of $[-\partial \log_{10}(\tau_m)/\partial T]^{-1/2}$ vs T for the bulk (●) and confined (○) α process, together with the corresponding VFT fits (solid lines) with $\Delta B=0$ and $\Delta T_0=-1.9$ K. Both frames: the ordinate scaling for τ_m in s is stated in units of $\mathrm{K}^{1/2}$.

with similar VFT parameters B and T_0), apart from the large offsets in $\log_{10}(\tau_m/s)$ seen in Fig. 3. For the low-temperature ($185 \leq T \leq 204$ K) behavior of the α process we find for the VFT parameters $A=14.9$, $B=545$ K, $T_0=139.9$ K for bulk NMEC and $A=15.5$, $B=545$ K, $T_0=138.0$ K for the CPG-NMEC samples. Regarding the temperature dependence of the α process in the vicinity of T_g, the effect of the pores can therefore be formally attributed to a change in T_0 by $\Delta T_0=-1.9$ K (see Fig. 7, lower panel). The resulting values for T_g, identified by the condition $\tau_g=\tau_m(T=T_g)=100$ s, are $T_g=172.2$ K and $T_g=167.2$ K for bulk and confined NMEC, respectively. Such a negative shift of the glass transition ($\Delta T_g=-5$ K in this case) is also observed for other polar liquids of low molecular weight, whereas propylene glycol and its oligomers indicate positive values for ΔT_g in the same 102 Å CPG.[15,16]

Within mesoscopic pores one might expect to find a portion of undisturbed dynamics in the inner pore space and a gradual frustration of molecular mobility towards the pore surface. In terms of the dielectric loss spectra this would correspond to a bulklike α peak but with a very broad and structureless low-frequency wing, very much in contrast to present and previous[15–17] findings. On the other hand, there exists a large body of experimental evidence by Isrealachvili,[26] Horn,[27] Granick,[28] and others, that the shear viscosity tends to diverge upon confining a liquid to several (~3) molecular layers. These results concur well with a separated slow relaxation attributed to a distinct surface layer. Very unlikely, however, is the picture of two consecutive surface layers in order to rationalize both additional peaks found in the CPG-NMEC samples.

For a complete understanding of the dielectric properties of a liquid inside a porous glass one has to account for the intrinsic heterogeneity of the system given by the different electric and dielectric properties of the SiO_2-glass matrix and of the liquid filler under study. A simplified model situation for such heterogeneity is composed of conducting spheres embedded in an insulating matrix and results in a Maxwell-Wagner-Sillars (MWS) polarization of the composite.[18] The MWS theory as formulated by Sillars[18,29] predicts for the complex dielectric function $\varepsilon_c^*(\omega)$ of the composite

$$\varepsilon_c^*(\omega)=\varepsilon_m^*(\omega)\frac{[n\varepsilon_f^*(\omega)+(1-n)\varepsilon_m^*(\omega)]+(1-n)[\varepsilon_f^*(\omega)-\varepsilon_m^*(\omega)]c_f}{[n\varepsilon_f^*(\omega)+(1-n)\varepsilon_m^*(\omega)]-n[\varepsilon_f^*(\omega)-\varepsilon_m^*(\omega)]c_f}, \tag{4}$$

with $\varepsilon_m^*(\omega)$ and $\varepsilon_f^*(\omega)$ being the dielectric functions of the glass matrix and the liquid filler, respectively. c_f is the volume fraction of the liquid and n is the depolarization factor in the range $0 \leq n \leq 1$. The factor n is used to account for uniform filler structures from prolate ($0 \leq n < \frac{1}{3}$, needles) to oblate ($\frac{1}{3} < n \leq 1$, disks) forms relative to the field. In our case, the branched and connected cylinders display random orientations, so that we use as an average value $n=\frac{1}{3}$, which actually represents spherical structures. As extreme departures from spherical symmetry we regard ellipsoids with axis ratios ranging from $0.1 \leq a/b \leq 10$, which corresponds to a range of n values from ~0.02 to ~1. According to Eq. (4), a (more than realistic) variation of n within $0.02 \leq n \leq 1$ alters the peak position of $\varepsilon_c''(\omega)$ only within ±0.5 decades.

Since all remaining parameters, c_f, $\varepsilon_m^*(\omega)$, and $\varepsilon_f^*(\omega)$, needed in Eq. (4) are experimentally determined, we can readily calculate the expected $\varepsilon_c^*(\omega)$, which resembles a Debye-type polarization process. The result that the peak position of $\varepsilon_c''(\omega)$ reflects the temperature dependence of the α process is the simple consequence of the well-known fact that the conductivity $\sigma_{dc}(T)$ of ionic tracers usually follows the trend of $\tau_m(T)$ of the α relaxation.[30] The calculated peak position of the MWS polarization is included in Fig. 3 as solid curve, indicating a satisfactory coincidence with process II of the three peaks. The calculated process strength also agrees within ±20% with the data. Since there exists a number of different approaches, by Hanai,[31] Looyenga,[32] and Bergman,[33,34] for calculating $\varepsilon_c^*(\omega)$ we have also compared these to the result of Eq. (4) and obtain very similar coincidences with the experiments. Moreover, alterations of ±50% in the process strength and ±1 in $\log_{10}(\tau_m)$ for the MWS results would still give no satisfactory agreement with one of the other peaks, I or III. Despite the simplifications and limitations to $c_f \leq 0.2,...,0.5$ of such approaches to heterogeneous dielectrics, we consider the above findings as a strong indication for the middle peak II being due to MWS polarization. This contribution to $\varepsilon^*(\omega)$ is thus a rather trivial effect of the liquid-glass heterogeneity and will not appear in other relaxation techniques.

The comparison between native and silanized pore surface as compiled in Fig. 4 indicates that mainly peak III is affected by surface modification, which replaces the $-OH$ groups by the more hydrophobic $-Si(CH_3)_3$. Volume effects as a consequence of this treatment are not expected because the surface coverage results in an additional $-Si(CH_3)_3$ layer of only ~1 Å average thickness.[21] We conclude that peak III arises from a distinct surface layer of NMEC with a strong impact of silanol groups on the dynamics at the surface. Despite this striking effect of silanization on peak III, we observe that the temperature dependence and width of the α process for a silanized surface equals $\tau_m(T)$ and width for a native pore surface, instead of restoring the bulk behavior (see lower panel of Fig. 4). As a consequence, the difference (ΔT_0 and ΔT_g) between the temperature dependences of the α relaxation times for bulk NMEC and CPG-NMEC should be understood as pure confinement effect, instead of surface induced effects which extend into the inner pore space.

Further support for an assignment of the additional peaks stems from the idea that partial filling of the pores is expected to have little effect on the surface layer, while the α process, if originating from the inner pore space, should be depressed in intensity. An important requirement for such an

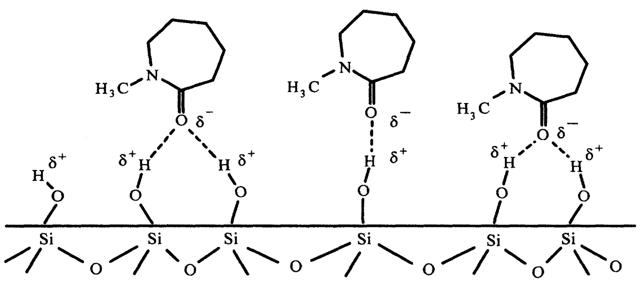

FIG. 8. Possible structure of NMEC molecules chemically trapped at the native CPG pore surface. The dipole moment ($|\mu|=4.2$ D) of NMEC is almost parallel to the C=O bond.

experiment is a sufficiently polar liquid, like NMEC, because effective surface wetting has to occur. Otherwise, only an overall, i.e., not peak specific, decrease of the dielectric signal will result. As expected, the experiment where only ~20% of the pore volume is occupied by the liquid displays a less pronounced but otherwise unaltered α process, whereas the intensity of peaks II and III are virtually maintained. This comparison in process strengths refers to identical geometric capacities, but without correcting for the liquid content. The invariance of the intensity of process III to the average liquid content in the pores strongly argues in favor of assigning this slowest relaxation to the liquid portion in the immediate vicinity of the glass surface, which is the thermodynamically preferred space in case of wetting materials. The further observation in Fig. 6 that process III is slowed down by another ~2 decades in the case of partially filled pores is probably the consequence of the missing more liquidlike material in the inner pore volume. In this situation the surface layer, which for 20% liquid content is on average ~3 monolayers thick, experiences two interfaces, NMEC-glass on one side and NMEC-gas on the opposite side. Regarding peak II, believed to reflect MWS polarization, the deviations in $\tau_m(T)$ can be understood as a signature of changes in the dc-conductivity mechanism which originate from reducing the liquid content.

The broadening and the variation of the temperature dependence of the α process revealed by dielectric spectroscopy on geometrically confined liquids is a generally accepted feature. The previous observation of additional peaks slower than the α relaxation has, however, lead to interpretations which contrast the present assignment. In a recent paper, Arndt and Kremer[17] claim peak II to reflect the surface layer, while peak III is attributed to MWS polarization. Their key argument is that relaxation strengths beyond that of the bulk α process cannot relate to relaxation processes of the liquid, whereas a MWS polarization can attain much higher peak intensities. We believe, however, that the results of our MWS calculations and of the experiments regarding silanization and partial pore filling are not compatible with such an interpretation.

In a very simplified view, Fig. 8 schematically indicates how NMEC molecules might reside on the native pore surface. It seems likely that hydrogen bonding between silanol groups and NMEC induces a strongly anisotropic structuring of the liquid in the immediate vicinity of the surface. Since rotation around the C═O bond possesses only little dielectric strength, the major dielectric contribution from a structure as in Fig. 8 should arise from a tilt motion with a high degree of molecular cooperativity. Within this picture the understanding of the similarity of $\tau_m(T)$ for peaks I and III is nontrivial. However, such a cooperative motion associated with relaxation peak III complies well with the observations of strongly increased relaxation times and enhanced dielectric strength $\Delta\varepsilon$ compared to the bulk α process. According to the Kirkwood-Fröhlich equation for rationalizing $\Delta\varepsilon$, a structural correlation of adjacent dipoles increases the effective dipole moment by $g^{1/2}$, where g is the Kirkwood correlation factor which is usually found in the range $0.1 \leqslant g \leqslant 10$.[35] The pure electrostatical effect of the presence of a dielectric interface is expected to be of minor importance in this context.[36,37] Experimental support for the strong impact of silanol groups on the behavior of the surface layer is gained from the above observation that the slowest peak III is entirely suppressed by silanizing the pore surface.

V. CONCLUSIONS

The study of a nonassociating liquid of low molecular weight within the 102 Å pores of controlled porous glass leads to several new features compared to the bulk NMEC liquid. The α process is subject to a broadening of the loss peak and to changes of its temperature dependence $\tau_m(T)$, where the confinement induced changes in $\tau_m(T)$ can be cast into ΔT_0 in the case of assuming a VFT dependence. The $\varepsilon^*(\omega)$ data of CPG-NMEC samples indicate three distinct peaks, whose temperature dependences differ mainly by their preexponential factors A. Because of its invariance to the liquid content in the pores and its disappearence for silanized surfaces we attribute peak III, which is 8 decades slower than the α process, to a surface layer of NMEC which is strongly influenced by the presence of silanol groups. The inherent cooperativity of such an ordered structure is believed to increase both the relaxation time and the dielectric relaxation strength. Since the CPG-liquid sample is a heterogeneous dielectric material, this composite displays a predictable MWS polarization, which coincides well with peak II. This middle peak is thus a rather trivial effect which appears only in conjunction with the application of electric fields. The temperature dependences of the α processes for native and silanized surfaces are identical but differ from the bulk behavior, whereas surface treatment has a strong impact on the dynamics at the surface. From this observation we conclude that the CPG-induced modifications of the α relaxation are pure confinement effects, rather than surface-induced effects which extend into the inner pore space.

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[1] *Molecular Dynamics in Restricted Geometries*, edited by J. Klafter and J. M. Drake (Wiley, New York, 1989).

[2] S. Gupta, D. C. Koopman, G. B. Westermann, and I. A. Bitsanis, J. Chem. Phys. **100**, 8444 (1994).

[3] K. P. Walley, K. S. Schweizer, J. Peanasky, L. Cai, and S. Granick, J. Chem. Phys. **100**, 3361 (1994).

[4] R. K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).

[5] *Dynamics of Disordered Materials*, edited by D. Richter, A. J. Dianoux, W. Petry, and J. Teixeira, Springer Proceedings in Physics Vol. 37 (Springer-Verlag, Berlin, 1989).

[6] K. L. Ngai and G. B. Wright, J. Non-Cryst. Solids **131-133**, (1991); K. L. Ngai, E. Riande, and G. B. Wright, *ibid.* **172-174**, (1994).

[7] *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994).

[8] E. Donth, *Relaxation and Thermodynamics in Polymers* (Akademie Verlag, Berlin, 1992).

[9] W. D. Dozier, J. M. Drake, and J. Klafter, Phys. Rev. Lett. **56**, 197 (1986).

[10] C. L. Jackson and G. B. McKenna, J. Non-Cryst. Solids **131-133**, 221 (1991).

[11] P. Pissis, D. Daoukakis-Diamanti, L. Apekis, and C. Christodoulides, J. Phys. **6**, L325 (1994).

[12] J. Dubochet, M. Adrain, J. Teixeira, C. M. Alba, R. K. Kadiyala, D. R. MacFarlane, and C. A. Angell, J. Phys. Chem. **88**, 6727 (1984).

[13] K. Hofer, E. Mayer, and G. P. Johari, J. Phys. Chem. **95**, 7100 (1991).

[14] P. Pissis, J. Laudat, D. Daoukaki, and A. Kyritsis, J. Non-Cryst. Solids **171**, 201 (1994).

[15] J. Schüller, Yu. Mel'nichenko, R. Richert, and E. W. Fischer, Phys. Rev. Lett. **73**, 2224 (1994).

[16] Yu. Mel'nichenko, J. Schüller, R. Richert, B. Ewen, and C.-K. Loong, J. Phys. Chem. **103**, 2016 (1995).

[17] M. Arndt and F. Kremer, in *Dynamics in Small Confining Systems II*, edited by J. M. Drake, J. Klafter, R. Kopelman, and S. M. Troian, MRS Symposia Proceedings No. 366 (Materials Research Society, Pittsburgh, 1995), p. 259.

[18] G. Bánhegyi, Colloid Polym. Sci. **264**, 1030 (1986).

[19] R. Schnabel and P. Langer, Glastech. Ber. **62**, 56 (1988).

[20] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry* (VCH, Weinheim, 1990).

[21] V. Erb, diploma thesis, Max-Planck-Institut für Polymerforschung, Mainz, 1993.

[22] S. Havriliak and S. Negami, Polymer **8**, 101 (1967).

[23] H. Vogel, Phys. Z. **22**, 645 (1921); G. S. Fulcher, J. Am. Chem. Soc. **8**, 339 (1925); **8**, 789 (1925).

[24] F. Stickel, E. W. Fischer, and R. Richert, J. Chem. Phys. **102**, 6251 (1995).

[25] F. Stickel, E. W. Fischer, and R. Richert (unpublished).

[26] H. K. Christenson, D. W. R. Gruen, R. G. Horn, and J. N. Israelachvili, J. Chem. Phys. **87**, 1834 (1987).

[27] R. G. Horn, S. J. Hirz, G. Hadziioannon, C. W. Frank, and J. M. Catala, J. Chem. Phys. **90**, 6767 (1989).

[28] W. Hu, G. A. Carson, and S. Granick, Phys. Rev. Lett. **66**, 2758 (1991).

[29] R. W. Sillars, J. Inst. Electr. Eng. **80**, 378 (1937).

[30] C. A. Angell, Annu. Rev. Phys. Chem. **43**, 693 (1992).

[31] T. Hanai, Bull. Inst. Chem. Res. Kyoto Univ. **39**, 341 (1961).

[32] H. Looyenga, Physica **31**, 401 (1965).

[33] D. J. Bergman, Phys. Rev. Lett. **44**, 1285 (1980).

[34] D. J. Bergman, Ann. Phys. **138**, 78 (1982).

[35] C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973), Vol. 1.

[36] M. Urbakh and J. Klafter, J. Phys. Chem. **97**, 3344 (1993).

[37] M. Urbakh and J. Klafter, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994).