Length Scale of Cooperativity in the Dynamic Glass Transition

M. Arndt,[1] R. Stannarius,[1] H. Groothues,[1] E. Hempel,[2] and F. Kremer[1]
[1]*Universität Leipzig, Fakultät für Physik,*
04103 Leipzig, Germany
[2]*Universität Halle, Fachbereich Physik,*
06099 Halle (Saale), Germany
(Received 31 March 1997)

The molecular dynamics in the glass transition of the “quasi”–van der Waals glass salol confined to nanopores (2.5, 5.0, and 7.5 nm) with lubricated inner surfaces is found to be faster (by up to 2 orders of magnitude) than in the bulk liquid. This effect of confinement is more pronounced for smaller pores. It reflects the cooperativity of molecular motions in the glass transition and enables its length scale to be determined quantitatively. [S0031-9007(97)04009-X]

PACS numbers: 64.70.Pf, 61.25.Em

Although the dynamic glass transition is an old problem of physics [1], it is still a challenging subject of interest from a scientific and technological point of view (for review see [2–5]). Recent research has extended the knowledge of the rich phenomenology of glassy systems but no unified theory is available at the moment. Next to free volume concepts [6] and mode coupling approaches [7], models that consider cooperativity are widely discussed [8–10]. The key idea of the latter is the existence of a length scale of cooperativity or correlation length ξ that increases with decreasing temperature [11]. It has been estimated to be a few nm in the vicinity of the calorimetric glass transition temperature [12].

A direct approach to prove the existence of a length scale involved in the dynamic glass transition is the investigation of the dynamic properties of liquids confined to distances of a few nm. Deviations from the bulk behavior should be observed if ξ reaches the size of the confining geometry. Such systems have attracted much interest from different points of view in recent years and have been addressed by a variety of experimental and theoretical approaches [13–18]. Especially nanoporous glasses have proven to be a successful tool for these studies [19–25]. It turns out in NMR [19,21], solvation dynamics [23], and dielectric relaxation experiments [20,22,25] that one observes a retarded layer of directly surface attached molecules and bulklike molecules inside the cavities. The interplay between these interfacial molecules and the bulklike molecules in the center of the pores can be described in terms of a dynamic exchange model [22,25]. A superposition of interface and volume effects is observed which cannot be interpreted straightforwardly in terms of cooperativity.

In order to investigate the predicted confinement effect without surface induced retardation effects it is necessary to neutralize the retarding influences of the surface attached molecules. For this aim we use nanoporous glasses with lubricated inner surfaces as confining environment. The dynamics of the low molecular weight glass-forming liquid salol (phenyl salicylate) confined to this system is studied by means of broadband dielectric spectroscopy (1×10^{-2}–1.8×10^{9} Hz).

Dielectric measurements are performed using a Solartron-Schlumberger frequency response analyzer FRA 1260 with a Novocontrol active sample cell BDC-S (1×10^{-2}–3×10^{6} Hz) and a Hewlett-Packard impedance analyzer HP 4291 A (1×10^{6}–1.8×10^{9} Hz). The sample temperatures are controlled with a nitrogen gas stream having a stability better than ±0.05 K. Details of the experimental setup may be found in Ref. [26]. Differential scanning calorimetry (DSC) measurements were carried out with a Perkin-Elmer series 7 thermal analysis system.

Reagent grade salol was obtained from Aldrich Chemical Company. Controlled porous glass from Geltech Inc. with specific pore sizes of 2.5, 5.0, and 7.5 nm and a narrow pore size distribution was used. According to a Brunauer, Emmett, and Teller (BET) analysis supplied by Geltech the data in order of increasing pore size are pore volume fraction 0.48, 0.63, and 0.70; and specific surface area 732, 522, and 367 $\mathrm{m}^2/\mathrm{cm}^3$. The pure silica porous glass slices used are disk shaped (diameter 10 mm, thickness 0.2 mm), so the outer surface is negligible compared to the huge inner surface. In order to remove water and other volatile impurities from the surface the porous glasses are evacuated to 10^{-5} mbar at 570 K for 24 h. After this procedure the samples are chemically treated inside the closed vacuum chamber using hexamethyldisilazane (Aldrich Chemical Company) for 25 min at 340 K and again evacuated for 24 h at 340 K. This treatment replaces the -OH groups on the glass surface with trimethylsilyl groups. We have confirmed this by means of IR spectroscopy. The pores are filled then with salol by capillary wetting during 48 h at 330 K. For that purpose the liquid is injected in the (closed) vacuum chamber by use of a syringe. After filling, both sides of the sample disks are covered with a thin (0.8 μm) aluminum foil to ensure a good contact to the electrodes of the sample capacitor.

0031-9007/97/79(11)/2077(4)$10.00 © 1997 The American Physical Society

Very recently, it has been demonstrated by means of dielectric hole burning experiments [27] that the dielectric data can be analyzed in terms of a relaxation time distribution of (spatially) distributed relaxators. We assume an ensemble of Debye relaxators with relaxation times τ and a distribution density $g(\log_{10}\tau)$. The imaginary part of the dielectric function is then given as

$$\epsilon'' = \epsilon_\infty + (\epsilon_{st} - \epsilon_\infty) \int \frac{g(\log_{10}\tau)}{1 + \omega^2\tau^2}\, d(\log_{10}\tau), \qquad (1)$$

where ϵ_{st} and ϵ_∞ denote the low and high frequency values of the permittivity. In order to obtain $g(\log_{10}\tau)$ the isothermal data of the dielectric loss ϵ'' are fitted to a superposition of Havriliak-Negami (HN) model functions [28] as illustrated in Fig. 1. The corresponding relaxation time distributions $g(\log_{10}\tau)$ as illustrated in the insets of Fig. 1 are calculated analytically from the HN-fit parameters. Identical results for $g(\log_{10}\tau)$ are obtained by applying an alternative fitting procedure based on a self-consistent regularization method [29].

Salol is known as a "quasi"–van der Waals glass-forming liquid because intramolecular H bonds are preferred [as they are sketched in Fig. 1(A)]. Figure 1 shows the dielectric loss curve of the bulk liquid at one selected temperature, together with the corresponding $g(\log_{10}\tau)$. One relaxation process is found which is connected with the dynamic glass transition [30]. In uncoated pores two additional loss processes are observed in the dielectric spectra [25]: a process which is connected with a Maxwell-Wagner polarization and an additional molecular relaxation process approximately 2 orders of magnitude slower than the dynamic glass transition [Fig. 1(B)]. This interfacial process is assigned to the motion of molecules that form H bonds to the surface of the pores. The two molecular processes are monitored in a bimodal relaxation time distribution $g(\log_{10}\tau)$.

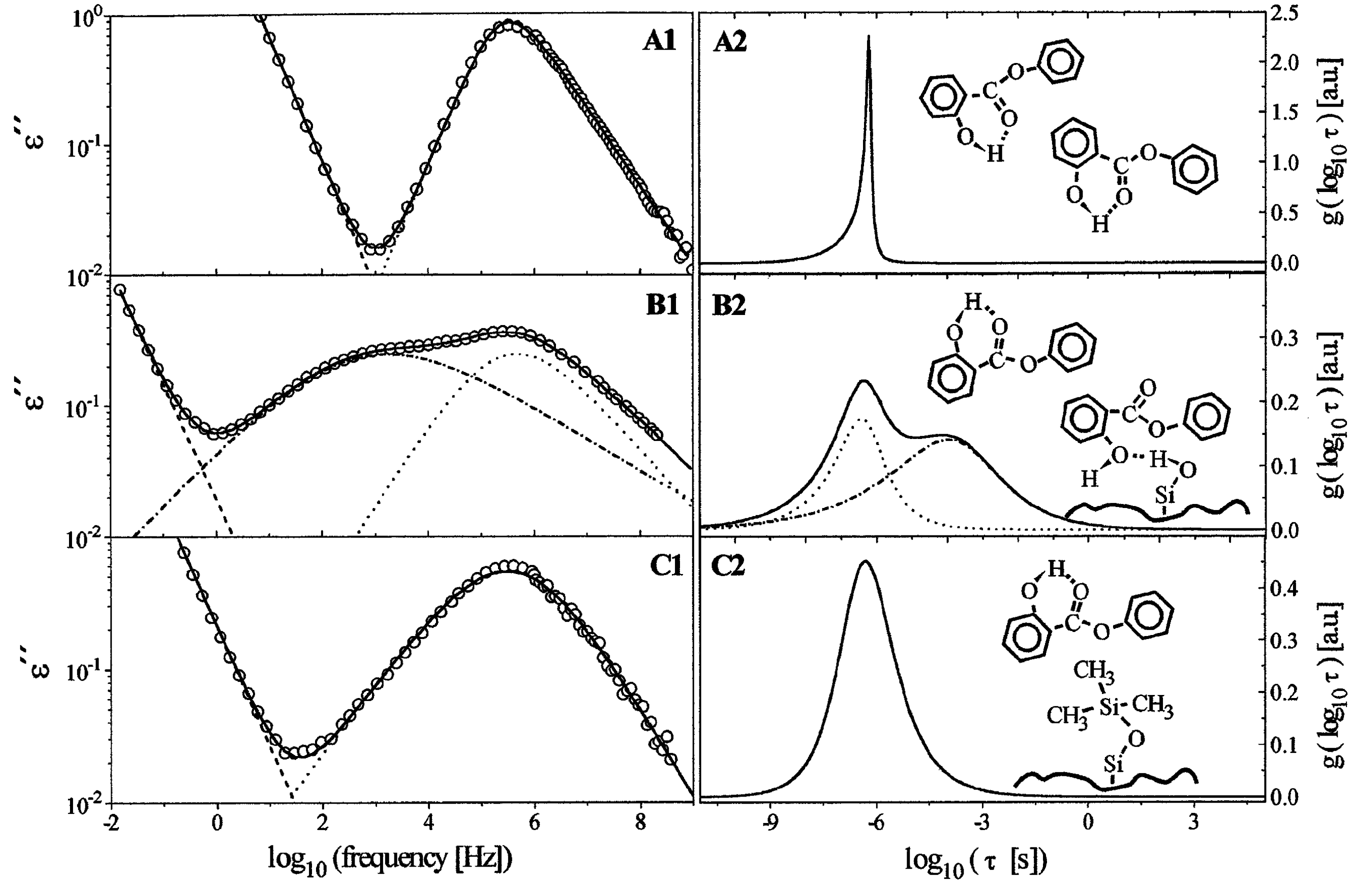

FIG. 1. Dielectric loss ϵ'' of salol at a temperature $T = 253$ K. The error of the measured data (○) is smaller than the size of the symbols. The dotted and dash-dotted lines indicate fits to the data according to Havriliak-Negami functions. The dashed lines correspond to conductivity contributions and loss processes caused by polarization effects. The plots on the right-hand side show the relaxation time distributions $g[\log_{10}(\tau)]$ that correspond to the relaxational processes. The sketches illustrate possible conformations of the molecules. (A)—bulk salol: The molecules form intramolecular H bonds (···), one relaxation process having the characteristic shape of $g[\log_{10}(\tau)]$ for a bulk glass-forming liquid is observed. (B)—salol confined to 7.5 nm uncoated pores: Salol molecules in the direct vicinity of the surface form H bonds (···) to the pore surface resulting in an additional interfacial relaxation process (dash-dotted lines) next to the relaxation of unbound molecules (dotted lines). The corresponding $g[\log_{10}(\tau)]$ has a bimodal shape (solid line). (C)—salol confined to 7.5 nm coated pores: The formation of H bonds is strongly suppressed. The resulting unimodal $g[\log_{10}(\tau)]$ is shifted to shorter relaxation times with respect to the bulk phase.

In the modified pores [Fig. 1(C)] the inner surface is covered with a hydrophobic coating so the formation of H bonds between liquid molecules and the pore surface is strongly hindered. This results in a complete suppression of the interfacial relaxation process. Figure 2 shows the relaxation time distribution of salol confined to the coated pores at different temperatures. At high temperatures $g(\log_{10}\tau)$ is broadened compared to the bulk relaxation due to various unspecific influences of the random confining material. With decreasing temperatures, $g(\log_{10}\tau)$ in the confined samples no longer follows the bulk curve but shifts to shorter relaxation times. This effect is more pronounced in smaller pores. The analysis of the dielectric strength of salol in the coated pores shows that the silane layer has a thickness of approximately 0.38 nm in all pore sizes.

We characterize the temperature behavior of the relaxation by the averaged relaxation time

$$\log_{10}\tau^* = \langle \log\tau\rangle_{\log_{10}\tau} = \frac{\int_{-\infty}^{+\infty}\log_{10}\tau\, g(\log_{10}\tau)\,d\log_{10}\tau}{\int_{-\infty}^{+\infty} g(\log_{10}\tau)\,d\log_{10}\tau}. \qquad (2)$$

The activation plot of the relaxation rate $1/\tau^*$ is compared for bulk and confined samples in Fig. 3. At high temperatures the relaxation rates of the confined liquids are identical to the bulk liquid in all pore sizes while with decreasing temperatures the relaxation rates in the confining geometry are shifted to higher frequencies compared to the bulk liquid; i.e., the glass temperature of the confined liquids is shifted to lower temperatures. This shift is more pronounced for smaller pores. A comparable effect is observed by means of DSC. The calorimetric glass temperature in the confining geometry is shifted 8, 11, and 15 K to lower temperatures in the 7.5, 5.0, and 2.5 nm pores, respectively (indicated by arrows in Fig. 3).

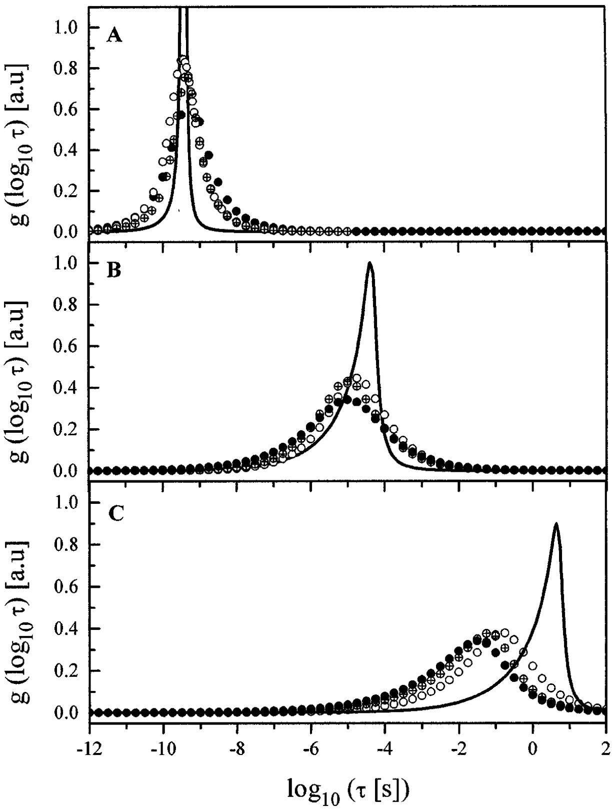

FIG. 2. Relaxation time distribution $g[\log_{10}(\tau)]$ for salol confined to 7.5 nm (○), 5.0 nm (⊕), 2.5 nm (●) pores with a hydrophobic coating and bulk salol (solid line) at different temperatures; (A) 305 K, (B) 243 K, (C) 223 K.

The confinement effect of relaxation rates being shorter in the confining geometry than in the bulk liquid can be unambiguously explained on the basis of the cooperativity of molecular reorientations in glass-forming van der Waals liquids: At high temperatures the range of cooperativity ξ is smaller than the diameter of the nanoporous restrictions. Hence no difference between the bulk and the confining geometry has to be expected. With decreasing temperature deviations from Arrhenius-type temperature dependence occur indicating the onset of cooperativity. The correlation length ξ increases until it becomes limited by the pore diameter ("hindered glass transition" [9]). Because of the lubricant coating of the inner surfaces the cooperatively rearranging molecules in the pores are not blocked and may reorient within the pore volume. In contrast, the reorientational dynamics in the bulk liquid is increasingly retarded due to the unhindered growth of ξ. This leads to a faster dynamics of the confined molecules compared to the bulk liquid.

Following the simple model described above the temperature dependence of the length scale of cooperativity can be estimated from the pore size dependence of the shift of the relaxation rate $1/\tau^*$. The relaxation rate starts to increase compared to the bulk rate when the length scale of cooperativity ξ reaches the size of the confining geometry. For the 2.5 nm pores deviations from the bulk rate are

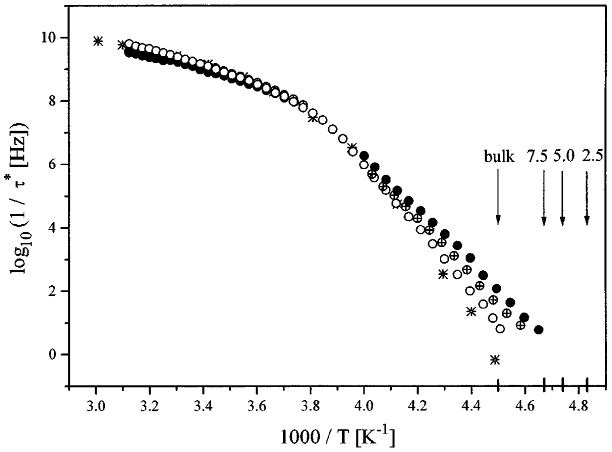

FIG. 3. Activation plot for salol confined to coated pores; 7.5 nm (○), 5.0 nm (⊕), 2.5 nm (●), and bulk salol (∗). The error of the data is smaller than the size of the symbols. The arrows indicate the calorimetric glass transition temperatures for the different pore sizes and bulk salol.

observed at 250 K. At lower temperatures even for salol in 7.5 nm pores a significant increase of the relaxation rate compared to bulk salol is observed so one can estimate the length scale of cooperativity to be greater than 7 nm in the vicinity of the calorimetric glass transition temperature.

In conclusion, we have presented results of broadband dielectric spectroscopy and differential scanning calorimetry of salol confined to nanopores with lubricated inner surfaces. Because of the lubricant coating, interface effects can be suppressed and confinement effects of the liquid in the restricted geometry become observable. The results can be consistently described in terms of cooperatively rearranging regions with dimensions growing with decreasing temperatures and reaching several nm diameter close to T_g.

Support by the *Deutsche Forschungsgemeinschaft* within the “SFB 294” and “SFB 416” is gratefully acknowledged.

[1] R. Kohlrausch, Pogg. Ann. Phys. **12**, 393 (1847).
[2] C. A. Angell, Science **267**, 1924 (1995).
[3] Special issue on *Relaxation in Complex Systems,* edited by K. L. Ngai and G. B. Wright [J. Non-Cryst. Solids **131-133** (1991)].
[4] Special issue on *Relaxation in Complex Systems,* edited by K. L. Ngai and G. B. Wright [J. Non-Cryst. Solids **172-174** (1994)].
[5] *Disorder Effects on Relaxational Processes,* edited by R. Richert and A. Blumen (Springer, Berlin, 1994).
[6] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959).
[7] E. Leutheuser, Phys. Rev. A **29**, 2765 (1984); W. Götze, in *Liquids, Freezing and Glass Transition,* edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991).
[8] D. Sappelt and J. Jäckle, J. Phys. A **26**, 7325 (1993).
[9] E. Donth, *Glasübergang* (Akademie Verlag, Berlin, 1981).
[10] T. R. Kirkpatrick and D. Tirumalai, Phys. Rev. A **40**, 1045 (1989).
[11] G. Adam and J. H. Gibbs, J. Chem. Phys. **28**, 373 (1965).
[12] E. W. Fischer, E. Donth, and W. Steffen, Phys. Rev. Lett. **68**, 2344 (1992).
[13] *Molecular Dynamics in Restricted Geometries,* edited by J. Klafter and J. M. Drake (John Wiley, New York, 1989).
[14] C. L. Jackson and G. B. McKenna, J. Chem. Phys. **93**, 9002 (1990).
[15] C. Schick and E. Donth, Phys. Scr. **43**, 423 (1991).
[16] *Dynamics in Small Confining Systems,* edited by J. M. Drake, J. Klafter, R. Kopelman, and D. D. Awschalom, MRS Symposia Proceedings No. 290 (Materials Research Society, Pittsburgh, 1993).
[17] *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).
[18] T. Fehr and H. Löwen, Phys. Rev. E **52**, 4016 (1995).
[19] G. Liu, Y. Li, and J. Jonas, J. Chem. Phys. **95**, 6892 (1991).
[20] J. Schüller, Yu. Mel’nichenko, R. Richert, and E. W. Fischer, Phys. Rev. Lett. **73**, 2224 (1994).
[21] S. Stapf, R. Kimmich, and R.-O. Seitter, Phys. Rev. Lett. **75**, 2855 (1995).
[22] R. Stannarius, F. Kremer, and M. Arndt, Phys. Rev. Lett. **75**, 4698 (1995).
[23] C. Streck, Yu. Mel’nichenko, and R. Richert, Phys. Rev. B **53**, 5341 (1996).
[24] R. Richert, Phys. Rev. B **54**, 15 762 (1996-II).
[25] M. Arndt, R. Stannarius, W. Gorbatschow, and F. Kremer, Phys. Rev. E **54**, 5377 (1996).
[26] F. Kremer *et al.*, Prog. Polym. Sci. **80**, 129 (1989).
[27] B. Schiener, R. Böhmer, A. Loidl, and R. V. Chamberlin, Science **274**, 752 (1996).
[28] S. Havriliak and S. Negami, J. Polym. Sci. C **14**, 99 (1966).
[29] H. Schäfer, E. Sternin, R. Stannarius, M. Arndt, and F. Kremer, Phys. Rev. Lett. **76**, 2177 (1996).
[30] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, Phys. Rev. Lett. **65**, 1108 (1990); G. Li, W. M. Du, A. Sakai, and H. Z. Cummins, Phys. Rev. A **46**, 3343 (1992).