# Glass Transition in Liquids: Two versus Three-Dimensional Confinement

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The molecular dynamics of glass-forming liquids is strongly affected by nm-scale confinements. Our dielectric data provide strong evidence both for the "cooperativity" concept and for the existence of two states (interfacial layer and volume liquid). With decreasing size of confinement the orientational relaxation associated with the glass transition becomes faster, and the glass transition temperature is lowered. These effects are stronger for 3D confined droplets than for 2D confined pores. However, the radius at which size effects cease, i.e., the cooperativity length, does not depend on the dimensionality of the confinement. [S0031-9007(98)05919-5]

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Confinement of liquids in geometries of mesoscopic dimensions gives rise to significant modifications of their structural and dynamic properties [1]. The investigation of confinement effects on the glass transition in glass-forming liquids is a challenging question of fundamental interest. It may provide a test of theories and models of the glass transition for which there is no generally accepted theory for the time being [2]. With the exception of the popular mode coupling theory [3], the existence of cooperatively rearranging regions (spheres of radius $\xi$) is a basic concept in several theories and models of the glass transition [4]. $\xi$, the "cooperativity" length or characteristic length of glass transition, increases with decreasing temperature. Close to the glass transition temperature $T_g$, $\xi$ can be indirectly estimated to be in the range of a few nanometers [2]. A direct consequence of the cooperativity concept is the existence of size effects [5]. Such effects should be expected for confined glass-forming liquids, if the cooperativity length becomes comparable to or larger than the confining length, and their experimental observation would yield $\xi$ most directly [5]. Differential scanning calorimetry (DSC), solvation dynamics measurements, and dielectric relaxation spectroscopy (DRS) have been used in recent years to study confinement effects on glass transition. Glass-forming liquids were two-dimensionally (2D) confined in controlled porous glasses (CPG) with pore radii ranging from a few to several nanometers; the results, however, are rather controversial [6–11]. Here we investigate both 2D and 3D confinement effects of the same liquids, i.e., for pores in CPG (2D) and droplets in butyl rubber (3D). We study the molecular orientational relaxation associated with the glass transition, i.e., relaxation frequency, shape of dielectric response, and glass transition temperature. We extrapolate the size at which the confinement effects cease and obtain an upper bound for the cooperativity length $\xi(T_g)$. Finally, our results for 3D and 2D confined glass-forming liquids are compared to those obtained with 1D confined thin polymeric and liquid crystal films recently [12–17].

In order to investigate confinement effects we take advantage of the broad frequency range covered by DRS. By means of a novel technique allowing temperature dependent calibration [18], we perform transmission measurements in the wide frequency range of $\nu = 5$ Hz–2 GHz and at temperatures from 100–300 K. Calibration standards and samples are placed in a shielded capacitorlike measurement cell.

Butyl rubber (BR) containing hydrophilic components [19] and CPG are the confinements used. In BR the liquid is confined in droplets (3D confinement). A diffusion process leads to the formation of these droplets, the size of which is limited by the counter pressure of the elastic matrix. With an increasing filling factor ($f = 0\%$–$30\%$), the droplet diameter increases from 7 to 11 nm as determined by means of small angle x-ray scattering [20]. The half-width of the respective particle size distribution is about one third of the mean diameter. The CPG used as 2D confinements were Gelsil from Geltech Inc. with specific pore sizes (diameters) of $d = 2.5$, 5.0, 7.5, and 20 nm. For comparisons we also show results obtained with Vycor glass (Corning) with a pore diameter of $d = 4.0$ nm. The glass-forming liquids chosen for this study are $N$-methyl-$\varepsilon$-caprolactan (NMEC), representing nonassociating liquids, and propylene glycol (PG), representing hydrogen bonded liquids. Details of the preparation of samples and of the measurements are given elsewhere [21,22].

In Fig. 1 we compare the dielectric response of bulk PG with that of PG confined in BR at 253 K (glass transition temperature for bulk PG, $T_g = 167$ K). The plot for bulk PG shows the $\alpha$ process associated with the glass transition. At low frequencies $\varepsilon'' \propto \nu^{-1}$ due to a dc conductivity ($\varepsilon'' = \sigma_{\mathrm{dc}}/\varepsilon_0\omega$, where $\varepsilon_0$ is the permittivity of free space, and $\omega = 2\pi\nu$). Also, the 2D confined PG exhibits such a dc contribution to the dielectric response, however, it does not appear in the 3D confinement, where nm droplets are completely surrounded by the insulating host. The plot for confined PG shows the $\alpha$ process

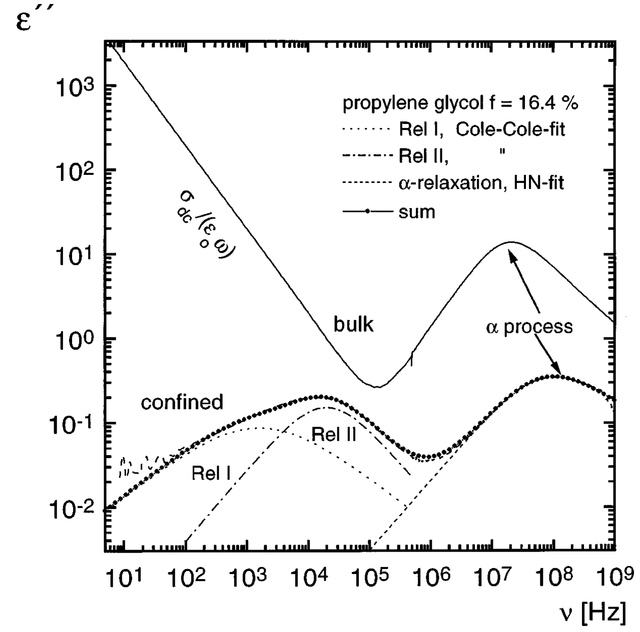

FIG. 1. Log-log plot of dielectric loss $\varepsilon''$ vs frequency $\nu$ for PG bulk and confined in BR (filling factor $f = 16.4\%$, mean droplet diameter $d = 10.2$ nm), both at 253 K.

and two additional relaxations at lower frequencies, Rel I and Rel II. This plot is typical for confined glass-forming liquids [7–10]. The two-shape-parameters Havriliak-Negami (HN) expression [9]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega/\omega_0)^{1-\alpha}]^\gamma} \tag{1}$$

gives satisfactory fits to the $\alpha$ process in both the bulk and the confined liquid. In this equation $\varepsilon^* = \varepsilon' - i\varepsilon''$ is the complex permittivity; $\Delta\varepsilon$ and $\omega_0$ are the intensity and the position of the relaxation process on the frequency scale, respectively. $\varepsilon_\infty = \varepsilon'(\omega \gg \omega_0)$, and $\alpha$ and $\gamma$ are shape parameters. In general, the one-shape-parameter symmetric Cole-Cole expression ($\gamma = 1$ in the HN expression) satisfactorily describes Rel I and Rel II. In agreement with previous work [8–10], Rel I and II are assigned to a slow liquid surface layer and to an interfacial Maxwell-Wagner-Sillars polarization, respectively. Support for this interpretation comes from Maxwell-Wagner-Sillars calculations for heterogeneous systems and from measurements on chemically modified and on partially filled CPG systems [9]. The observation of Rel I is in agreement with a two-states model, distinguishing between viscous surface layer and inner mobile layers (inner sphere). In addition, the relaxator strength $\Delta\varepsilon$ of the $\alpha$ process increases overlinearly with increasing $f$ (for details on these TSDC measurements on BR samples we refer to Ref. [22]). Also, this effect is expected within the two-states model, where the percentage of molecules belonging to the inner mobile sphere increases with increasing droplet size. As a direct consequence of this model our data provide strong evidence for, the $\alpha$ process refers only to the inner sphere, i.e., to dimensions smaller than the size of pores/droplets.

In the following we focus on the $\alpha$ process. Figure 2 shows the Arrhenius plot for bulk PG and for PG confined in Gelsil glasses. The relaxation frequency $\nu_0$ refers to the frequency where the maximum of the loss peak in $\varepsilon''$ appears. The lines represent fits of the Vogel-Fulcher-Tamman (VFT) expression to the experimental data,

$$\nu_0 = A \cdot \exp\left(-\frac{B}{T - T_0}\right), \tag{2}$$

with temperature-independent empirical parameters $A$, $B$, and $T_0$ [9]. In a 2D confinement of randomly oriented pores the observed effective relaxation frequencies can be shown to equal those of the confined liquid [23]. This does not hold for a 3D confinement, where the boundary conditions cause an altered field distribution that affects the effective $\nu_0$. In order to correct for this mixture effect we have evaluated the permittivity of the confined droplets, $\varepsilon_c$, using the Hanai-Bruggeman formula [24]: $(\varepsilon_m/\varepsilon_{\text{eff}})^{1/3} \cdot (\varepsilon_{\text{eff}} - \varepsilon_c)/(\varepsilon_m - \varepsilon_c) = 1 - f$, where $\varepsilon_{\text{eff}}$ and $\varepsilon_m$ denote the measured permittivity of the effective system and of the BR matrix, respectively. The obtained $\nu_0$ curves are similar to those of Fig. 2. We observe that at a fixed temperature, $\nu_0$ is significantly higher in the confined liquid than in the bulk one. For the same system, $\nu_0$ decreases with increasing size of confinement towards the bulk behavior. Moreover, the relaxation rates for bulk and confined liquids approach each other with increasing temperature, suggesting weakening and disappearance of confinement effects

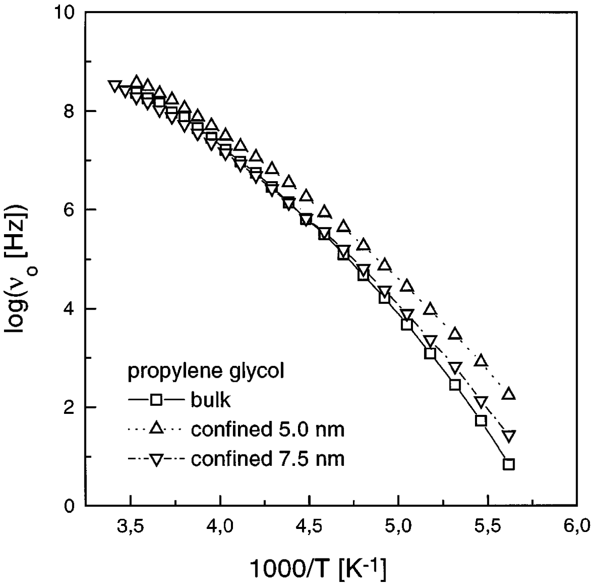

FIG. 2. Arrhenius plot (semilogarithmic plot of frequency of maximum dielectric loss, $\nu_0$, against reciprocal temperature, $1/T$) for the $\alpha$ process in PG bulk and PG confined in Gelsil glasses. The lines are VFT fits to the experimental data.

at temperatures far above $T_g$. These results can be understood on the basis of the cooperativity concept in the configurational entropy model of glass formation. Adam and Gibbs developed this model for a bulk system [4]. At high temperatures the cooperativity length $\xi$ is infinitesimally small. It increases with decreasing temperature and finally diverges for $T \rightarrow T_0$ as does the relaxation time $\tau = (2\pi\nu_0)^{-1}$ when the molecular processes slow down. At $T_0$ the cooperative region comprises the whole sample ($\xi = r_{\text{bulk}} = \infty$). In a confined system $\xi$ becomes comparable to the system size already at a higher temperature $T_r$, i.e., $r = \xi$ holds for all temperatures $T_r \geq T \geq T_0^{\text{conf}}$. All the molecules in the confined sample (e.g., the inner mobile layers, $r \leq d/2$) take part in the cooperative dynamics and will relax faster compared to bulk. Above $T_r$, $\xi$ is smaller than the size of the confined sample and decreases towards zero with increasing temperature [2,4]. Thus, with increasing system size or temperature, confinement effects weaken, and finally the dynamical behavior of the bulk system is observed (see Fig. 2).

Extrapolation of the Arrhenius plots to the relaxation time $\tau = 100$ s ($\nu_0 = \frac{1}{628}$ Hz) allows one to determine $T_g$ [7–10]. Since the confined liquids relax faster (see above), they have to be cooled to lower temperatures in order to slow down their relaxation. Figure 3 shows $\Delta T_g = T_g(\text{bulk}) - T_g(\text{confined})$ vs size of confinement $d$ for PG in BR and in CPG. $T_g$ is lower in the confined liquid, and the shift increases with decreasing $d$. For the same $d$, $\Delta T_g$ is larger in BR (3D) than in CPG (2D). For both systems $\Delta T_g$ becomes zero at about $d = 10$–$12$ nm. According to the above explanations, the confinement effects are expected to disappear when $\xi \leq r \leq d/2$, i.e., from our experimental data we obtain an upper bound for the cooperatively length $\xi(T_g^{\text{bulk}}) \leq 5$–$6$ nm. Since $\xi$ is a characteristic length of the glass-forming liquid, it does not depend on the dimensionality of the confinement. Similar results were obtained with NMEC, the main differences being that (i) $\Delta T_g$ vanishes at about 20–25 nm [corresponding to $\xi(T_g^{\text{bulk}}) \leq 10$–$12.5$ nm] and that (ii) the decrease of $T_g$ with decreasing size of confinement is smaller. For comparison, dielectric measurements on salol confined in Gelsil yielded $\xi(T_g^{\text{bulk}}) > 7$ nm [10]. TSDC measurements on NMEC in Vycor glass (both native and treated with hexamethyldisilazane) show that $\Delta T_g$ is not affected by surface modification [25], so that the lowering of $T_g$ is a pure confinement effect [6,9].

Similar shifts of $T_g$ to lower temperatures have been measured by DSC in several liquids confined in CPG. They have been assigned to a faster relaxation due to a lower density of the liquid in the pores [6]. This might be conceivable in systems where already existing cavities are partially filled. However, a molecular diffusion process leads to the formation of our 3D confined droplets [19]. They arise against the counter pressure of the elastic rubber matrix so that a reduction of the density can be excluded. In addition, the relaxation times of confined and bulk liquid become equal at high temperatures far above $T_g$ (see Fig. 2). Thus, neither the 2D nor the 3D confined liquid exhibits a noticeably reduced density. On the other hand, DSC measurements on liquids confined in microemulsions [26] and hydrogels [27] show a significant broadening of the glass transition [6] but no shift of $T_g$ to lower temperatures as compared to bulk liquids. Microemulsions represent an interesting 3D confinement, but possibly there may be no temperature shift because of strong hydrophilic interaction. Small shifts to both higher and lower temperatures have been reported by means of DRS in several liquids confined in CPG [7–10].

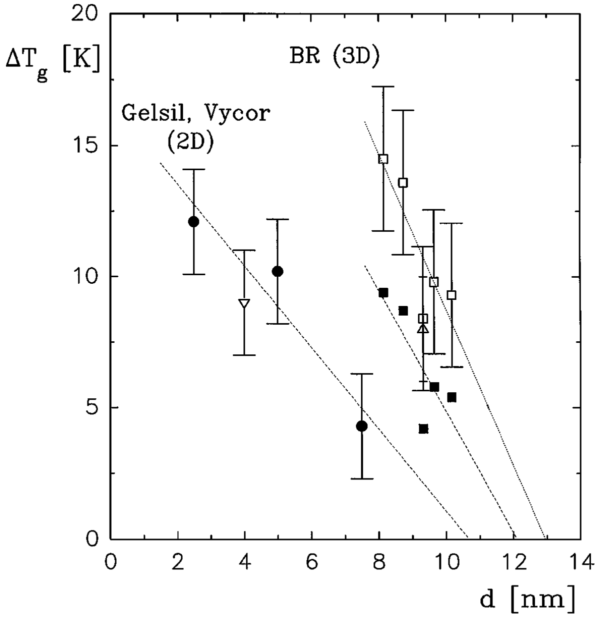

FIG. 3. Glass transition temperature depression, $\Delta T_g = T_g(\text{bulk}) - T_g(\text{confined})$ vs size of confinement (nominal pore/droplet diameter $d$) for PG in BR and in CPG. The half-width of the droplet size distribution in BR is FWHM $\simeq \frac{1}{3}d$. For the 3D confined liquid both the measured effective values (open squares) and the results of an effective medium analysis (filled squares) are displayed (see text). For the 2D confinement the effective values equal those of the confined liquid. $\triangle$ and $\nabla$ denote TSDC data for PG in BR and in Vycor glass, respectively (thermally stimulated depolarization currents, see Ref. [7]). Vertical bars indicate experimental errors. The lines are to guide the eyes.

It is interesting to compare our results on 2D and 3D confined liquids with those obtained with 1D confined polymers [12–16]. We expect confinement effects in 1D to be less strong. As a consequence, they are more easily suppressed or even overcompensated by other mechanisms. Several experimental techniques have been used to measure glass transition properties of thin polymeric films, usually deposited on a substrate. Depending on film thickness and on substrate material, shifts of $T_g$ to both lower [12,13] and higher [13,14] temperatures have been measured. Confinement effects, polymer-substrate interactions, and the presence of a free surface (as well as density reduction in the film [12]) were used to explain the observed changes of $T_g$. In fact, strong polymer-substrate interactions extending deep into the polymer sample can overcompensate pure confinement effects and may be responsible for $T_g$ shifts to higher temperatures. Measurements on freely standing polystyrene films, however, show that, compared to bulk, $T_g$ decreases linearly with decreasing film thickness [15]. With respect to 1D confinement and substrate interactions it is interesting to mention dielectric and DSC studies on semicrystalline poly(ethylene terephtalate), where amorphous regions are 1D confined by crystalline lamellae [28,29]. The results were discussed within the concept of cooperativity and provided estimates of the cooperativity length $\xi$ [29].

A commonly observed feature of confined liquids and polymers is that, independent of the measured physical property, the response at $T_g$ becomes broader compared to bulk [6–10,16,26–29]. Interestingly, this effect has also been observed for Se confined in zeolithes [30]. Our studies show that two parameters are necessary to describe the shape of the dielectric response at $T_g$, i.e., $\alpha$ and $\gamma$ in the HN expression Eq. (1) [31]. The asymmetric form of the response (different slopes at frequencies below and above the peak frequency $\nu_0$ in Fig. 1), typical for the bulk liquid [31], is observed also with the liquids confined in BR, whereas a clear shift towards symmetric response is observed with liquids confined in CPG. The latter resembles the behavior of semicrystalline polymers, a point which deserves further investigation [32].

Summarizing, our results show that the orientational relaxation of the molecules associated with the glass transition becomes faster, and $T_g$ shifts to lower temperatures when glass-forming liquids are confined in mesoscopic 2D and 3D volumes. Confinement effects are stronger in 3D than in 2D confinement and disappear with increasing temperature or size. They can be understood on the basis of the cooperativity concept for the glass transition [4], and they are in qualitative agreement with results of computer simulations [33] and with theoretical predictions [34]. The overall response of the liquid is described by a two-states model, i.e., the aforementioned effects refer to the inner mobile layers. The radius for which these pure confinement effects disappear is an upper bound for the cooperativity length. For PG, a hydrogen bonded liquid, we obtain $\xi(T_g^{\mathrm{bulk}}) \leq 5\text{–}6$ nm independent of the dimensionality of confinement. For NMEC, a nonassociating liquid, the decrease of $T_g$ with decreasing size of confinement is smaller and $\xi(T_g^{\mathrm{bulk}}) \leq 10\text{–}12.5$ nm. The two-states model must be quantitatively worked out, before these and similar measurements are used to evaluate more accurately the cooperativity length.

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