Molecular dynamics in thin glassy films

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In this Chapter we present a study of orientational relaxation dynamics of thin films of the glass-former [B] (shown in Fig. 2.1) as a function of temperature and film thickness. The relaxation is probed by second-harmonic generation (SHG) after release of a poling electric field. From the measured decays of the effective normalised second-order susceptibility and their fitting with a stretched exponential we can determine the distribution of relaxation times in the system. As temperature decreases from above the glass transition, we observe that the width of the distribution first increases under confinement, but that deeper in the glassy state, confinement has no effect anymore on the dynamics.

6.1 Introduction

From the measurements performed with x-ray reflectivity on thin films of glass formers, presented in Chap. 3, we have seen that by restricting a glass former into a thin film, the glass transition significantly widens. We have interpreted this as originating from an increase of the inhomogeneity of the dynamics in the system.
To obtain a direct evidence for the increase in inhomogeneity under confinement and study in detail how confinement affects the dynamics of the system, we have examined the reorientation dynamics of glass-former [B] (see Fig. 2.1) in thin films using second-harmonic generation measurements.

Other glassy systems have been studied with this technique [62, 126, 135, 145, 146], most of them being polymeric materials. In [126] the measurements probe the reorientation dynamics of a chromophore that is either dissolved in the hosting material or attached to the polymer main chain by a flexible spacer. The interest in these non-linear optical polymer comes from their potential technological applications as inexpensive alternatives to inorganic non-linear optical crystals and for several new applications, as for example optical storage or electro-optical devices.

In one of the above mentioned works on side-chain polymer [62], the effect of confinement was studied in thin supported films as a function of temperature. It was found that, at all temperatures, the average relaxation time is essentially independent of the film thickness, while the width of the distribution of the relaxation times increases as thickness decreases. The widening of the distribution was however found to be the same over the whole temperature range considered ($T_g - 13^\circ C < T < T_g + 25^\circ C$).

We have used a similar method to study the dynamics in thin films of compound [B]. The principle of the experiment is the following. The films to be studied are first brought in the liquid phase and a strong DC poling field $E_p$ is then switched on. This field tends to align the dipoles carried by the side-groups of compound [B] along the direction of the field (Fig. 6.1).

After sufficient time to reach the equilibrium orientation, the films are cooled down at the desired temperature holding the poling field on. In this state, the film generates a second-harmonic signal for a s-in-s-out polarisation configuration (see Sec. 4.1.2). By release of the field (see Fig. 6.1) at time $t = 0$ the field-induced orientational order disappears in the course of time by the randomisation of the dipoles orientation. This leads to a decrease of the SH signal to zero. So the reorientation dynamics of the system can be followed by measuring the SH signal $I_{ss}$. The square root of the $I_{ss}$ is directly proportional to the degree of polar ordering in the system through the effective polarisability ($\chi_{ss}$) of the film (see Eq. 4.11). The measured $\chi_{ss}(t)$ as a function of time is normalised to the value before the switching off the poling field ($\chi_{ss}(0)$). The resulting normalised second-order susceptibility is fitted using the phenomenological stretched exponential response function (KWW
Figure 6.1: Schematic representation of the orientation order of the polar branches in the glass former with applied poling field (left) and after removal of the field and complete relaxation (right). The poling field $E_Y$ is perpendicular to the optical plane (XZ) defined by the incident and SH beams (see also Fig. 4.1)

law Eq. 1.9):

$$\chi_{NO}^{(2)}(t) = \chi^{(2)}(t) = e^{-(t/\tau)\alpha}$$ (6.1)

The relaxation functions are determined over a range of 11 orders of magnitudes in time from 1 $\mu$sec onwards. The ability of characterising reorientation dynamics over a wide range of time scales is crucial because relaxation can occur, as shown in Sect. 5.4, within 1 sec after switching off the DC field and because to measure the decay accurately, it must be measured over a wide range of times.

With the above measurement method, the state from which the relaxation starts is determined by the applied poling field. For the range of poling fields we have used, $\chi_{ss}(0)$ is proportional to the field strength [62, 147]. In principle, the measured relaxation times can be expected to depend on the degree of order of the starting state of the relaxation, thus on $E_p$ [128]. We have not studied this dependence and have only one value of $E_p$. 
Figure 6.2: Schematic representation of a substrate with gold electrodes. The DC external field is provided by a grounded high voltage power supply. The dependence of the electric field on the position inside the gap is shown at the top.

6.2 Experimental procedure

Thin films of compound [B] represented in Fig. 2.1 were deposited by spin coating onto a fused quartz substrate following the procedure described in Chap. 2. To be able to apply an electric field parallel to the substrate, the quartz plates were first patterned with two planar electrodes separated by a gap $d$ of 1 mm. The electrodes were obtained by first depositing a thin (10 nm) layer of chromium, which has a high affinity for silica and then depositing a second thick (100 nm) gold layer. Both depositions were made by standard chemical vapor deposition\(^1\). With the gold coating we obtained substrates with a high chemical resistance to the cleaning process with bi-chromate sulfuric acid solution (see Sec. 2.4.1). The quality and thickness of the electrodes has been verified with atomic force microscopy.

\(^1\)We kindly thank M.M. Groeneveld from University of Amsterdam for metals depositions
A high DC electric field was applied between the two electrodes as shown in Fig. 6.2. For poling the films, we used a constant voltage $V$ of 1.9 kV. The electric field produced in the gap is perpendicular to the electrode edges and parallel to the substrate surface. The intensity profile of this field depends on the distance from the edges [148] (see Fig. 6.2). In the middle of the gap the electric field is minimum and equal to $E_p = \frac{2V}{\pi d}$, which corresponds to $1.2 \cdot 10^6$ V/m. Around this minimum the field is constant within 1% in a region of width $d/5 = 200 \mu m$ in our case. This width is sufficiently large for our measurements, which are all performed with a projected laser beam area of $\sim 100 \mu m$ in diameter. We assume therefore that the electric field is uniform in the probed surface area. As seen in Sect. 4, the degree of polar ordering induced by the poling field is proportional to the applied field. Therefore a higher field is expected to increase the ordering and the initial SH signal before the field is switched off. Nevertheless we have to limit the applied voltage to 1.9 kV because higher fields cause arching between the two electrodes, which destroys the samples. The high-voltage power supply limited the current during the transient regime just after switching the electric field on or off to 10 mA.

Samples were thermally treated following the procedure schematically presented in Fig 6.3. To eliminate the solvent from the deposited films, samples were annealed
first at 45 °C for 5 hours. They were then heated above the glass transition to 120 °C where they were kept for at least 15 minutes. After switching on the external field the temperature was brought to the desired value and then kept constant during the experiment. All temperature ramps were conducted at 0.25 Kmin⁻¹. To facilitate solvent removal and provide a clean atmosphere, the sample chamber was fluxed continuously with dry nitrogen.

The second-harmonic signal was measured following the protocol described in detail in Chap. 5. The optical setup is shown in Fig. 4.4. In the experiments reported in this Chapter, we have set the applied electric field and the polarisations of the in-coming and out-going waves perpendicular to the incident plane of the laser light (see Fig. 6.1 and Sec. 4.1.3).

6.3 Results

We have examined the dependence of the reorientation dynamics as a function of two parameters: temperature and film thickness. In the following, we first present the results concerning the temperature dependence of the dynamics in a thick film (as-spun thickness \( h_0 = 116 \) nm). From the thermal expansivity measurements we have presented in Chap. 3, we expect a bulk-like behaviour for the molecular dynamics of such a thick film. We can therefore compare our dynamic measurements with the expected behaviour around the glass transition temperature of a bulk glassy system.

In the second part of this Section, we examine how the dynamics at different temperatures varies as the film thickness decreases. From the broadening of the glass transition we have reported in Chap. 3, which is a sign of an increased inhomogeneity of the film, we expect a broadening of the distribution of the relaxation times as the film thickness decreases.

6.3.1 Temperature-dependence of relaxation dynamics

The decay of the SH signal as a function of time was collected for several temperatures ranging from 130 °C to 60 °C. Our temperature control unit did not allow us to reach to high temperatures, excluding measurements far into the liquid phase.

In Fig. 6.4 we plot the time dependence of the effective non-linear susceptibility \( \chi_{ss} \) normalised to its value before the poling field is switched off at time \( t = 0 \), for a 116 nm-thick film. We show for clarity the results only for the temperatures just below (100 °C) the nominal bulk glass transition temperature determined by DSC \( (T_g = 106 \) °C) and deep into the glass phase (60 °C). From the observed decays it is clear that any contribution to \( \chi_{ss} \) from electric-field-induced second-harmonic
6.3 Results

Figure 6.4: Normalised second-order susceptibility vs. time for a 116 nm-thick film (as-spun thickness) at (○) 60 °C ($T_g - 46$) and (△) 100 °C ($T_g - 6$). Solid lines represent the best mean-square fit using Eq. 6.1.

generation (see Sect. 5.4) can be neglected. Indeed, for all temperatures, the SH signal does not decrease for several decades in time. A possible contribution of EFISH would result in an immediate jump of the signal to a lower value, as fast as the poling field $E_p$ drops to zero ($\sim 100$ ns, see Sect. 5.2.1). We conclude then, that the observed decays have to associate solely to reorientation dynamics of the non-linearly polarisable units.

Data are fitted with the stretched-exponential KWW law given by Eq. 6.1. The characteristic time $\tau$ and the stretch exponent $\beta$ obtained at the different temperatures are given in Tab. 6.1. From the values of $\beta$, it is obvious that the relaxation process is highly non-exponential.

Another way to characterise the dynamic behaviour of the system is to calculate an average reorientation time $\langle \tau \rangle$ as is generally done for polymer systems from dynamic optical or dielectric measurements [32, 33, 34, 92, 135]:

$$\langle \tau \rangle = \int_0^\infty \exp \left[ - \left( \frac{t}{\tau} \right)^\beta \right] dt = \frac{\tau \Gamma (1/\beta)}{\beta}$$

where $\Gamma$ is the gamma function (Tab. 6.1). For $\beta = 1$ (single exponential), $\langle \tau \rangle$ is equal to $\tau$. For all temperatures $\langle \tau \rangle$ is rather large. Even for the highest temperature ($T = 120^\circ C = T_g + 14^\circ C$) the average relaxation time lies above the value generally
Table 6.1: Values of the characteristic time $\tau$ and stretch exponent $\beta$ obtained by fitting the experimental relaxation with Eq. 6.1 and average relaxation $\langle \tau \rangle$ time calculated with Eq. 6.2, for the different temperatures considered for a 116 nm-thick film.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\tau$ (sec)</th>
<th>$\beta$</th>
<th>$\langle \tau \rangle$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.46 -10^6</td>
<td>0.26</td>
<td>29 -10^6</td>
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<tr>
<td>80</td>
<td>36 -10^3</td>
<td>0.32</td>
<td>250 -10^3</td>
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<td>90</td>
<td>16 -10^3</td>
<td>0.28</td>
<td>220 -10^3</td>
</tr>
<tr>
<td>100</td>
<td>1.1 -10^3</td>
<td>0.34</td>
<td>6.2 -10^3</td>
</tr>
<tr>
<td>120</td>
<td>160</td>
<td>0.31</td>
<td>1.24 -10^3</td>
</tr>
</tbody>
</table>

associated to the macroscopic glass transition $\langle \tau \rangle_{T_g} = 100$ sec.

The values of $\beta$ exhibit little temperature dependence. We saw in Sec. 1.3.2 that the stretch exponent $\beta$ is a measure of the width of the distribution of the relaxation times in the film: when $\beta$ decreases, the width of the distribution becomes larger.

To visualise how the distribution of relaxation times varies with the temperature, we have calculated this distribution using the following procedure [139, 149]. We consider the stretched-exponential response function (Eq. 6.1) as being a sum of exponential relaxations (see Eq. 1.11):

$$\chi^{(2)}_{NO}(t) = \sum_i g_i e^{-(t/\tau_i)}.$$  \hspace{1cm} (6.3)

The distribution of relaxation times can then be defined by a discrete distribution [150]:

$$G(\tau) = \sum_i g_i(\tau_i) \delta(\tau - \tau_i)$$ \hspace{1cm} (6.4)

where $g_i$ are the weights of the delta functions composing the distribution. $G(\tau)$ can be calculated numerically using a recursive computer algorithm [149].

In Fig. 6.5 we present the distribution of relaxation times $G(\tau)$ calculated\(^2\) from the fitting parameters of the real-time relaxation decays listed in Tab 6.1. The measured relaxation decays at low temperatures do not decay to 0 at the largest experimental time (Fig. 6.4). Calculating distribution of relaxation times using then

\(^2\)We thank D. Moroni (UvA) for writing the code for the computer algorithm and for running the calculations.
high characteristic time $\tau$ evaluated with the KWW fitting law (Eq. 6.1) introduces weights $g_i$ for times longer than the measured ones. Thus the contributions to the distribution function at times $\log(\tau) > 6$ have to be taken as purely a result of the computation but not strictly related to the experimental evidence. These calculations confirm the trend indicate by Tab 6.1 for the average relaxation time and the width of the distribution. For the considered film thickness, the width of the distribution does not show a particular trend at temperatures larger than 80 °C. Only at the lowest temperature measured (60 °C) a slight widening of the distribution is visible. When temperature increases, the peaks of the distribution move from long to short times by almost four orders of magnitude in time in the explored temperature window. Note that the characteristic time $\tau$ corresponds approximately to the maximum of the distribution, while the average calculated with Eq. 6.2 is equal to the average calculated from the distribution $G(\tau)$. This confirms the consistency of our data analysis.

The wide distributions of relaxation times shown in Fig. 6.5 confirms the fact that to make an accurate evaluation of the distribution $G(\tau)$, experimental relaxation decays covering many orders of magnitude in time are needed. Indeed, the relaxation time distributions cover 14 orders of magnitude in time ($10^{-4} - 10^{10}$ sec) for the studied range of temperatures.
6.3.2 Size-dependence of the relaxation dynamics

To investigate the effect of confinement we carried the same relaxation experiment as presented in Sec. 6.3.1 for films with a lower thickness. In Fig. 6.6 we show the signal decay measured at 120 °C and 60 °C for a 17 nm-thick film (as-spun thickness).

The decay measured at 120 °C presents an interesting feature: the SH signal exhibits a first decay in the short time domain. The use of the KWW equation to fit the data appears to be only a first approximation. The data are not properly described in the msec time window and, a general double stretched exponential law would be more suitable. It seems that, under our experimental conditions, it is possible to discriminate different relaxation processes. Measuring relaxation dynamics around and below the bulk glass transition means in principle probing the α relaxation process (see Chap. 1). Nevertheless, at high temperatures, the α process does not necessary screen all other faster processes (see Fig. 1.2). These modes observed at high temperature can have different origins. One possible interpretation is to identify in this mode the fast β process, related to a local mobility (see Sec. 1.2).

Given the small contribution of possible fast processes (observed only at high T), we fitted in first approximation all decays with a single stretched exponential function using Eq. 6.1. Fitting with a double stretched exponential the data at high T hardly changes the parameters for the α-process. Resulting fitting parameters...
Figure 6.7: Distribution of relaxation times for a 17 nm-thick film from the parameters in Tab. 6.2: 60 °C (○), 90 °C (●), 100 °C (△), 110 °C (□), 120 °C (●) and 130 °C (▽). The solid lines are a guide to the eye.

\[
\tau \text{ and } \beta \text{ together with the calculated average relaxation time } \langle \tau \rangle \text{ are reported in Tab. 6.2. The corresponding distribution of relaxation times } G(\tau) \text{ are plotted in Fig. 6.7.}
\]

The distribution obtained in the glass phase are slightly wider than the ones obtained with the 116 nm-thick film. They also show a clear increase of the exponential character (increase of \( \beta \)) for the highest temperature measured, which results in a sharper distribution of relaxation times for \( T=130 \, ^\circ \text{C} \) in Fig. 6.7. Note that for this temperature the distribution function moves towards shorter times and \( \langle \tau \rangle < 100 \) sec.

To increase the effect of confinement, we repeated the above experiments with an even thinner film. We have chosen a film thickness similar to that of the thinnest film studied by x-rays reflectivity, namely a 10 nm-thick (as-spun) film. The only difference with the thicker films was that the annealing temperature was 110 °C instead of 120 °C (see Fig. 6.3), due to the instability of the film at higher temperatures (see Sec. 3.2.2). Fig. 6.8 shows the relaxation for the 10 nm-thick film at 90 °C and 110 °C. For this film thickness experimental data are in general of lower quality with a higher scattering of the points. This is mainly due to the low value of the SH signal intensity in the oriented state at \( t < 0 \). Analysing ultra-thin films reduces the number of molecules \( (N_s) \) probed by the input laser beam, reducing the sensitivity
Figure 6.8: $\chi_{NO}^{(2)}$ vs. time for a 10 nm-thick film (as-spun thickness) at 90 °C ($T_g-16$) (○) and °C ($T_g+4$) (□) 110. Solid lines represent the best mean-square fit using Eq. 6.1.

Figure 6.9: Distribution of relaxation times for a 10 nm-thick film from the parameters in Tab. 6.2: 60 °C (○), 90 °C (○), 100 °C (△) and 110 °C (□). The solid lines are a guide to the eye.
6.4 Discussion and conclusion

We summarise our results on the dynamics of thin films by plotting the temperature dependence of the average relaxation time $\langle \tau \rangle$ (Fig. 6.11) and the stretch exponent $\beta$ (Fig. 6.12) for all the films we have measured.

The first important question arising from these measurements is whether the measured reorientation dynamics of the non-linearly polarisable groups is coupled with the glassy dynamics of the molecules as a whole.

An element of answer can be found in the values of $\beta$ for the thickest film exhibiting a bulk-like behaviour. The values are rather scattered but remain in

<table>
<thead>
<tr>
<th>$h(0)$</th>
<th>T ($^\circ$C)</th>
<th>$\tau$ (sec)</th>
<th>$\beta$</th>
<th>$\langle \tau \rangle$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17 nm</td>
<td>60</td>
<td>$1.5 \cdot 10^6$</td>
<td>0.24</td>
<td>$43 \cdot 10^6$</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>$170 \cdot 10^3$</td>
<td>0.21</td>
<td>$15 \cdot 10^6$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>$38 \cdot 10^3$</td>
<td>0.20</td>
<td>$3.7 \cdot 10^6$</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>$2.9 \cdot 10^3$</td>
<td>0.24</td>
<td>$93 \cdot 10^3$</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>160</td>
<td>0.32</td>
<td>$1.1 \cdot 10^3$</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>39</td>
<td>0.56</td>
<td>65</td>
</tr>
<tr>
<td>10 nm</td>
<td>60</td>
<td>$6 \cdot 10^6$</td>
<td>0.26</td>
<td>$110 \cdot 10^6$</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>$5.9 \cdot 10^3$</td>
<td>0.22</td>
<td>$320 \cdot 10^3$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>$2.8 \cdot 10^3$</td>
<td>0.21</td>
<td>$190 \cdot 10^3$</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>61</td>
<td>0.28</td>
<td>$7.8 \cdot 10^3$</td>
</tr>
</tbody>
</table>

Table 6.2: The same as Tab. 6.1 for a 17nm- and 10 nm-thick film.
the interval 0.25-0.35. If we take for the value at \( T_g \) the average of the measured values, we obtain \( \beta(T_g) \sim 0.30 \), which is close to the value for bulk poly(propylene glycol) (see Tab. 2.1). This can be expected from the fact that compound [B] carries four hydroxy groups per molecules and should belong to the most fragile hydrogen-bonded glass-formers. We unfortunately lack enough data at temperatures larger than \( T_g \) to determine the fragility \( m \). Another element of answer can be found in the Arrhenius plot (see Fig. 1.2) of \( \langle \tau \rangle \) as a function of the inverse temperature (Fig. 6.11). \( \langle \tau \rangle \) increases exponentially with \( 1/T \) as expected for a glassy material.

From the above, we can conclude that the reorientation dynamics we observe, corresponds to what is expected for a glass-former. The reorientation of the non-linearly polarisable groups is probably strongly coupled to that of the rest of the molecules, since the flexible spacer between the central rigid group and the polarisable side-groups contains only three atoms (see Fig 2.1). The fact that the reorientation dynamics of side-groups is coupled to the \( \alpha \)-relaxation process has also been demonstrated in a polymeric system with a flexible spacer of four atoms [139]. The same coupling has also been demonstrated for chromophores dissolved in a polymer without any covalent bonding with the polymer chains [135]. However this could be due to strong steric interactions between the chromophores and the chains, which are less likely to take place with a low-molecular weight glass-former as compound [B].

The dynamic behaviour we have observed deviates, however, from the expectations on two points. The first one is that even at temperatures above the bulk glass transition temperature \( T_g \) (as measured by DSC), the average relaxation time \( \langle \tau \rangle \) is longer than the one corresponding to the standard definition of \( T_g \): \( \langle \tau \rangle T_g = 100 \) sec. We saw in Chap. 3 that there is no evident variation of \( T_g \) under confinement. So the high values of \( \langle \tau \rangle \) cannot be explained by an increase of \( T_g \).

The origin of the long relaxation times might be related to the fact that the non-polarisable side-groups are polar mesogenic units. Ordinary non-glassy liquid crystals based on the same cyanobiphenyl units exhibits also a very slow reorientation dynamics in ultra-thin films (thickness below 10 nm) [141, 142, 144]. The reason for this slow dynamics is not clear. One possible explanation could be the electrostatic correlation between the dipoles carried by the cyanobiphenyl groups [143] (see also Sec. 5.4), although no direct evidence for such a correlated dynamics has been found yet.

The second unexpected feature in the observed dynamics (in particular in thick films) is the fact that the time dependence of the observed relaxations remains strongly stretched at temperatures above the bulk glass transition temperature. We
Discussion and conclusion

Figure 6.10: Distribution of relaxation times at 100 °C ($T_g$-6) for a 10 nm (□), 17 nm (+), 25 nm (○), 41 nm (×), 70 nm (○) and a 116 nm (△) thick films. The solid lines are a guide to the eye.

could expect an increase of the stretch exponent $\beta$ indicating a narrowing of the distribution as temperature increases. The fact that we do not observe this narrowing might simply be due to the limited range of temperature that we can explore above $T_g$. When we have managed to performed experiments at slightly high temperatures (130 °C with the 17 nm-thick film), we indeed observed an increase of $\beta$. Similar results were found on polymer systems [135, 136], where $\beta$ does not vary significantly in the glassy phase, while for temperature above $T_g$, $\beta$ was increasing with temperature.

Our experimental results allow a discussion on the main purpose of our study, namely the effect of confinement on the dynamics of glass-formers. Let us start with the average relaxation time $\langle \tau \rangle$ (Fig. 6.11). At high and low temperature, $\langle \tau \rangle$ hardly depends on the film thickness. At intermediate temperatures around $T_g$, there is a large scatter without a specific variation with film thickness. This is likely due to the limited relevance of $\langle \tau \rangle$ when the distribution of relaxation times $G(\tau)$ becomes very wide. Variations in the actual shape of the distribution can have a strong influence on $\langle \tau \rangle$ while the location of the maximum of $G(\tau)$ hardly moves. This can be seen in the plot of the distribution of relaxation times for different film thickness at $T = 100$ °C (Fig. 6.10). Except for the thickness of 17 nm, maxima hardly are shifted with respect to one another (less than one order of magnitude),
Figure 6.11: *Average relaxation time* \( \langle \tau \rangle \) *vs. inverse temperature* for 10 nm (□), 17 nm (+), 25nm (○), 41 nm (×), 70 nm (○) and 116 nm (△) thick films.

Figure 6.12: *Stretch exponent* \( \beta \) *vs. temperature* for 10 nm (□), 17 nm (+), 25nm (○), 41 nm (×), 70 nm (○) and 116 nm (△) thick films.

but the asymmetric widening of \( G(\tau) \) for the thin films leads to differences in \( \langle \tau \rangle \) of two orders of magnitude. So the average relaxation time \( \langle \tau \rangle \) is not the most relevant
parameter to describe the variation of the distribution of relaxation times with film thickness. One should rather look at the width of the distribution, which is related to the stretch exponent $\beta$ (Fig. 6.12).

The summary of the results in Fig. 6.12 show that we can distinguish three distinct temperature regions exhibiting different behaviours:

- **high temperatures** ($T \gtrsim 120 \, ^\circ C$): although the number of measurements we could perform in this range is small, it is clear that thickness has little influence on the dynamics. This can be understood from the fact that at 120 °C, in the liquid phase, the dynamics can only be little affected by size effects. Eventually the dynamics will be modified at small thickness (below 10 nm) by the presence of the free surface and film-substrate interface. The effect is quite likely not large enough to be observed with our experiments.

- **intermediate temperatures** ($70 \, ^\circ C \lesssim T \lesssim 120 \, ^\circ C$): in this temperature range, there is an influence of the film thickness on the dynamics. First of all the stretch exponent $\beta$ of the thinnest films (10 nm and 17 nm) significantly decreases as temperature decreases and reaches a minimum at around 100 °C and then slightly increases again (Fig. 6.12). The decrease of $\beta$ indicates a widening of the distribution of the relaxation times. This widening is also observed for intermediate thicknesses at $T = 100 \, ^\circ C$, but the effect is smaller and decreases as the film thickness increases. Since this widening is not observed in the thickest film (116 nm-thick) we can conclude that it is due to an increase of the inhomogeneity of the films under confinement. This is in agreement with our observation of a broadening of the glass transition as the film thickness decreases (see Chap. 3). Note also that the temperature range in which $\beta$ is decreased in the thinnest films, with respect to the value in thick films, corresponds to the temperature range in which the glass transition takes place in the thinnest films studied with x-ray reflectivity. This is indeed the temperature range in which one expects the inhomogeneity to be the largest, with part of the film in the liquid state and the rest in the glassy state. Since the average relaxation time varies very rapidly in the vicinity of the glass transition, the difference between the dynamics in the different parts of the system is then the largest.

- **low temperatures** ($T \lesssim 60 \, ^\circ C$): the difference in dynamics between films at different thicknesses diminishes as temperature decreases below 100 °C and becomes unmeasurable at approximately 60 °C. Although we have not performed measurements at lower temperatures because the relaxation of the
system becomes extremely long, we can expect that this independence on temperature also occurs below 60 °C.

Following the argument in the discussion of the intermediate temperatures, we can say that 60 °C is the temperature at which the glass transition is completed in the whole film (for the thinnest films we have measured). The inhomogeneity of the dynamics induced by confinement becomes then equal to or smaller than the intrinsic inhomogeneity of the dynamics in bulk and thick films.

Our finding that $\beta$ becomes independent of film thickness at low temperatures is in contrast with the results of Torkelson et al. [62] on polymer films. They found little influence of temperature on the difference in value of $\beta$ for thin and thick films. This might however be due to the fact that they only performed measurements for temperatures above $T_g - 10 ^\circ C$, while we measured down to $T_g - 46 ^\circ C$.

In the above discussion, we have not considered the role of the cooperative length $\xi$ and its temperature dependence. From the model presented in Sec. 3.4.2, we know that the existence of $\xi$ introduces an inhomogeneity of the system for film thicknesses close to $\xi$.

The original theory of Adam and Gibbs of cooperative motion [20] predicts a divergence of $\xi$ at a temperature below $T_g$ (corresponding to $T_{VFT}$ in Eq. 1.2). This implies that $\xi$ should increase as temperature decreases. This means that as temperature decreases, the effect of confinement on the heterogeneity of the dynamics should start appearing at larger thicknesses and, for a given thickness, the inhomogeneity should increase as temperature decreases. This is however not what we have observed. One explanation for this is that $\xi$ does not increases as temperature decreases, or at least not much. This has actually been observed in colloidal suspension using confocal microscopy [40, 39]. In such a system, the glass transition is obtained by increasing the density of particles. The size of fast relaxing clusters (which can be compared to cooperatively rearranging regions) was found to remain constant when the density increases beyond the glass transition. Unfortunately, no data is available on the temperature dependence of $\xi$ below $T_g$ in molecular systems.

In the framework of the simple model presented in Sec. 3.4.2, making the cooperative length $\xi$ independent of temperature, makes also the relaxation time $\tau_\infty$ in bulk and the degree of inhomogeneity in the film independent of temperature. We could introduce a variation of $\tau_\infty$ with temperature in a phenomenological way by imposing the appropriate temperature dependence of the parameter $\alpha_\infty$, which is the energy barrier per molecule that needs to be overcome for allowing for a re-
laxation process [113]. There is however no obvious way of obtaining a dependence of the distribution of relaxation times in the films as a function of temperature in agreement with our experimental results.

So the simple model simply based on the idea that motion is cooperative over a certain length scale is not able to explain all the dynamic feature of thin glassy films, although it explains qualitatively some of them.

From the questions we have asked ourselves at the beginning of this thesis (see Sec. 1.5), we have given an answer to how the dynamics of these system and the distribution of relaxation times are modified when the size of the system decreases. We have also shown in Chap. 3 how macroscopic properties changes with size. We can qualitatively link the two types of information and explain most features we have observed. We miss however a real model of the dynamics of the system that could make quantitative predictions.