Molecular dynamics in thin glassy films

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Glass Former in Confined Geometry by X-ray Reflectivity

X-ray reflectometry was used to measure the temperature dependence of the thickness of ultrathin films of two low-molecular-weight glass formers [104]. In bulk samples, this type of expansivity measurements reveals the presence of a glass transition by a sudden break of slope. We have observed a broadening of the glass transition in films thinner than roughly 150 Å, indicating an inhomogeneous distribution of relaxation times in these films. Our results are explained by confinement effects and interpreted in the framework of a theoretical model based on the concept of collective dynamics over a cooperative length.¹

¹This work have been performed in collaboration with Ph.D. student Nicolas R. de Souza
3.1 Introduction

Among the several existing theories on the glass transition, the theory introduced by Adam and Gibbs [20] proposes the concept of cooperative motion. The idea of a length scale for the cooperativity is easily associated to some sort of finite size effect (see Fig. 1.5). Indeed, the dynamics of glass-forming molecules should strongly be modified when they are confined in systems with a size of the same order of magnitude of the cooperative length. As a consequence, one expect changes in macroscopic properties related to the dynamic behaviour of molecules, such as the glass transition and the expansivity of the material.

We have adopted thin films as confining geometry because this facilitates direct access to the system. One way to locate the glass transition temperature in a substance is to detect the changing in a physical property such as the specific volume, enthalpy, viscosity or refractive index, as a function of temperature $T$. We have chosen to monitor the volume while scanning the temperature. The expansivity coefficient $\alpha = d(\ln V)/dT$ is essentially constant in both the liquid and glass phases but with different values. The curve $\ln V(T)$ presents then two straight lines below and above $T_g$ and a break of slope at $T_g$. In the case of thin films we can only probe the out of plane expansion perpendicular to the substrate by monitoring the temperature dependence of the thickness $h(T)$. The measured expansivity is then in principle different from the three dimensional volume expansivity because we do not take into account the in-plane expansion. However the temperature dependence of the out-of-plane expansivity will show the same feature as that of the volume expansivity. For the limited temperature range that we have used, we can consider the thickness variation as linear in $T$ and the expansion coefficient is then defined by $\alpha = (1/h) dh/dT$. For $h$ below $\sim 100$ nm, x-ray reflectometry is a suitable technique for measuring film thicknesses.

In thin films the expansion coefficient $\alpha$ has been observed to depend on the film thickness. Former experiments [74, 75, 77, 79] have shown different $\alpha$ dependencies, qualitatively related to the sample-substrate interaction. Evaluation of the behaviour of $\alpha$ can then give an indication on the strength of the interaction with the substrate and its influence on the molecular dynamics at the interface. From the temperature dependence of the expansivity, it is also possible to determine the width of the glass transition. It is simply the width of the temperature region in which $\alpha(T)$ changes from its values in the liquid and glass phases.

As explained in the first Chapter, confinement effects (see Sec. 1.4.1) and interaction with the substrate (see Sec. 1.4.3) induce an inhomogeneous dynamics in thin films. As a consequence, different parts of the film should have different aver-
age relaxation times, and therefore different glass transition temperatures, leading to a broadening of the glass transition of films observed as a whole. However such a broadening has not been observed in most previous measurements of the glass transitions of supported polymer films [73, 74, 75] and also not in free-standing films [64]. Only Kawana & Jones [70] found an increase of the glass transition width as the film becomes thinner. The fact that this broadening is not observed in the very same experiments, is explained by the presence at the free surface of a layer with a lower glass transition temperature.

No clear evidence for a similar effect had ever been found in low-molecular-weight glass-formers. In this Chapter we present an experimental evidence of such a broadening observed in the temperature dependence of the film expansivity with two low molecular weight materials.

3.2 Experimental procedure

3.2.1 X-ray reflectivity

X-ray diffraction is used since the '30s as a powerful technique to probe the structure of condensed matter and lately also for soft condensed matter as polymers (for a review see [105]). The advantage of this sort of radiation is the high penetration depth (several hundreds of Å) and the good spatial resolution.

Reflectivity from interfaces

When x-ray radiation interacts with matter, it gets scattered by electrons present in the material. This scattering is governed by Maxwell's equations. In the case of an interface between two media, this scattering results in both a reflection and refraction of the incident wave. The x-ray scattering by an interface was rigorously derived by Parrad already in the '50s [106] using Maxwell's equations to describe the interference between the incident and scattered waves. In the dynamical theory, a key property to describe the scattering of a wave incident on a flat interface between air and a material, is the refractive index \( n \) of the material

\[
n = 1 - \delta + i\beta = 1 - \frac{\lambda^2 r_0}{2\pi} \rho + i\frac{\lambda\mu}{4\pi}
\]  

(3.1)

where \( \lambda \) is the wavelength of the x-rays, \( r_0 \) is the classical electron radius (2.82 \( \cdot 10^{-8} \) Å), \( \rho \) is the electron density in the material, and \( \mu \) the mass absorption coefficient of the medium. Typical values for \( \delta \) are on the order of \( 10^{-6} \) for low-molecular-weight solids and polymers. Values of \( \beta \) are usually \( 10^2-10^3 \) times smaller than \( \delta \).
Therefore, in first approximation, the imaginary part, describing the absorption of x-rays by the material, can be neglected. Another assumption is that the scattering is purely elastic with no change of the energy of the x-ray photons [105]. For x-rays, \( \lambda \) is on the order of 1 Å which means that \( n \) is close to 1 (the value of \( n \) in vacuum).

At the interface between air (refractive index \( n_a = 1 \)) and a material with refractive index \( n_m \), assumed to be sharp and smooth, the incident angle \( \theta_a \) and the refraction angle \( \theta_m \) (See Fig. 3.1) obey Snell’s law

\[
 n_m \cos \theta_m = n_a \cos \theta_a \Rightarrow \cos \theta_m = (1/n_m) \cos \theta_a \quad (3.2)
\]

For most materials \( \delta \) has positive value, thus \( n_m < n_a = 1 \). This implies that, for a given wavelength \( \lambda \), there is a critical angle \( \theta_c \) of incidence below which the radiation experiences total external reflection. Applying Eq 3.2 and excluding absorption, we have \( \cos \theta_c = 1 - \delta \), which can be approximated for small angles to \( \theta_c = \sqrt{2\delta} \). \( \theta_c \) is thus directly dependent on the material’s electron density. For \( \theta > \theta_c \) the incident x-ray wave is both reflected and refracted. In a reflection geometry, the reflected wave vector \( k_{rf} \) is in the same plane as the incident wave vector \( k_i \) and the normal to the surface \( \hat{z} \), and the detection angle is the same as the incident angle \( \theta_a \). The wave vector transfer for the reflection on the air side is defined as

\[
 q_{z,a} = k_{rf} - k_i. \quad (3.3)
\]

Since we assumed elastic scattering: \( |k_i| = |k_{rf}| = |k| \) and \( q_{z,a} = 4\pi \rho = q_{z,a}^2 - q_c^2 \). The wave vector transfer for the refracted wave \( q_{z,m} \) has a different length than \( q_{z,a} \) because of the difference in electron density between the material and the air [105]:

\[
 q_{z,m}^2 = q_{z,a}^2 - 4\pi \rho = q_{z,a}^2 - q_c^2. \quad (3.4)
\]
3.2 Experimental procedure

Figure 3.2: Schematic representation for multiple reflections and refractions of x-rays with incident angle $\theta_a$ in a thin film of thickness $h$.

The reflection coefficient for a sharp interface is given by

$$r_{a,m} = \frac{q_{z,a} - q_{z,m}}{q_{z,a} + q_{z,m}}$$

and the reflectivity of such an interface is given by the Fresnel equation

$$R(q_{z,a}) = r_{a,m}r_{a,m}^* = \left[ \frac{1 - \sqrt{1 - (q_{z,a}^2/q_{z,m}^2)}}{1 + \sqrt{1 + (q_{z,a}^2/q_{z,m}^2)}} \right]^2.$$  (3.6)

In our experiments we have used thin supported films and in this case the reflection at both the air-material interface and material-substrate interface have to be considered (see Fig. 3.2). For a slab model of a thin film of thickness $h$ with uniform density, and supported by an infinitely thick substrate, the Fresnel reflection coefficient of the whole system takes into account the multiple reflections of the wave inside the film

$$r = \frac{r_{a,m} + r_{m,s} \exp(2iq_{z,m}h)}{1 + r_{a,m}r_{m,s} \exp(2iq_{z,m}h)},$$

and the reflectivity becomes

$$R(q_{z,a}) = \frac{r_{a,m}^2 + r_{m,s}^2 + 2r_{a,m}r_{m,s} \cos(2q_{z,m}h)}{1 + r_{a,m}^2 + r_{m,s}^2 + 2r_{a,m}r_{m,s} \cos(2q_{z,m}h)}.$$  (3.8)

where $r_{m,s}$ is the reflection coefficient of the material-substrate interface. From Eq. 3.8 we can already get some insight in the expected dependence of the reflectivity on the wave vector transfer $q_{z,a}$ for $q_{z,m} > q_c$. $R(q_{z,a})$ will vary as $q_{z,a}^{-4}$ and present in addition periodic oscillations known as Kiessig fringes. By differencing Eq. 3.8, it
can be easily seen that the distance $\Delta q_{z,a}$ between minima yields the film thickness $h = \pi/\Delta q_{z,m} \propto \pi/\Delta q_{z,a}$. Another important information is that the amplitude of the oscillations depends on the contrast of density at both interfaces through the reflectivity coefficients $r_{a,m}$ and $r_{m,a}$ of both interfaces. The larger the contrast, the larger the oscillations.

**Roughness**

The model used above applies only to flat surfaces while in reality interfaces are usually rough. To take into account the surface roughness, the Fresnel reflectivity coefficient given in Eq. 3.5 can be corrected with a Debye-Waller factor that assumes a Gaussian distribution of the height deviation of the interface with respect to its mean position. For example, the air-material interface will have a reflectivity coefficient

$$r_{a,m} = \frac{q_{z,a} - q_{z,m}}{q_{z,a} + q_{z,m}} \exp \left( -\frac{1}{2} q_{z,a} q_{z,m} \langle \sigma_{a,m} \rangle^2 \right)$$

(3.9)

where $\langle \sigma_{a,m} \rangle^2$ is the mean square deviation of the position of the interface. This is equivalent to convolute the infinitely sharp interface profile with a smoothing function for the electron density profile versus the depth $z$. Taking in consideration the roughness contribution for both interfaces has two main consequences for the reflectivity: $R(q_{z,a})$ decays more rapidly than $q_{z,a}^4$ and the amplitude of the Kiessig fringes becomes smoother at high $q_{z,m}$.

**Experimental setup**

The reflectivity measurements were done in a specular geometry, schematically represented in Fig. 3.3. Measurements were performed on a Philips X'Pert MPD diffractometer based on a Cu x-ray tube and equipped with a hot stage. The rotation angle $\theta$ of the sample is then varied while keeping it equal to half the rotation angle $2\theta$ of the detector. Data were collected in the range $2\theta = 0.2^\circ - 5^\circ$ with a resolution of 20 mdeg ($\sim$250 points per spectrum). The signal was measured by photon counting. The counting statistics of the reflectivity profile is a determining factor for defining the quality of the data, thus it is important to have high counting rate for every range of the spectrum. Specular scans span several decades of photon intensities. To take into consideration the extreme differences in intensity of the

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2We thanks H. Schenk (University of Amsterdam) for use of his reflectometer and W. Molleman and P. Verschuren for technical assistance.
3.2 Experimental procedure

reflected x-rays at different \( \theta \) we attenuated the incident flux by mean of Plexiglas filters. The scanned \( \theta \) range was then divided in four overlapping windows in which we used different filter thicknesses. We constructed a master plot over the whole \( \theta \) range by overlapping the data, starting from high \( \theta \). Background noise (relevant at high \( \theta \)) has been subtracted.

Data analysis

The most common way of analysing the measured reflectivity curves is to assume a model for the density profile of the sample, calculate the corresponding reflectivity curves and then tune the model parameters in order to fit the experimental curves. We adopted a three layer model: a semi-infinite air layer, a glassy material layer and a semi-infinite quartz layer for the supporting substrate. For the fits (with the simulated annealing technique) we assumed uniform electron densities throughout the three different layers. We kept the air and quartz layers density fixed (defined through the quantity \( 1 - \text{Re}(n) \)) and the adsorption (defined through \( \text{Im}(n) \)) and fitted the rms roughnesses of the two interfaces, the film thickness and density. Moreover we could also fit the instrumental resolution, the overall scaling factor, the critical angle \( \theta_c \) and the ratio between the offset of the substrate to the center of the beam and the beam size itself.

Modeling and fitting of the experimental spectra were performed using the software SPEEDO \(^3\). The code is based on a non-linear least-square technique implemented with a dynamically optimised Monte Carlo method [107] (so-called simulated

\(^3\)SPEEDO was developed by Mike Knewston at the Department of Physics of Carnegie Mellon University in Pittsburgh, Pennsylvania, USA
annealing) and leaves the freedom of using a variable number of layers for modeling the experimental system, with several fitting parameters. To determine the quality of the fitting of a x-ray profile with \( p \) number of data points, we used the \( \chi^2 \) function

\[
\chi^2 = \frac{1}{p+1} \sum_{i}^{p} \frac{(R_{i,m} - R_{i,c})}{\sigma_i^2}
\]

(3.10)

where \( R_{i,m} \) and \( R_{i,c} \) are the measured and calculated reflectivity for a given scattering vector \( q_z \), and \( \sigma_i^2 \) is the variance. Eq. 3.10 shows that the number of points \( p \) (\( \sim 250 \) in our spectra) is a key factor to reduce \( \chi^2 \).

### 3.2.2 Sample preparation

We have used the glass-forming H-bonded materials shown in Fig. 2.1: compounds [A] and [B] have a glass transition respectively at 78 °C and 106 °C as measured by DSC at 20 Kmin\(^{-1}\) with \( T_g \) being defined as the onset of \( C_p \) change upon heating [91].

The films we have studied were obtained by spin-coating, from solutions of the glass forming materials in cyclopentanone with different concentrations, on fused quartz plates. This method gives uniform films whose structure is quenched by the instantaneous evaporation of the solvent. Thicknesses as spun ranging from 100 Å to 1300 Å were analysed. Films with thicknesses between a monolayer (30 Å) and 100 Å presented dewetting upon heating [101]. After spin-coating, the films were allowed to equilibrate by annealing at 130 °C for 90 min. The thinnest film of compound [A] (thickness 99 Å) was annealed at 110 °C because it dewets at higher temperatures. Data for the expansivity measurements were collected upon approaching and crossing \( T_g \) from above during the cooling cycle. During the whole experiment the films were kept under inert atmosphere of nitrogen.

Due to the long time necessary for an x-ray spectrum to be collected, the cooling of the sample occurred in steps. After each temperature step, the sample was first allowed to equilibrate for 40 minutes before the reflectivity was collected. The average cooling rate was of 0.1 Kmin\(^{-1}\). We have chosen the smallest average temperature scanning rate possible, giving a reasonable collection time and isothermal condition for the data collection. It is important to note that in an out of equilibrium system, as in the case of a glassy phase, the sample thermal history becomes important for the reproducibility of the measurements. In experiments with a continuous scanning of temperature, the width of the glass transition was found to depend mainly on the fragility of the substance [108], but it also decreases as the temperature scanning rate decreases [109].
### 3.3 Results

All measured films were stable during temperature scanning. Good parameters to evaluate the stability are the mean square roughnesses of the material-substrate and air-material interface. The films presented the same rms roughness of the material-substrate interface (~4.5 Å) while the roughness of the free surface slightly varied from one film to the other (6-13 Å) but remained constant for each film during the experiments.

#### Typical x-ray reflectivity curves obtained with a 99 Å thin film (as-spun) of compound [A] are shown in Fig. 3.4 for different temperatures during the temperature cycle. The plots clearly show the Kiessig fringes. The distance between successive minima is inversely proportional to the film thickness. The amplitude of these peaks slightly decreases at high wave vector transfer $q_z$ due to roughness of the film interfaces. A first shrinking of the film upon the first heating is clearly visible. It is due to the equilibration of the structure quenched during the spin-coating. The reduction in thickness is proportional to the initial thickness and is on average ~10 % for all the analysed films of both materials. During the cooling procedure, the film further shrinks but at a rate depending on temperature. The thermal behaviour of the expansivity depends strongly on the temperature range under observation, whether it is above or below the glass transition temperature.

The temperature dependence of the film thickness $h(T)$, obtained by fitting the x-ray data, is shown in Fig. 3.5 for the 99 Å, 136 Å and 1308 Å thick films of compound [A]. Like all other films, they present a more or less constant slope of $h(T)$ at the highest and lowest temperatures, namely the liquid and glass regions, with a slope variation in the region around the bulk glass transition $T_g\text{bulk}$. In the low temperature region, the thickness increases very weakly with temperature. Within experimental error, the expansivity coefficient for the glass phase $\alpha_{\text{Glass}} = (1/h)\, dh/dT$ seems independent of the film thickness. In the high temperature region, the expansivity coefficient for the liquid phase $\alpha_{\text{Liq}}$ is easily determined as all samples present a high, almost constant increase of the thickness. Note that for the thinnest film (as-spun thickness 99 Å), the liquid phase is not yet reached at the highest measurable temperature. This implies that we can only determine a lower limit for the expansivity coefficient $\alpha_{\text{Liq}}$ in the liquid phase and for the transition width.

To evaluate $\alpha_{\text{Liq}}$ we fitted the experimental variation of $h(T)$ by a 'minimal' model assuming an exponential law for the expansivity $\alpha(T)$ between the plateaux
Figure 3.4: Representative x-ray specular reflectivity curves for an initially 99 Å thick film of compound [A] during a cooling cycle. Intensities are plotted vs. the wave vector \( q_z \). For clarity, the curves are offset and plotted using every three data point in the data set of each spectrum. From bottom to top: as spun at room temperature, 110 °C, 90 °C, 70 °C, 30 °C. The solid lines represent the best fits as described in the text. Error bars are within point size.

of its extreme values \( \alpha_{\text{Liq}} \) and \( \alpha_{\text{Glass}} \):

\[
\begin{align*}
\alpha(T) & = \alpha_{\text{Glass}} + \frac{\alpha_{\text{Liq}} - \alpha_{\text{Glass}}}{1 + \exp \left[ \frac{T_{\text{inf}} - T}{\Delta} \right]} \\
h(T) & = h_c \exp \left[ \alpha_{\text{Liq}} T + \Delta (\alpha_{\text{Liq}} - \alpha_{\text{Glass}}) \log \left( 1 + e^{\frac{T_{\text{inf}} - T}{\Delta}} \right) \right]
\end{align*}
\] (3.11)

where \( T_{\text{inf}} \) is the inflexion point of the exponential, \( \Delta \) is the width parameter and \( h_c \) is a constant. The model gives a fairly constant value for \( \alpha_{\text{Glass}} = 0.8 \cdot 10^{-4} \text{ K}^{-1} \). We observe a dependence of the expansion coefficient in the liquid phase with film thickness. The values of \( \alpha_{\text{Liq}} \) as a function of film thickness for compound [A] are given in Tab. 3.1 and plotted in Fig. 3.6. Compound [B] presents the same trend as compound [A] although the obtained values show more scatter.

The data in Fig. 3.5 clearly shows a broadening of the glass transition with decreasing thickness. In thick films the glass transition is restricted to a limited region
Figure 3.5: Left: measured thickness versus temperature for films of compound \([\text{A}]\). The as-spun thicknesses were of 99 Å (top), 136 Å (middle) and 1308 Å (bottom). Solid lines represent the best fitting using Eq. 3.11. Right: corresponding dependence of \(\alpha(T)\) deduced from the fit of the experimental data on the left, showing also how the width \(w\) of the transition is defined.

while for thinner films it extends over several decades in temperature. To quantify this broadening, we have measured the width \(w\) of the glass transition as the width of the temperature domain in which the expansivity \(\alpha\) deviates by 5 % from its extreme values \(\alpha_{\text{Liq}}\) and \(\alpha_{\text{Glass}}\) (in between onset \(T_-\) and endpoint \(T_+\) in Fig. 3.5). For the thinnest film we took the endpoint as the highest temperature measured
Glass Former in Confined Geometry by X-ray Reflectivity

<table>
<thead>
<tr>
<th>$h$ as spun (Å)</th>
<th>$w$ (K)</th>
<th>$\alpha_{\text{Liq}} = (1/h) \frac{dh}{dT} \cdot 10^4 (K^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.75 ± 0.09</td>
<td>≥42</td>
<td>≥26.6</td>
</tr>
<tr>
<td>136.1 ± 0.1</td>
<td>59.5 ± 5</td>
<td>15.6 ± 0.1</td>
</tr>
<tr>
<td>299.9 ± 0.2</td>
<td>52.5 ± 2.5</td>
<td>11.52 ± 0.06</td>
</tr>
<tr>
<td>770.8 ± 0.15</td>
<td>29.5 ± 2.5</td>
<td>8.59 ± 0.25</td>
</tr>
<tr>
<td>1308.0 ± 0.1</td>
<td>23.0 ± 2.5</td>
<td>6.03 ± 0.22</td>
</tr>
</tbody>
</table>

Table 3.1: Calculated width of the glass transition and thermal expansivity $\alpha_{\text{Liq}}$ of the liquid phase for compound [A].

...to estimate the lowest possible value for $w$. The errors reported in Tab. 3.1 take into consideration the temperature resolution used for the collection protocol. The results for $w(h)$ are plotted in Fig. 3.7 for compound [A], confirming the trend seen in Fig. 3.5. $w(h)$ increases as the thickness decreases and all data points lie above the width $w_{\text{bulk}} = 7$ K evaluated by measurement of the isobaric heat capacity $C_p$ on bulk samples with a cooling rate of 20 Kmin$^{-1}$.

The evaluation of the glass transition temperature $T_g$ needs a specific consideration. It can be mainly determined in three different ways:

- By the intersection of the straight parts of the $h(T)$ plot corresponding to the glass and liquid phase. This way, typically used in x-ray reflectivity or ellipsometry experiments, is generally successful for data in which the temperature dependence of the thickness in the liquid phase is clearly a straight line. This is not the case for several films, making it impossible to evaluate $T_g$ properly for all films.

- By the onset temperature $T_a$ at which $\alpha(T)$ starts deviating from $\alpha_{\text{Glass}}$, as often used in calorimetric measurements with specific heat $C_p$. This method gives scattered data around the bulk value without a specific trend: $T_g = T_{g_{\text{bulk}}} \pm 10^\circ C$.

- By the inflexion point $T_{\text{inf}}$ in Eq. 3.11, as also done in calorimetry measurement. Except for the thinnest film (for which the liquid phase is not reached), the obtained values remain within a few degrees equal to $T_{g_{\text{bulk}}}$.

So, whatever the method we use, we find no clear dependence of $T_g$ on film thickness. If $T_g$ varies, it stays in the range $[T_{g_{\text{bulk}}-10^\circ C}, T_{g_{\text{bulk}}+10^\circ C}]$. 
3.4 Discussion and conclusion

Our results allow us to draw several conclusions concerning the thickness dependence to the following properties of thin glass films: the expansivity in the liquid phase, the width of the glass transition, and the location of the glass transition. In the following, we discuss each of these aspects in comparison with results obtained in other systems and with predictions of a simple model. In Chap. 6, we will compare the macroscopic behaviour discussed in the present Chapter with the information on the molecular dynamics obtained by dynamic second-harmonic generation.

3.4.1 Expansivity coefficient of the liquid phase

The measurements show that the expansivity coefficient of our system in the liquid phase decreases with increasing film thickness (see Fig. 3.6). Other research groups have analysed the temperature dependence of the thermal expansion coefficient of polymeric materials, finding contradictory results. Early experiments by Orts et al. [75] using x-ray reflectivity on thin films of polystyrene (PS) supported by an oxydised Si surface and kept in vacuum, showed no dependence of $\alpha_{\text{Liq}}$ with
film thickness. Later results [73, 74, 77, 110] on polymers having weak or strong interaction with the solid substrate did show a dependence of $\alpha_{\text{Liq}}$ on film thickness. Keddie [73] used a stable hydrogen-passivate crystalline silicon substrate but conducted his ellipsometry measurements and thermal treatments in air. In this work they found an increasing expansivity for the liquid phase with decreasing thickness. On a similar system, but using x-ray reflectivity and analysing the sample in vacuum, Wallace et al. observed the opposite effect: a decreasing expansivity for the liquid with decreasing thickness [77]. They explained the diverging results by the difference in the nature of the substrate: conducting the measurements in air, as Keddie did, generates a silicon oxide layer which has a much smaller interaction with the polymer chains than the hydrogen passivated Si. The fact that a strong interaction of the polymer chain with the supporting substrate leads to a decrease of the expansivity coefficient with decreasing film thickness, is confirmed by studies of PMMA on passivated Si [74] (measured by neutron reflectivity under vacuum), where the effect was observed for both the melt and the glass, and by the behaviour of poly(2)vinylypyridine on SiO$_2$ (measured by x-ray reflectivity under vacuum) [110]. On the other hand when the material-substrate interaction is weak like in the case of PS on SiO$_2$ actually studied by Keddie [73], the expansivity coefficient for the liquid phase increases with decreasing thickness.

Figure 3.7: Glass transition width $w$ for compound [A] vs. the as-spun film thickness $h_0$. The dotted line represents the bulk value measured by DSC [91].
Summarising these results, molecules having strong attractive interactions with the substrate show a decrease of the thermal expansivity with decreasing film thickness. Conversely, systems presenting weak interactions with the substrate, exhibit the opposite behaviour. As far as our low molecular weight glass-formers can be compared to polymeric materials, the fact that we have measured an increase of the expansivity for the liquid phase for decreasing thickness, indicates that our systems are comparable to the second situation, meaning that our molecules have little interaction with the fused quartz substrate. This is in agreement with previous dynamic measurements on ultrathin films of compound [B]. Monolayers exhibited a measurable dynamics even at 90 °C below the bulk $T_g$ while increasing the film thickness led to an exponential increase of the relaxation time [58]. This shows that the slowing down of the molecular dynamics due to the interaction with the wall is significantly smaller than the slowing down due to the presence of the surrounding glass-former molecules. As a consequence of the above, in terms of molecular dynamics, at least in first approximation, we only need to take into account confinement effects and we can use a symmetric model of thin films as in the case of freely suspended films.

The $\alpha_{\text{Liq}}(h)$ dependence in Fig. 3.6 can be fitted with a scaling law:

$$
\alpha_{\text{Liq}}(h) = \alpha_{\text{Liq} \infty} + \frac{C}{h}
$$

with $\alpha_{\text{Liq} \infty} = 4.9 \cdot 10^{-4} \text{ K}^{-1}$ and $C = 0.19 \text{ ÅK}^{-1}$. Scaling laws inversely proportional to the size of the system, are often found in systems involving finite size effects, such as clusters [111]. In first approximation Eq. 3.12 describes pretty well the experimental behaviour though more data would be required to evaluate with more precision the dependence law for $\alpha_{\text{Liq}}(h)$.

The question arises why $\alpha_{\text{Liq}}$ increases when the thickness $h$ decreases in glass-formers with small interactions with the supporting substrate. There is unfortunately no model allowing to relate the dependence of $\alpha_{\text{Liq}}$ on $h$ with the behaviour of the molecules inside the films. We can only say that the fact that for small $h$, $\alpha_{\text{Liq}}$ is different than the bulk value means that the obtained liquid state in the thin film is different that the bulk liquid state, at least in part of the film. For normal liquids, we would actually expect such size effects to appear at much smaller thicknesses. However our measurements are limited to a small temperature range above $T_g$ in which the behaviour of the liquid phase starts changing towards that of a glass.

We can however remark that the influence of the interaction with the substrate on $\alpha_{\text{Liq}}(h)$ corresponds to the intuitive expectation. In systems with a strong interaction with the supporting substrate, the overall dynamics of the system is slowed down with respect to that in bulk (see Sec. 1.4.3, so the system has a more “glassy”
character than bulk. Conversely, a system with little interaction with the substrate have a dynamics corresponding to a bulk liquid at a higher temperature, at least at the interface of the film. This leads to a larger value of $\alpha_{\text{Liq}}(h)$ than in bulk.

Finally, we emphasize that in the above discussion, the qualification of "strong" or "weak" interactions of the molecules with substrate is actually relative to the strength of the intermolecular interaction. In Chap. 5, we will see that in a system in which the intermolecular interactions are weaker, namely an ordinary liquid crystal, the effect of the interactions with the substrate become important in the dynamics of the system.

### 3.4.2 Width of the glass transition

The expected inhomogeneity of the molecular mobility in films should intuitively have some consequences for the glass transition: different parts of the film should have different average relaxation times, and therefore fall out of equilibrium at different temperatures, leading to a broadening of the glass transition of films observed as a whole. Our experimental data clearly show such a behaviour when the film thickness decreases (see Fig. 3.7). To our knowledge this is the only evidence of such broadening report so far in films of low-molecular-weight glass-formers. For polymers, the only report of an increase of the glass transition width as films become thinner is that of Kawana and Jones about supported polystyrene films [70]. To determine the transition width, they plotted the ratio $\alpha(T)/\alpha_{\text{Liq}}$ and determined the onset $T_+$ and the endpoint $T_-$ of the temperature domain in which $\alpha(T)$ varies abruptly between the nearly constant values in the liquid and the glass phases. They mainly found a decrease of the endpoint $T_-$ and a small increase of the onset $T_+$. For a film thickness of 100 Å, $(T_+ - T_-)$ becomes approximately 60 °C, which is close to the width we found at this thickness. However in our case, the average of the onset and endpoint does not vary much with film thickness. This is probably due to the fact that in our case the glass transition temperature varies little with film thickness while in supported polystyrene film $T_g$ decreases by about 30 °C for a 100 Å-thick film. Kawana and Jones explained their results in the framework of a three-layer model with a layer with an increased mobility at the free surface and a layer with reduced mobility at the interface with the substrate [70, 112].

Layer models have also been used to explain the broadening of the distribution of the relaxation times observed with dielectric spectroscopy in low-molecular-weight glass-formers confined in pores [82]. However these models are not realistic since they imply an abrupt change in mobility at the interface between the different layers. Models with a continuous variation of the mobility should be more suitable [66].
3.4 Discussion and conclusion

So to interpret the broadening of the glass transition that we have observed experimentally, the expected variation of the relaxation time \( \tau(z) \) across films of different thicknesses \( h \) can be calculated using the theoretical model developed by Jérôme [113] and based on the idea that the dynamics of glass-formers is collective over the length scale \( \xi \). This characteristic length \( \xi \) can be seen as the radius of a collectively rearranging region. If this region is in the bulk, the characteristic relaxation time of this region is

\[
\tau = \tau_0 \exp \left[ \alpha'_\infty N_\infty \right]
\]

(3.13)

where \( \tau_0 \) is a constant, \( N_\infty \) is the number of molecules in the region and \( \alpha'_\infty \) is a factor inversely varying with the mobility of the molecules.

When the glass forming material is confined in a thin film, molecules do not have the same surrounding across the film: both the mobility factor \( \alpha' \) and the number of molecules in a cooperatively rearranging region depend on the distance from the interface. In the model of Jérôme, the relaxation time \( \tau(z) \), is a continuous function given by:

\[
\tau(z) = \tau_0 \exp \left[ \int_{V(z)} \alpha'(Z)n(Z) \right]
\]

(3.14)

where the integral is taken over the collectively rearranging region \( V(z) \) located within a radius \( \xi \) around the molecule considered positioned in \( z \). \( n(Z) \) is the number of molecules in volume \( V(z) \) at a distance \( Z \) from the surface. The local mobility factor \( \alpha'(z) \) is proportional to the bulk value \( \alpha'_\infty \) and to the effective number of molecules \( N(z) \) present in \( V(z) \) compared to the number of molecules \( N_\infty \) present in a cooperatively rearranging region located in bulk:

\[
\alpha'(z) = \alpha'_\infty \frac{N(z)}{N_\infty}
\]

(3.15)

The resulting dependence of the relaxation time \( \tau \) as a function of position \( z \) and film thickness \( h \) is shown in Fig. 3.8. The relaxation time is presented in terms of

\[
T(z, h) = (\alpha'_\infty N_\infty)^{-1} \ln \left( \frac{\tau(z, h)}{\tau_0} \right)
\]

(3.16)

which is mainly the logarithm of the relaxation time normalised by the bulk value. In Fig. 3.8 the distances are normalised to \( \xi \). \( 2z/h = 0 \) corresponds to the center of the film and \( 2z/h = \pm 1 \) to the interfaces. From this plot we can draw the following conclusions regarding the inhomogeneity of the film:
• For $h \gg \xi$, the calculations show that the dynamics is uniform across the film, except for a thin region close to the surfaces: the glass transition of the film should then be as sharp as in bulk.

• As $h$ decreases towards $\xi$, the dynamics becomes more and more inhomogeneous and one expects the glass transition to become wider.

• For $h \leq \xi$, the dynamics is predicted to become homogeneous again but with a relaxation time distribution centered at shorter times, then the glass transition should sharpen again but take place at a lower temperature.

The experimental data are in good agreement with this model since the glass transition exhibits a widening as the thickness $h$ decreases. The wide transition presented by the thinnest analysed films suggests that even these films have a thickness larger than $\xi$. We can therefore speculate that the cooperative length $\xi$, at temperatures around the glass transition, should be below 100 Å for our systems. In principle, we expect the glass transition to sharpen again, as the films become thin enough. Unfortunately this prediction cannot be verified on our experimental system due to the instability of thinner films. Moreover, it could happen that for this sharpening to be observed (e.g. with $h \sim \xi/3$), the system should be confined to dimensions below the molecular size.
3.4.3 Location of the glass transition

In the thin films of our materials, we found no clear indications of glass transition temperature depression with respect to its bulk value. There are two explanations for this. The first one is that we cannot determine the glass transition with enough precision from our data. The second one is that the deviation we can actually expect is rather small. Considering that the interaction of our molecules with the substrate is small (see Sec. 3.4.1), we expect a decrease of \( T_g \) when the thickness decreases. The largest decrease of \( T_g \) reported in the literature was observed with ortho-terphenyl in pores with a diameter of 40 Å [72]. With our system, we can only study films with a thickness larger than 100 Å. Moreover, our films are only confined in one dimension, while pores are confined in two dimensions, and it is known that the change in glass transition temperature is larger if the system is confined in more dimensions (see Chap. 1).

Since the model presented in the previous Section gives only relative values for \( \langle r \rangle \) through the normalised quantity \( T \) (Eq. 3.16), it is very difficult to make any predictions of the glass transition temperature \( T_g \) from the results shown in Fig. 3.8. Qualitatively, the model predicts a decrease of \( T_g \) as the thickness decreases. However, we cannot calculate by how much and below which thickness we should observe this decrease. So we cannot compare our experimental results with predictions concerning \( T_g \).