Dynamics of glass-forming materials confined in thin films

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Abstract. By considering the effect of confinement of the collective motion of glass-forming molecules, we show how the relaxation time of molecules is expected to vary across a thin film and as a function of the film thickness. The results of these calculations are compared with available experimental data.

1. Introduction

The glass transition and the dynamics of glass-forming molecules have been the subjects of numerous studies [1,2]. An important motivation for these studies is that of trying to understand why a glass is a glass, namely a liquid whose viscosity and characteristic relaxation time have become so large that it appears solid on the experimental timescale. Numerous models have been developed to account for the huge increase of the viscosity that is observed in a supercooled liquid as temperature decreases towards the glass transition. One idea that is common to many models is that this dynamic behaviour is due to the collective character of molecular motion in these materials. This idea is expressed in different terms: collectively rearranging regions [3–6], aggregates or clusters [7–9], 'backflow' collective motion [10].

In this article, we will adopt the description in terms of collectively rearranging regions. In this framework, molecules are considered to rearrange collectively over a certain length scale, called the cooperative length ξ. This means that to allow for the motion of one molecule, all of the molecules located within a distance ξ from this molecule must rearrange together. As ξ increases, the number of molecules implied in such collective rearrangements increases, and the probability of occurrence of a collective movement decreases. The increase of relaxation time observed as the glass transition temperature is approached from above comes from an increase of ξ.

A good deal of indirect and direct experimental evidence for the presence of collective molecular motion has been obtained. Most of it has been obtained by studies of the behaviour of glass-forming liquids confined in pores and thin films [11–15]. The idea behind these experiments is that as a glassy material is confined over dimensions smaller than the cooperative length, the size of the system determines the number of molecules that are involved in collective rearrangements. It is then possible to follow how the dynamic properties of the system vary as a function of this number.

To analyse such data, it is however necessary to model how the dynamic properties of confined systems vary as a function of the size of the system. One can distinguish two types of effect. As was already said, decreasing the size of the system decreases the number of molecules involved in the collective relaxation. This effect is a pure confinement effect that

increases the mobility of the molecules. The dynamics has indeed been found to speed up for several low-molecular-weight systems as their size decreases below a few nm [11–14]. The same phenomenon has been observed with confined polymers but for sizes ten times larger; it seems however that this phenomenon has a different origin for polymers, probably linked to the chain character of the molecules [16–21].

Another effect arises from the feature that the molecules located at the interface with the walls limiting the system interact with these walls. If this interaction is strong, the dynamics of the interfacial molecules is much slower than in the bulk [13, 22–31]. If the size of the system decreases, the proportion of molecules affected by the walls in creases, and the overall dynamics of the system slows down. This effect has been observed for several systems [21, 32–34].

To our knowledge, there has only been one modelling of the dynamics of confined glassy systems, namely in pores [25, 28]. It considered however only the effect of interactions with the limiting walls and not that of the confinement itself. In the present article, we concentrate on the effect of confinement on the cooperative motion of glass-forming molecules. We present calculations showing how the dynamics of glass-forming molecules is expected to vary within a film as a function of the film thickness and of the position of the molecules inside the film.

2. The principle of the calculation

If one considers the slowing down of glass-forming materials as arising from an increase of the size of collectively rearranging regions, the relaxation time of these regions should strongly depend on the number of molecules that these regions contain. We call this number N_∞ for a bulk system. Since collectively rearranging regions are spheres of radius ξ, we have $N_\infty \propto 4\pi\xi^3/3$. To ensure a Vogel–Fulcher dependence of the relaxation time τ and the viscosity of the system, τ should depend exponentially on N_∞:

$$\tau = \tau_0 \exp(\alpha_\infty N_\infty) \tag{1}$$

where τ_0 is a material constant. α_∞ is a measure of the mobility of the molecules: it is related to the free-energy barrier per molecule which has to be overcome in order to allow for the transition of the region considered from its original state to another state. In the original derivation of equation (1) given by Adam and Gibbs [4], α_∞ is related to the configurational entropy of the region. The fact that the activation energy $\alpha_\infty N_\infty$ is proportional to the number of molecules in a collectively rearranging region is also consistent with recent simulation results [35]. The precise nature of α_∞ is not important for the rest of our calculation.

Let us now consider a film of glass-forming material of thickness d, either limited by free surfaces (free-standing film), or limited by walls with which the molecules have little interaction. We consider this film to be uniform in the directions parallel to the surfaces. We call the axis perpendicular to the surfaces the Z-axis, with $Z = 0$ corresponding to the middle of the film and $Z = \pm d/2$ corresponding to its surfaces (figure 1).

The collectively rearranging regions might be truncated in the film (figure 1) if they are close enough to one of the surfaces: their volume $V(Z)$ and the number of molecules $N(Z)$ that they contain depend on the position Z of their centre. Moreover the environment of the molecules depends on their location in the film, and so does their mobility. This means that the barrier $\alpha(Z)$ that has to be overcome per molecule to allow for a relaxation process also depends on Z. The relaxation time of a molecule located at a position Z in a film becomes then

$$\tau(Z) = \tau_0 \exp\left[\int_{V(Z)} \alpha(z)n(z)\,\mathrm{d}z\right] \tag{2}$$
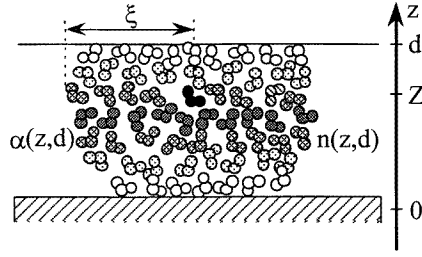
Figure 1. A schematic representation of a collectively rearranging region of volume $V(Z, d)$ around a molecule (in black) located at altitude Z in a film of thickness d. In this region, there are $n(z, d)$ molecules at altitude z with an associated energy barrier $\alpha(z, d)$.

where the integral is taken over the collectively rearranging volume $V(Z)$ located within a radius ξ around the molecule considered, and $n(z)$ is the number of molecules in $V(Z)$ located at position z. In this calculation we neglect the weaker Z-dependence of the factor τ_0 outside the exponential.

To perform the calculation of $\tau(Z)$, we need the expression for $\alpha(Z)$. If we consider that the mobility of the molecules varies within a film because the number of molecules in the collectively rearranging regions varies, the value of $\alpha(Z)$ at a certain altitude Z should be proportional to the number of molecules $N(Z)$ inside the region $V(Z)$. We can therefore write

$$\alpha(Z) = \alpha_\infty \frac{N(Z)}{N_\infty}. \tag{3}$$

Substituting equation (3) in equation (2) gives an analytical expression for the relaxation time τ as a function of position Z and film thickness d.

3. Results

We present here the results of the calculations of the relaxation time of molecules as a function of their position Z in a film and of the film thickness d. These results are presented in terms of the quantity

$$\mathcal{T}(Z, d) = (\alpha_\infty N_\infty)^{-1} \ln\left(\frac{\tau(Z, d)}{\tau_0}\right) \tag{4}$$

which is essentially the logarithm of the relaxation time normalized by the corresponding value in the bulk. All lengths are normalized by the cooperative length ξ. This means that the material and temperature dependences of the relaxation time are contained in the corresponding dependences of $\alpha_\infty N_\infty$ and ξ. In figure 2 we show the dependences of the relaxation time of the molecules in the middle of a film ($Z = 0$) and at the surfaces ($Z = d/2$) as functions of the film thickness, and in figure 3 the dependences on the normalized position $2Z/d$ for different film thicknesses. The analytical formulae for $\mathcal{T}$ are given in the appendix.

At all positions Z, the logarithm of the relaxation time first increases quadratically with film thickness d, then the increase becomes linear, and finally it saturates at a certain value. In the middle of a film ($Z = 0$), this saturation starts at thicknesses of about 2ξ, and the relaxation time becomes exactly the bulk one for films thicker than 4ξ. At the surface ($Z = d/2$), the saturation starts at around $d \approx \xi$ and ends at $d = 2\xi$. The value at which the surface relaxation time saturates is significantly smaller than the bulk value. As expected, surface molecules are more mobile than bulk ones. Another interesting feature is that for films thinner than $\xi/2$,
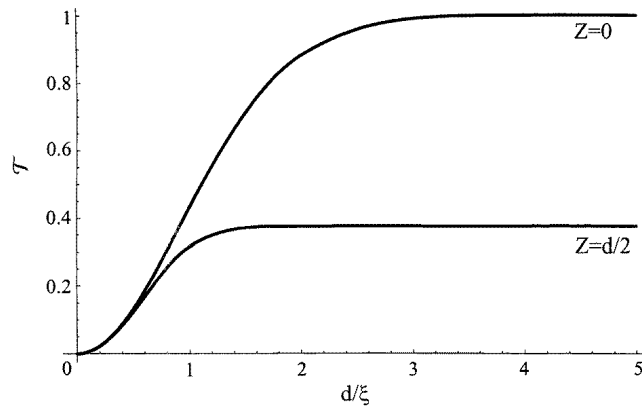
Figure 2. The normalized logarithm of the relaxation time $\mathcal{T}(Z, d)$ (equation (4)) for $Z = 0$ (the middle of film) and $Z = d/2$ (the surface) as functions of the normalized film thickness d/ξ.
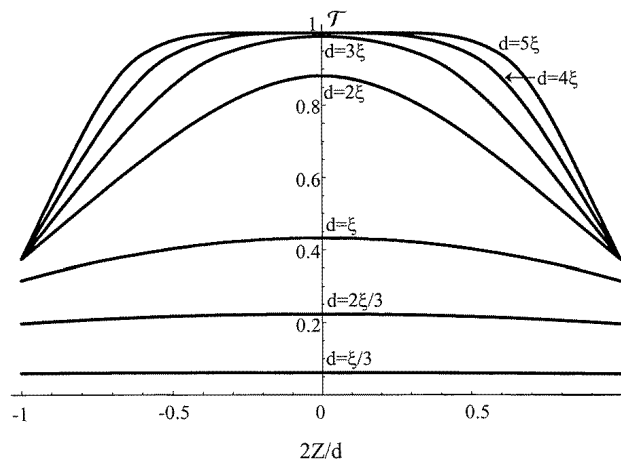

Figure 3. The normalized logarithm of the relaxation time $\mathcal{T}(Z, d)$ (equation (4)) as a function of the normalized position $2Z/d$ for different film thicknesses .

the relaxation time hardly depends on the position Z. This is because in such thin films all molecules along a normal to the film rearrange collectively. As the film thickness increases, the difference between the mobility of the molecules at the surface and that in the middle of the film increases. For very thick films ($d > 4\xi$), the effect of the surfaces extends over a distance 2ξ from the surfaces.

Since most experiments performed on confined glass systems probe the average dynamics of the system, it is also useful to calculate the average $\mathcal{T}^*(\tilde{d})$ of the quantity $\mathcal{T}$ as a function of the normalized film thickness $\tilde{d}$. For film thicknesses d larger than ξ, this average of the logarithm of the relaxation time is found to vary as $1 - 177/280\tilde{d}$. As d decreases further, $\mathcal{T}^*$ shows a strong inflection and tends to 0. The same trends are valid for glasses confined in cylindrical pores of diameter d. For large $\tilde{d}$, $\mathcal{T}(Z, d)$ (where Z is now the distance to the centre of a pore) is in first approximation given by the same formulae as in the case of a thin film. The $1/\tilde{d}$ dependence of $\mathcal{T}^*(\tilde{d})$ holds then only to first order in $1/\tilde{d}$.

4. Comparison with experiments

In this section we compare the prediction of our model with available experimental data on the dependence of the relaxation time for small glass-forming molecules in thin films. There are only few data available on the effect of the film thickness and the position of the molecules in the film, namely on the dependence of the relaxation time of interfacial molecules as a function of the thickness of the film that they belong to [15]. We also compare our theoretical results with the average relaxation time of salol molecules in lubricated pores of different sizes [13].

4.1. Interfacial relaxation time versus film thickness

These measurements were done with a liquid-crystalline glass former deposited by spin coating from a solution on fused quartz plates. In this deposition process, the solvent evaporates very quickly, leaving behind a film quenched in an amorphous state and not equilibrated. The subsequent appearance of a polar ordering at the interface with the substrate is followed by second-harmonic-generation measurements (for more details, see [15]). This interfacial relaxation is found to be exponential with a characteristic time growing exponentially as the film thickness increases (figure 4). For comparison, liquid-crystalline cyanobiphenyl molecules, which are similar to the liquid-crystalline groups of the glass-forming molecule studied but form no glass, show no dependence of their reorientation time at the interface with fused quartz plates over the film thickness range 20–200 Å [36].
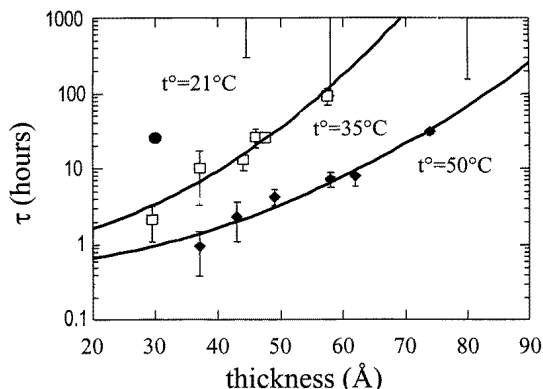

Figure 4. The thickness dependence of the interfacial relaxation time τ at three different temperatures below the bulk glass transition temperature $T_g = 110$ °C [38]. The lines correspond to least-squares fits to $\tau(d, T) = \tau_0(T) \exp(d/d_0(T))^2$.

The thickness of the measured films, which is tuned by the concentration of the solution, was determined by x-ray reflectivity measurements. This thickness remained constant during all of the dynamic measurements. X-ray reflectivity measurements also show that the density of the films is uniform within the films and remains so during the dynamic measurements. This absence of structural features across the films is expected since the spin-coating process quenches the films in a fully amorphous state. Films that were annealed at temperatures above the bulk glass transition temperature did not show any layering either. This layering is expected in the case of correlations in the positional order. The film density is also independent of the film thickness, showing that the observed changes in relaxation time are not due to density changes.

At room temperature, which is 90 °C below the bulk glass transition temperature of 110 °C, monolayers (corresponding to a thickness of 30 Å) are still relaxing within a day. This shows that the substrate has little effect on the dynamics of the interfacial molecules as regards their interaction with the rest of the material. So we can neglect the effect of the substrate interaction and apply the calculations presented above, which take only confinement into account.

Since measurements were made only for very thin films ($d < 80$ Å), it is likely that the film thickness is small with respect to the cooperative length. Our calculations then predict that the logarithm of the relaxation time should increase quadratically with film thickness. The experimental results are consistent with this dependence (figure 4).

The fact that we are in the regime of small thicknesses with respect to the cooperative length also explains why an exponential relaxation of the interfacial molecules is observed, instead of the usual stretched-exponential relaxation seen in glasses [1,2]. If one thinks that the stretched-exponential behaviour is due to spatial heterogeneities (see e.g. [37] and references therein), this means that spatial heterogeneities have been removed. This can indeed be the case, since the environment of the molecules has been made very similar for all of the molecules by the strong confinement between two surfaces. Moreover, from our calculations, we expect all of the molecules to have the same relaxation time (figure 3). If one thinks that the stretched-exponential behaviour is due to the cooperative character of the dynamics, this means that the dynamics is not cooperative any longer (see Ngai [39]). This is also the case, since the effective cooperative length, which is given by the film thickness, is very small.

4.2. Average relaxation time versus pore size

These measurements were performed using dielectric spectroscopy on porous glass (pore sizes 2.5, 5.0, and 7.5 nm) filled with salol. The pore walls were covered with silyl groups to prevent strong interactions between the glass-forming molecules and the walls [13]. This ensures that observed changes in the dynamics are only due to confinement effects.
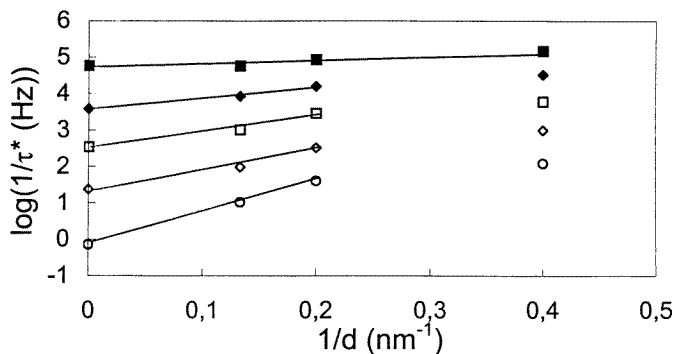

Figure 5. The dependence of the inverse average relaxation time $\log(1/\tau^*)$ on the inverse pore size $1/d$ for salol in lubricated pores at different temperatures [13]: (■) 242.8 K, (◆) 237.5 K, (□) 232.7 K, (◇) 227.4 K, (○) 222.6 K. The lines are linear fits to the data at 242.8 K and for $1/d < 0.2$ nm^{-1} at the other temperatures.

From the dielectric spectroscopy data, one gets in particular the temperature dependence of the average relaxation time τ^* defined by averaging the logarithm of the relaxation time. The temperature dependence of this average is affected by the pore size for temperatures below 256 K: $\log(1/\tau^*)$ decreases more slowly in pores than in the bulk as temperature decreases towards the bulk glass transition temperature of 222.2 K [13]. From these data, we have

determined the dependence of $\log(1/\tau^*)$ as a function of the inverse size of the system $1/d$ (figure 5). At high temperature ($T = 242.8$ K), $\log(1/\tau^*)$ depends linearly on $1/d$ over the whole range of thicknesses measured. For lower temperatures, this linear dependence only holds for small values of $1/d$ ($1/d < 0.2$ nm^{-1}). The departure from linearity for larger values of $1/d$ increases as temperature decreases.

This behaviour is in agreement with the predictions of our calculations of

$$\mathcal{T}^*(\tilde{d}) = (\log \tau^*(\tilde{d}) - \log \tau_0)/(\log \tau_{\text{bulk}}^* - \log \tau_0)$$

as a function of $\tilde{d} = d/\xi$. $\mathcal{T}^*(\tilde{d})$ is linear in $1/\tilde{d}$ for small $\tilde{d}$, and so is $\log \tau^*(\tilde{d})$ with a slope varying with $\log \tau_{\text{bulk}}^*$, in agreement with figure 5. Since ξ increases as temperature decreases, $\tilde{d}$ decreases for a given pore size d. This means that as temperature decreases, the departure from the linear law $\log \tau^*(d) \propto 1/d$ starts at lower values of $1/d$ and gets more pronounced for a given $1/d$, again in agreement with the trends observed in figure 5.

4.3. Summary

We have shown by a simple calculation how the collective dynamics of glass-forming molecules is expected to be modified by confinement, and compared the results obtained with available experimental data. There is however more experimental work to be done to test all of the predictions of these calculations.

Acknowledgments

Appendix

We give in table A1 the value of $\mathcal{T}(Z, d)$ (equation (4)) as a function of the normalized film thickness $\tilde{d} = d/\xi$ and the normalized position $\tilde{Z} = Z/\xi$ of molecules in a film. The expressions for the functions f_i ($i = 1$–6) are

$$f_1(\tilde{d}, \tilde{Z}) = \frac{3}{8} + \frac{27\tilde{d}}{80} + \frac{9\tilde{d}^2}{256} - \frac{\tilde{d}^3}{32} + \left(-\frac{27}{40} - \frac{9\tilde{d}}{64} + \frac{3\tilde{d}^2}{16}\right)|\tilde{Z}| + \left(\frac{9}{64} - \frac{3\tilde{d}}{8}\right)|\tilde{Z}|^2 + \frac{|\tilde{Z}|^3}{4}$$

$$f_2(\tilde{d}, \tilde{Z}) = \frac{1}{2} + \frac{3\tilde{d}}{10} - \frac{\tilde{d}^3}{32} + \frac{3\tilde{d}^4}{512} - \frac{\tilde{d}^6}{20\,480} + \left(-\frac{3}{5} + \frac{3\tilde{d}^2}{16} - \frac{3\tilde{d}^3}{64} + \frac{3\tilde{d}^5}{5120}\right)|\tilde{Z}|$$

$$+ \left(-\frac{3\tilde{d}}{8} + \frac{9\tilde{d}^2}{64} - \frac{3\tilde{d}^4}{1024}\right)|\tilde{Z}|^2 + \left(\frac{1}{4} - \frac{3\tilde{d}}{16} + \frac{\tilde{d}^3}{128}\right)|\tilde{Z}|^3$$

$$+ \left(\frac{3}{32} - \frac{3\tilde{d}^2}{256}\right)|\tilde{Z}|^4 + \frac{3\tilde{d}|\tilde{Z}|^5}{320} - \frac{|\tilde{Z}|^6}{320}$$

$$f_3(\tilde{d}, \tilde{Z}) = \frac{3\tilde{d}}{5} - \frac{\tilde{d}^3}{16} + \frac{3\tilde{d}^4}{256} - \frac{\tilde{d}^6}{10\,240} + \left(\frac{-3\tilde{d}}{4} + \frac{9\tilde{d}^2}{32} - \frac{3\tilde{d}^4}{512}\right)|\tilde{Z}|^2$$

$$+ \left(\frac{3}{16} - \frac{3\tilde{d}^2}{128}\right)|\tilde{Z}|^4 - \frac{|\tilde{Z}|^6}{160}$$

$$f_4(\tilde{d}, \tilde{Z}) = -\frac{1}{8} + \frac{51\tilde{d}}{80} + \frac{9\tilde{d}^2}{256} - \frac{\tilde{d}^3}{16} + \frac{3\tilde{d}^4}{512} - \frac{\tilde{d}^6}{20\,480} + \left(-\frac{3}{40} - \frac{9\tilde{d}}{64} + \frac{3\tilde{d}^3}{64} - \frac{3\tilde{d}^5}{5120}\right)|\tilde{Z}|$$

$$+ \left(\frac{9}{64} - \frac{3\tilde{d}}{4} + \frac{9\tilde{d}^2}{64} - \frac{3\tilde{d}^4}{1024}\right)|\tilde{Z}|^2 + \left(\frac{3\tilde{d}}{16} - \frac{\tilde{d}^3}{128}\right)|\tilde{Z}|^3$$

$$+ \left(\frac{3}{32} - \frac{3\tilde{d}^2}{256}\right)|\tilde{Z}|^4 - \frac{3\tilde{d}|\tilde{Z}|^5}{320} - \frac{|\tilde{Z}|^6}{320}$$

$$f_5(\tilde{d}, \tilde{Z}) = -\frac{1}{4} + \frac{27\tilde{d}}{40} + \frac{9\tilde{d}^2}{128} - \frac{\tilde{d}^3}{16} + \left(\frac{9}{32} - \frac{3\tilde{d}}{4}\right)|\tilde{Z}|^2$$

$$f_6(\tilde{d}, \tilde{Z}) = \frac{9\tilde{d}^2}{16} - \frac{9\tilde{d}^4}{64} + \frac{7\tilde{d}^6}{640} + \left(\frac{-9\tilde{d}^2}{16} + \frac{3\tilde{d}^4}{32}\right)|\tilde{Z}|^2$$

Table A1. The value of $\mathcal{T}$ as a function of $\tilde{d}$ and $\tilde{Z}$.

$\tilde{d}$	$\tilde{Z}$	$\mathcal{T}$
$\tilde{d} > 4$	$\tilde{d}/2 - 1 < |\tilde{Z}| < \tilde{d}/2$	f_1
	$\tilde{d}/2 - 2 < |\tilde{Z}| < \tilde{d}/2 - 1$	f_2
	$0 < |\tilde{Z}| < \tilde{d}/2 - 2$	1
$3 < \tilde{d} < 4$	$\tilde{d}/2 - 1 < |\tilde{Z}| < \tilde{d}/2$	f_1
	$2 - \tilde{d}/2 < |\tilde{Z}| < \tilde{d}/2 - 1$	f_2
	$0 < |\tilde{Z}| < 2 - \tilde{d}/2$	f_3
$2 < \tilde{d} < 3$	$2 - \tilde{d}/2 < |\tilde{Z}| < \tilde{d}/2$	f_1
	$\tilde{d}/2 - 1 < |\tilde{Z}| < 2 - \tilde{d}/2$	f_4
	$0 < |\tilde{Z}| < \tilde{d}/2 - 1$	f_3
$1 < \tilde{d} < 2$	$1 - \tilde{d}/2 < |\tilde{Z}| < \tilde{d}/2$	f_4
	$0 < |\tilde{Z}| < 1 - \tilde{d}/2$	f_5
$0 < \tilde{d} < 1$	$0 < |\tilde{Z}| < \tilde{d}/2$	f_6

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