Introduction

Human beings have been using natural glasses since the origins, producing daily tools like knives and arrow tips manufactured with the volcanic glass, obsidian [1]. But it is only in the past few thousands of years that man has started producing objects from sand (silicates). Glass-blowing is an even more recent discovery of mankind. We all have in mind a common sense of what a glass is, thinking usually of transparent silica based glasses, used in windows, bottles, glasses etc. Moreover there are now many applications that make use of high purity silica, such as optical fibers or bioactive implants.

In modern times the definition of a glass was extended to a more general class of materials. One defines as glasses all materials which, upon cooling from the liquid phase, do not undergo a classical crystallisation phase transition but become progressively more viscous, leading to a solid amorphous phase. This wider definition includes many other natural and synthetic materials present in our daily life: most polymers, glass ceramics, amorphous semiconductors, some proteins and several materials obtained with exotic new techniques, such as amorphous metals or alloys, dense colloidal suspensions, supercooled emulsions and many others. Understanding the nature of glasses has now become an issue that is not only of use for the work of the glass-blower, but also for the manufacturing and use in everyday life of plastic objects or more sophisticated technological devices. It is also important to
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She shed light on the behaviour of natural products and their ability not to crystallise far below their melting points. This property is exhibited, for example, by glycol used in cars as an antifreeze agent, but also in the body fluids of insects that need to survive in extreme cold or arid conditions. Besides these intuitive and practical applications, the understanding the glass phase remains a puzzling problem in condensed matter physics and in the last decades it has become the centre of increasing interest and ongoing research. The increasing attention for this unsolved problem has been sustained by the recent availability of appropriate experimental tools, as well as significant theoretical developments. Moreover, the ever growing simulation capacities of computers, offers nowadays conditions closer to realistic systems in size, temperature and time scale.

Although the word "freezing" is often used in the description of the glass transition, we should bear in mind that at temperatures below the glass transition, the dynamics does not stop. This is demonstrated by all aging phenomena such as stabilisation processes taking place at temperatures below the glass transition (eg. enhancing the mechanical strength). This applies to commonly used materials like polymers, which can have a glass transition temperature that is not far above room temperature. Sometimes the implications can be of practical interest, for instance the size change of an old plastic ruler. For other materials, such as common window glasses ($T_g \sim 800^\circ$C), they are far too deep into the glass phase to relax over human time scales at room temperatures. In particular, the fact that stained-glass windows of 12th century cathedrals are thicker at the bottom than at the top is probably due to the manufacturing technique and certainly not to a gravitational flow of the glass in 800 years [2, 3]. This flow would indeed only occur on geological time scales.

1.1 Glass transition

In the liquid phase of glass formers, the viscosity and any sort of relaxation time increase enormously upon cooling. Relaxation times eventually become longer than the experimental time scale, which is essentially the time during which the system is allowed to equilibrate after a change of an external parameter or constraint. As a consequence, no changes are observable anymore in the system and the structural configuration of the liquid appears to freeze. The temperature at which the dynamic arrest takes place is the so-called glass transition temperature $T_g$. The value of $T_g$ depends on the considered experimental time scale: the longer the system is allowed to equilibrate, the lower the temperature below which no changes take place in the
1.1 Glass transition

Figure 1.1: Schematic plot of the structural entropy vs. temperature for a liquid cooled below the melting point. $T_m$ is the melting temperature, $T_{g1}$, $T_{g2}$ and $T_K$ are the glass transition temperatures corresponding to different cooling rates.

allowed equilibration time. In experiments in which a property is followed in time after a sudden change of experimental conditions (e.g. temperature jump, switching an external field on or off, etc.), the experimental time scale is simply the time over which the system evolution is followed. In experiments in which conditions are changing at a constant rate (e.g. heating or cooling), the experimental time scale is inversely proportional to this rate. In this respect, the glass transition is seen to be kinetic in nature. Indeed, by studying static properties, it is impossible to discriminate between a glass and its corresponding liquid: neither of them presents the long range order typical of a crystalline phase.

Let us consider in more details the cooling of a glass-forming liquid. Fig. 1.1 schematically represents the behaviour of a macroscopic thermodynamic property, as structural entropy (or specific volume), versus temperature. Upon cooling from the liquid phase, the system does not undergo a transition into the crystal phase, but is supercooled below the melting point. The thermodynamic property follows the extrapolation to lower temperatures of the law observed in the liquid phase. With further cooling, the dynamics of the molecules is slowed down so much that they cannot explore their whole phase space anymore. This breaking of ergodicity leads to a deviation from the equilibrium configuration of the system. The temperature at which this happens is defined as the kinetic glass transition temperature $T_g$. As the temperature is further decreased, any rearrangement becomes impossible at
the experimental time scale and the molecules are stuck in a structural state out of equilibrium, with an entropy higher than that of the crystalline phase. If the cooling rate is lower, the system gets more time to equilibrate. Therefore the glass transition will occur at a lower temperature and the entropy of the glassy state will be closer to that of the crystal. Eventually, at a certain cooling rate the entropies of the glassy and crystalline states will coincide. The extrapolated temperature at which this happens is known as the Kauzman temperature $T_K$ (Fig. 1.1). By continuing to reduce the cooling rate, a stage is in principle reached where the entropy becomes zero (or even negative), at a temperature above zero. This is the so-called entropy paradox by which the third law of thermodynamics is violated.

Since the value of the glass transition temperature depends on the way it is measured, more or less standard conditions have been adopted to determine $T_g$ experimentally [4]. In dilatometry measurements, consisting in following the dependence of the specific volume as a function of temperature (as explained above), $T_g$ is measured with temperature cycling rates between 1 and 20 Kmin$^{-1}$. The same cooling rates are used for differential scanning calorimetry (DSC), which is actually the most common technique for measuring $T_g$. In this case, the specific heat capacity of the material is measured as a function of temperature, with the glass transition characterised by a sudden increase of the heat capacity (see also Sec. 2.3.1). Another way of defining $T_g$ is to consider the temperature at which the average relaxation time of the system equals a given value taken as the experimental time scale (see Sec. 1.2). This time scale is fixed by convention to 100 sec. How much $T_g$ changes if this value varies depends very much on the material considered (see next Section and Fig. 1.3). Similarly people use also measurements of the shear viscosity $\eta$ of the material, defining $T_g$ as the temperature at which $\eta$ reaches the value of $10^{13}$ poise. Since the values of $T_g$ measured by these different methods agree quite well, databases give generally "the" value of $T_g$ for a given material, without specifying the experimental conditions.

Another consequence of the fact that the glassy state is not a thermodynamic equilibrium state is that the exact state of the system depends on the history of the sample [5]. So to perform experiments with glass-forming materials in a reproducible way, it is necessary to first anneal the system at high temperature in the liquid state, which is an equilibrium state. This gives a well-defined starting point that is independent of the history. Then the system should be brought to the desired temperature following a well-defined procedure (generally a constant cooling rate).
1.2 Relaxation dynamics

The glass transition described above takes place as the characteristic structural rearrangement time exceeds the experimental time scale. This behaviour stresses the importance of dynamics as a key factor in this process, disconnecting it from structural considerations.

The term “relaxation time” that we have used so far, should be taken in a wide sense: it can be any kind of characteristic time that describes dynamic processes in complex fluids. These processes, will first, of all include the rotational and translational motion of the molecules. In a simple liquid, the characteristic rearrangement time $\tau$, corresponding to such motion, depends exponentially on the inverse temperature. In a so-called Arrhenius plot of log $\tau$ as a function of $1/T$, a straight line is obtained. In a glass-former, the Arrhenius plot gets a more complex structure (Fig. 1.2), because motion takes place on very different times scales [6]. Already in the high temperature range (low $1/T$), different relaxation processes take place. The molecular transient process $A$, bifurcates into the high-temperature process $a$ (also known as $\alpha\beta$), which is well described by the mode coupling theory (MCT) from

![Figure 1.2: Modified Arrhenius plot of the logarithm of the relaxation time $\tau$ vs. inverse temperature $1/T$ for a moderate glass-forming liquid. The different curved correspond to different relaxation processes (see text): (A) molecular transient process, (a) high temperature process, (b) boson peak, (c) cage rattling, (α) structural relaxation and (β) local slow relaxation.](image-url)
Götze [7], and into the cage rattling $c$ mode (also known as fast $\beta$) that corresponds to local motion of molecules inside cages formed by the surrounding molecules. The boson peak $b$ (detected by neutron scattering) is also present in the supercooled phase, and is temperature independent, as is mode $c$. The boson peak is associated with a low-frequency vibrational mode or group of modes. At the crossover temperature $T_C$, a bifurcation takes place. The structural relaxation process, known as the $\alpha$ process, becomes significantly slower than the local (slow) $\beta$ relaxation identified in the '70s by Johary-Goldstein. In the supercooled liquid other more exotic modes can be identified, especially when the glass former is a complex system such as a polymer [8]. The descriptions of these systems is beyond the scope of this thesis and will not be included in the discussion.

The crossing of the glass transition is associated with the slowing down of the structural relaxation corresponding to the $\alpha$ process, which is the dominant mode. Different laws are used to describe the temperature dependence of the corresponding relaxation time. They are all adaptations of the Arrhenius law observed in simple liquids, which describes the temperature dependence of the relaxation time with a simple exponential law [9]

$$
\tau = \tau_0 \exp \left[ \frac{E_a}{k_B T} \right],
$$

where the energy $E_a$ is the temperature-independent activation energy, i.e. the energy to be overcome by a molecule in the relaxation process and $\tau_0$ is a constant for the system. For glass dynamics, a phenomenological adaptation was suggested in the '20s with the Vogel-Fulcher-Tammann (-Hesse) law [10, 11, 12]

$$
\tau = \tau_{VFT} \exp \left[ \frac{B}{T - T_{VFT}} \right],
$$

where $B$, $\tau_{VFT}$ and $T_{VFT}$ are constants. These laws were interpreted a few decades later with a microscopic model considering the free space in between molecules (so-called free volume theory). The parameter $B$ gives the strength of the non-Arrhenius character of the dynamics. $T_{VFT}$ is a characteristic temperature below the observed glass transition temperature. Other laws have been proposed to fit the temperature dependence of experimental relaxation times, like power laws

$$
\tau = \tau_0 \exp \left[ \frac{T - T_{VFT}}{T_{VFT}} \right]^{\delta}.
$$
For polymer systems the equivalent of Eq. 1.2 is often used for the average relaxation time (so called Williams-Landel-Ferry (WFL) law)

\[ \langle \tau \rangle = \langle \tau \rangle_{T_g} \exp \left[ \frac{-C_1(T - T_g)}{C_2 + T - T_g} \right] \tag{1.4} \]

where \( C_1 \) and \( C_2 \) are positive constants.

The deviation from the Arrhenius law has been quantified by Angell [13] using the concept of fragility. Angell plotted the shear viscosity, which is proportional to \( \tau \), versus reduced inverse temperature \( T_g/T \), defining \( T_g \) as the temperature at which the viscosity reaches \( 10^{12} \) Pa·s (=\( 10^{13} \) poise) [9, 13, 14, 15]. With this scaling, he obtained a masterplot in which the viscosity of all the considered substances falls on common non-Arrhenius curves for similar values of a parameter \( m \) called fragility. Fig. 1.3 shows a schematic representation of the equivalent plot for the relaxation time \( \tau \). This is actually a modified Arrhenius plot. \( T_g \) is then defined by \( \tau T_g = 100 \) sec. The lines correspond to the dependence of \( \tau \) for different values of the fragility \( m \), calculated using Eq. 1.2 written in the following form:

\[ \log \tau = \log \tau_{T_g} - m_0 + \frac{m_0^2(T_g/T)}{(m - (m - m_0)T_g/T)} \tag{1.5} \]

with

\[ m_0 = \frac{B}{(T_g - T_{VFT}) \ln 10} \]

\[ m = \frac{B T_g}{(T_g - T_{VFT})^2 \ln 10} = m_0 + m_0^2 \ln 10 \frac{T_{VFT}}{B}. \tag{1.6} \]

\( m \) is actually the slope of the curve \( \log \tau \) versus \( T_g/T \) at \( T = T_g \):

\[ m = \left. \frac{d \log \tau}{d(T_g/T)} \right|_{T = T_g}, \tag{1.7} \]

The parameter \( D = B/T_{VFT} \) is called the strength parameter. \( m_0 \) is the lower limit found for \( m \) in strong glasses. It corresponds to an Arrhenius behaviour \( \tau = \tau_A \exp(E_A/T) \) with \( \tau_A = \tau_{T_g} \exp(-m_0 \ln 10) = 10^{-14} \) sec. Materials with a high fragility \( m \) (small strength parameter \( D \)) are typically polymers, while silica, known to be a strong glass former, has a fragility \( m = 20 \).

\section{1.3 Models of glass formation}

So far, we have dealt with the macroscopic behaviour of glassy materials, but of course, the question arises why these systems exhibit such a slowing down of dynamics. A deep detailed knowledge of the nature of the glass transition is still
lacking and reaching it is a challenging goal. Many theories have been proposed [16, 17, 18, 19] and revisited, but all fail to explain the whole collection of typical features of the glass transition. Somehow each theory applies to a limited range of conditions, either thermodynamic or kinetic. Theories like the original or the successive elaborations of Mode Coupling Theory (MCT) are more suitable in describing the origins of the dynamic slowing down, taking place far above the glass transition. Since we are interested in the behaviour of confined glassy systems around and below the glass transition, we need a theoretical model applicable over the whole relevant temperature range and in which size plays a prominent role.
1.3.1 Cooperatively rearranging regions and dynamic heterogeneities

One of the widely used theories of the glass transition is that of Adams and Gibbs [20], which is based on the concept of cooperatively rearranging regions, CRR. As the temperature of a liquid decreases towards the glass transition state, the motion of the molecules is no longer independent, but the dynamics becomes correlated over a certain number of molecules. The spatial extent of this correlation is generally defined as the cooperative length $\xi$. As depicted in Fig. 1.4, the CRRs can be thought of as regions where the dynamics, either rotational or translational, is collective, i.e. all the molecules in the region need to move together to allow some restructuring. As the temperature approaches and crosses $T_g$, the length $\xi$ diverges exponentially at a temperature $T_b$ lower than $T_g$. As $\xi$ increases, relaxations become more and more unlikely and the average relaxation time increases dramatically. The temperature dependence of $\xi$ is related to that of the configurational entropy that becomes zero at $T = T_b$. A later model of Ngai [21] considered the CRRs as not being independent but having mutual interactions. This extension of the model is suitable for explaining calorimetric and dielectric experimental data.

Parallel to the development of theories based on the idea of cooperative motion, other models focused on explaining the fact that the dominant $\alpha$-relaxation is highly non-exponential. This non-exponentiality can be related to the superposition of relaxation processes with different relaxation times. This gave rise to the notion of dynamic heterogeneities, composed of slow and fast relaxing regions [22]. The contours of these regions probably fluctuate along with the relaxation rate inside

Figure 1.4: Sketch of a cooperatively rearranging region, growing as temperature decreases. The cooperative length $\xi$ is indicated by the arrows.
the regions [23].

Collectively rearranging regions and dynamic heterogeneities are actually related concepts. CRRs are, in fact, fast relaxing regions surrounded by slow or immobile molecules. So the length scale of heterogeneities and the cooperative length should essentially be the same. Both simulation and experiments have been used to provide evidence for the existence of such a length scale and to evaluate it.

Simulations

Computer simulations were already attempted several decades ago (see eg. [24]), but it is only recently that computing power has made it feasible to simulate sufficiently large systems of glass-formers [2, 25]. The advantage of computer simulations is that the positions of particles are known at every simulation step, making it possible to calculate different characteristics of the system, such as time-dependent density correlation functions. Spatially correlated heterogeneities have been found by molecular dynamics (MD) simulations of Lennard-Jones binary systems [26] as well as by Monte Carlo simulations [27]. An original finding is that CRRs would not have a compact shape but instead a string-like structure [28].

Experiments

Several established techniques can be found in literature, to determine directly or indirectly the characteristic length associated to dynamics in bulk glass-formers, although the associated meaning differs from one author to another. Some consider a characteristic length as the size of clusters present in the system, while others use the correlation length from density-density correlations.

Long-range optical inhomogeneities were found by Rayleigh-Brillouin spectroscopy on ortho-terphenyl, an unusual but widely studied glass-former [29]. Samples with clusters were prepared by opportune control of the thermal history. The dynamic cluster sizes were determined by assuming a density fluctuation model for the rotational relaxation time. The temperature dependence of the length scale $\xi(T)$ in the temperature range $[T_g, T_g + 80^\circ \text{C}]$ was found to be a power law

$$\xi(T) \sim (T - T_{VT})^{-\nu}$$

(1.8)

with $\nu = 0.69$ [30].

In polymeric materials studied by NMR [31], the molecular dynamics is dependent on the polydispersity and is non-Arrhenius. This was interpreted by the
formation of clusters containing a few chain units, appearing already at temperatures far above $T_g$. Multidimensional NMR has proven to be a more powerful technique for identifying such heterogeneities and their spatial and temporal fluctuations [22]. With a specifically selected series of excitation pulses, it is possible to probe molecules with a higher or lower mobility [23, 32, 33], which provides a selectivity in mobility similar to that obtained using computer simulations [28]. The main advantage of this experimental technique is to probe the length scale of the dynamic heterogeneities in a non-perturbative way. At temperatures just above $T_g$, this length scale was found to be around 3 nm in poly(vinylacetate) [23] and 1 nm in glycerol [32]. Another interesting piece of information on collective motion can be derived from studies of the high-frequency relaxation modes, such as the cage rattling and/or the boson peak ($c$ and $b$ modes in Fig. 1.2). These modes give information on the character of the corresponding motion. These processes are of vibrational nature and can be analysed using inelastic coherent neutron scattering [34]. Atomic motions at small wave numbers correspond to a length scale of several times the nearest neighbours’ atomic distance. Experiments on Ca$_{0.4}$K$_{0.6}$(NO$_3$)$_{1.4}$ revealed the existence of randomly flowing collective displacement of a large number of neighbouring atoms.

Other methods to probe heterogeneous dynamics are dielectric and optical measurements. A special dielectric technique consists in following the recovery process in the dielectric spectra after inducing a non-resonant spectral burning in the studied material [35]. The refilling of the spectral holes is consistent with the existence of short-living spatial heterogeneities. A physical localisation of slower molecular ‘clusters’ was also obtained by measuring dielectric fluctuation at the nanometer scale performed by using an AFM tip as the sensor [36].

Similar to the dielectric hole burning, photobleaching techniques allow one to observe heterogeneities in glass-formers by following the recovery of dynamically selected molecules. The rotational dynamics of dilute optical probes can be followed after appropriate photobleaching of the more mobile probe molecules in a sample [37]. The relaxation profiles are consistent with the presence of spatial heterogeneities.

But it is only recently that an optical experiment has provided direct evidence of the presence of spatial heterogeneities in mesoscopic systems. Van Blaaderen [38] and Weeks [39] observed fast relaxing regions surrounded by slow ones in polydisperse colloidal hard-sphere suspensions [38] using confocal fluorescence microscopy on specially prepared fluorescent silica colloids [40].

Characteristic lengths have also been determined by analysing calorimetric heat capacity scans, applying a fluctuation theory of the glass transition [41, 42]. The
obtained values at $T_g$ or just above it, are of the order of a few nanometers, both for low-molecular weight and polymeric systems. These values are slightly larger than those determined with NMR or simulation techniques [43]. This could be explained by the fact that the size of the dynamically distinguishable sub-units probed by the latter techniques, only represent a upper limit for the size of CRRs.

1.3.2 Non-exponentiality

If a system is dynamically heterogeneous, this implies that there is a certain distribution of the relaxation times in the system. As a consequence, the time relaxation of any property will not be a single exponential. Observable relaxations of a physical quantity $\Phi$ are often fitted by the Kohlrausch-Williams-Watts (KWW) law:

$$\Phi(t) = A e^{-(t/\tau)^\beta},$$

(1.9)

where $A$ is a constant and $\tau$ is a characteristic relaxation time. The stretch exponent $\beta$ is related to the width of the distribution of relaxation times, and $\tau$ is a characteristic relaxation time. If $\beta = 1$, $\Phi(t)$ becomes a single exponential law and corresponds to a Dirac distribution of relaxation times peaked at $\tau$. A decreasing value of $\beta$ below 1 indicates a widening of the relaxation times distribution.

A broad distribution of relaxation times is generally considered as being at the origin of the non-Arrhenius temperature dependence of the $\alpha$-relaxation time. The link between non-Arrhenius behaviour and non-exponential relaxation is strengthened by the rather good correlation between the exponent $\beta$ (Eq. 1.9) and the fragility $m$ (see Sec. 1.2). In a plot of $m$ vs. $\beta$, most materials with $\beta < 0.8$ fall on the line [9]

$$m = 250 - 320\beta$$

(1.10)

It has long been debated whether the non-exponential character of glassy dynamics is due to intrinsic non-exponential dynamics, with all regions in the material presenting a complex dynamics, or whether it is the result of heterogeneities with a distribution of fully exponential relaxation functions throughout the system. In the heterogeneous dynamics scenario, we can describe the system as being made of a distribution of relaxators $i$ (that can be visualised as nanoscopic regions within the glass-former) having a defined time constant $\tau_i$

$$\Phi(t) = \sum_i g_i e^{-(t/\tau_i)},$$

(1.11)
where \( g_i \) is the probability density of the relaxators \( i \) with relaxation time \( \tau_i \). In the case of intrinsic non-exponentiality, one assumes that the relaxation of each relaxator is non-exponential and described by a response function \( f(t, \tau) = \exp\left[-(t/\tau)^{\beta_{int}}\right] \) with an exponent \( \beta_{int} \) and a distribution function \( g_{\beta_{int}} \) of these exponents [44]. The total response function of the system is then

\[
\Phi(t) = \sum_i g_{\beta_{int}} \exp\left[-(t/\tau_i)^{\beta_{int}}\right],
\]

with \( 0 < \beta \leq \beta_{int} \leq 1 \).

There are several theoretical and experimental studies validating the heterogeneous dynamics scenario (Eq. 1.11) (see [45, 46, 47]), although the apparent distribution of relaxation times is not necessarily associated to regions of different densities and entropies. On the other hand, local dielectric measurements performed with an AFM tip found that the dynamics is non-exponential in individual homogeneous regions [36].

Relaxation processes other than the \( \alpha \)-relaxation, related to individual molecular mobility, have been proven to be spatially uniform, both above and below the glass transition. This is particularly the case for the \( \beta \)-relaxation, which shows spatial uniformity [48].

### 1.4 Dynamics in confined geometries

Generally speaking, confining a system to a scale comparable to a characteristic length scale inside the system, results in significant deviations of the structural and dynamical properties with respect to the bulk. In glass-formers, the concept of cooperativity suggests that the dynamics of the system should be modified if the size of the system becomes comparable to the cooperative length \( \xi \). In this size range, it is the size of the system that determines the size of cooperatively rearranging regions (Fig. 1.5) and therefore the dynamic behaviour of the system. The cooperative length in several low-molecular weight glass-formers has been estimated to be of the order of a few nanometers for temperatures approaching \( T_g \) from above. Theories predict that this length should increase as temperature decreases. So one expects modifications of the dynamic behaviour in glassy systems with sizes in the mesoscopic range. In the following we review the known effects of confinement on the dynamic behaviour of glass-formers. Thereby we make a distinction between two different effects. The first one (referred to as pure confinement or pure geometrical effect) comes from the change in the size of the system, disregarding the way this size is imposed. This effect of size on the dynamics and the glass transition is discussed
in the next two sections. In the last Section, we discuss the role of the interactions with the confining walls that have to be taken into account in most experimental realisations of confinement.

1.4.1 Effect of pure confinement on dynamics

Taking into account only pure geometrical effects (without interactions with walls) and assuming the presence of cooperatively rearranging regions of size $\xi$, we can intuitively expect the following changes in the dynamic behaviour of glass-formers when they are confined in thin films. For thicknesses rather large with respect to $\xi$, confinement only affects molecules in the vicinity of the surfaces (Fig. 1.5). Surface molecules belong to cooperatively rearranging regions that are smaller than the ones present in bulk. Therefore their relaxation should be faster than that of molecules in the middle of the system. As the size of the system decreases, the proportion of molecules affected by the surfaces increases. As a consequence, the distribution of relaxation times in the system should broaden towards the short time scales leading to a decrease of the mean relaxation time. When the film thickness becomes comparable with $\xi$, all molecules are affected by confinement and the size of the cooperatively rearranging regions is determined by the size of the system. Decreasing the size even more down to a molecular size will make the system homogeneous again, with all molecules having essentially the same environment. However, the relaxation time will be smaller than the value in bulk, because the motion of the molecules becomes essentially individual again.
Most of the experiments performed on low-molecular-weight glass-formers confirm the above qualitative picture. They have been performed using porous glass for 2-D confinement and cavities in butyl rubber for 3-D confinement. Possible attractive interactions with walls are then suppressed by silanisation of these walls [49].

The characteristic time corresponding to the $\alpha$ orientational relaxation, as measured by dielectric spectroscopy, is generally decreasing as the size of the system decreases [49, 50, 51, 52, 53, 54]. Translational diffusion measured by NMR also tends to increase under confinement, but to a lesser extend than rotational motion [54]. The reduction in relaxation time is larger for 3-D confinement than for 2-D confinement, but it appears at approximately the same system size [51, 52, 53]. The expected broadening of the distribution of relaxation times is also observed with dielectric spectroscopy [49, 50, 52, 53, 55, 56]. Similar results were obtained also in Monte Carlo simulations [57].

There are very few results on systems confined down to the molecular size, and they are rather contradictory. In molecularly thin films, the reorientational dynamics was observed to be exponential [58], which suggests a narrow distribution of relaxation times. On the contrary, ethylene glycol confined in zeolite pores as small as 7 Å in diameter still showed a bulk-like dynamic behaviour [59].

From the effects of size on the dynamics, it is possible to make an estimation of the cooperative length $\xi$. The value of $\xi$ for salol in the vicinity of the calorimetric glass transition temperature was estimated to be $\geq 70$ Å [50]. Similar values of $\xi$ at $T_g$ were obtained for another H-bonded material (propylene glycol, with $\xi \leq 60$ Å) and for the non-associating liquid $N$-methyl-$\epsilon$-caprolactam ($\xi \leq 120$ Å) [60]. These values are larger than the ones measured in bulk systems (see Sec. 1.3.1).

There is much more work done on polymeric materials confined in thin films, but it concerns mainly the glass transition (see Sec. 1.4.3) and not the dynamics itself. One advantage of polymers is the possibility of studying free-standing films, in which interactions with a wall are totally absent. The relaxation dynamics has been studied in such films made of a high-molecular weight polystyrene (Mw=767kDa) using photon correlation spectroscopy [61]. The mean relaxation time was found to be significantly lower than in bulk while the relaxation dynamics followed the same stretched exponential as in bulk. In contrast a significant broadening of the distribution of the relaxation times has been observed in films supported by a substrate [62, 63].

Other measurements probe only the dynamics close to the free surface, using different techniques, but the results are very contradictory: some experiments show
an enhanced mobility at the free surface (which would lead to a broadening of the
distribution of relaxation times in thin films) while others show no sign of such an
enhancement [64, 65].

We should however keep in mind that the behaviour of polymeric systems cannot
really be compared with that of low-molecular weight systems. As already mentioned
in Sec. 1.2, polymers are also subject to several effects directly linked to the con-
finement of chains in a finite space. This is underlined for instance by the strong
molecular weight dependence of all confinement effects [64, 65].

1.4.2 Effect of pure confinement on the glass transition

The variation of the distribution of relaxation times in confined systems should
result in changes of dynamic macroscopic properties. If the relaxation time distribu-
tion shifts towards shorter time scales and the average relaxation time \( \langle \tau \rangle \) becomes
smaller then the temperature, at which \( \langle \tau \rangle \) becomes equal to the experimental time
scale \( \langle \tau \rangle =100 \) sec), decreases. So we expect to observe a decrease of the glass
transition temperature \( T_g \). Such a decrease has indeed been observed, both in low-
molecular weight glass formers [66, 67, 68] and polymeric systems [69, 70, 71]. How-
ever the glass transition temperature shifts is significantly smaller in low-molecular
weight systems than in polymers. In the first category of materials, the most pro-
nounced \( T_g \) depression, registered for salol in a 2.5 nm pore size, was of 15 °C [72].
The largest shifts in polymers (70 °C) was observed in polystyrene free-standing
films [71].

From the broadening of the distribution of relaxation times, we expect that
different parts of a confined system would exhibit a glass transition at different
temperatures. This inhomogeneity of the glass transition temperature is generally
used as an explanation for the decrease of the overall glass transition temperature in
polymer films [64, 65]. This inhomogeneity should lead to a broadening of the glass
transition. Surprisingly enough, such a broadening has only been observed in one
study of supported polymer films [70]. In all others and in studies of free-standing
polymer films, such a broadening has not been observed [64, 73, 74, 75]. This is one
of the main puzzles in the field. For low-molecular-weight glass formers, a smearing
out of the transition region has been observed by calorimetry in o-xylene dispersed
in a microemulsion, although artifacts due to changes in the heat flux through the
dispersed medium cannot be excluded [76]. In thin films, there was no study of
the glass transition till our measurements presented in Chap. 3, so the question was
totally open.
1.4.3 Effect of interactions with a wall

So far we have concentrated our discussion on the effect of pure geometrical confinement. In experiments, however, this confinement has generally to be imposed by walls to obtain a stable system. It is known by now that the interactions between the glass-forming molecules and the walls can have a strong influence on the dynamics. This conclusion is mainly drawn from studies performed in polymer systems. In free-standing films of polystyrene, in which such interactions are absent, the decrease of the glass transition temperature \( T_g \) under confinement is large (up to \( 70 \, ^\circ C \)) [71]. When the films are supported by oxidised silicon wafers and glass, which have rather small interactions with polystyrene, the shift in \( T_g \) decreases significantly (\( \sim 30 \, ^\circ C \)) [64]. When the films are supported by hydrogen-passivate silicon wafers, which interact strongly with polystyrene, \( T_g \) increases as the size of the system decreases [77].

The same increase is observed in all other systems with strong polymer-substrate interactions [78, 79] while the opposite behaviour is observed in systems with small interactions [63, 69, 70, 79, 80, 81].

Effects due to the walls have also been observed for low-molecular-weight glass-formers confined in pores with bare walls. The broadening of the distribution of relaxation times towards the long time scales has been interpreted as the result of a lower mobility of the molecules in contact with the walls, due to their strong interaction with walls [49, 55, 82, 83].

1.5 Aim of our work and outline

The origin of the formation of glasses is still a puzzle. The idea that motion is collective explains several features of glass formation, but many questions remain open, in particular on the length scale at which collective motion takes place. The existence of this length scale implies that the size of the system should have a significant influence on the dynamics of the system. This raises several questions. \textit{How is the dynamics affected if we reduce the size of the system around or below the cooperative length? How is the distribution of the relaxation times then modified? What are the consequences for the glass transition?}

As reviewed in the previous section, research aiming at answering these questions has concentrated on two types of systems: polymers in thin films and low-molecular-weight glass-formers in porous media. Because of their chain character, polymers exhibits bulk dynamic processes and a behaviour under confinement that is specific to these materials rather than generic for glasses in general. Confinement in porous media introduces curvature effects and is not well defined in size because of
the polydispersity in pore sizes and the presence of pore junctions. To overcome these problems, we have studied the dynamic behaviour of low-molecular-weight glass-formers in thin films. We have chosen two hydrogen-bonded glass-formers, with a fairly simple chemical structure, from which we can expect relatively simple relaxation processes.

Thin films are easy to prepare by direct deposition or coating (as we used) on open surfaces, allowing us to prepare homogeneous samples with a well-defined thickness over large areas. Moreover the sample reproducibility is very good due to the easy control of sample preparation conditions like cleaning of the substrate or control of the external environment. Last but not least, intrusive and destructive investigative probes as well as non-destructive ones, like the probes we have used, can directly be applied on thin films.

In Chap. 2 we present the physico-chemical characterisation of the two materials synthesized for our purpose. The preparation of the films by spin coating and the subsequent characterisation of the films by atomic force microscopy are also discussed.

Chap. 3 is dedicated to a study of macroscopic properties of the films, namely the thermal expansivity and the glass transition. The dependence of the film thickness versus temperature was determined by x-ray specular reflectivity for a wide range of as spun thicknesses. We show that confinement significantly modifies the behaviour of the films for thicknesses below ~100 nm. We use a simple model to qualitatively interpret our results in term of the distribution of relaxation times inside the system.

Among non-destructive techniques, linear and non-linear optical techniques are widely used, the latter being more powerful and presenting a wide variety of possible applications. One of the materials we have studied carries non-linearly polarisable units. We used this specific substance for carrying out second-harmonic generation (SHG) measurements on thin films similar to those used in Chap. 3. The basic theory of this optical technique is presented in Chap. 4.

SHG was used to probe reorientational dynamics of the non-linearly polarisable groups after orienting them with an external strong DC electric field. The relaxation response was followed over 11 orders of magnitude in time, covering time scales from 1 µsec up to several days. Chap. 5 shows how such a wide time range could be obtained experimentally. Measurements at time scales below 1 sec required a specific signal collection method involving switching the external DC field in short time, synchronisation with the signal collection, and the measurement of very low signals. An example of application of this technique is shown, which allows us to resolve dynamic feature of liquid crystalline thin films in the microsecond domain.
In Chap. 6 we present our results for the relaxation dynamics of glass-formers as a function of temperature and film thickness. The measured relaxation functions are fitted with a stretched exponential law, from which we determine the distribution of relaxation times in the film. These results are compared with the macroscopic measurements performed in Chap. 3.