Summary

"It is therefore probable that, at the right cooling rate, all or at least most substances, even if in small amounts, can be transformed into the glass state."

G. Tammann, 1933.

The statement of Tammann, besides being 70 year old, can give an idea of the importance of the glass phase as a relevant state of matter.

The common sense of the word glass is associated to the silica and derivated glasses with which human beings make objects such as windows, bottles, monitors, lamps bulbs etc. The most modern scientific definition of a glass is much wider and includes all the liquids that upon a proper cooling procedure fall out of equilibrium. The viscosity of the liquid increases exponentially and the molecules undergo a freezing-in of the dynamical configuration, but does not crystallise. The temperature at which this occurs corresponds to the glass transition temperature $T_g$. With such a definition many other materials also of daily use are included, such as polymers (plastics), glass ceramics, amorphous semiconductors, some proteins and other more sophisticated materials. In this perspective, understanding the origin of the glass phase becomes of significant value as a theoretical achievement and for all practical applications. In the last few years the glass transition became one of the most studied topics in soft condensed matter physics, ranking among the first for the amount of published papers. Most of the studies concern experimental studies while little has been achieved in theoretical models.

Among the available theoretical the cooperative model of Adam and Gibbs model has gained a lot of consideration. Such a model is based on the concept of cooperatively rearranging regions. Upon cooling of a liquid from a high temperature,
the motion of the molecules becomes no longer independent but correlated over a certain number of molecules in a radius $\xi$. As the temperature further decreases the cooperative length $\xi$ is thought to increase. The introduction of a size as relevant variable in the study of the glass transition suggests that the overall size of the system should be an important parameter.

In this thesis we consider the effects of changing the size of the system on the dynamics of glass materials at temperatures above and below the glass transition. The presence of interfaces/walls affects the dynamics introducing inhomogeneity throughout the material.

Known studies in literature often focus in polymeric materials that are more directly of practical use or allow producing free-standing films as confining geometry. On the other hand they have the drawback of not being molecular model systems due to the complexity of the dynamics, once experimental results are compared to theoretical models or computer simulation. For this reason we adopted two low-molecular-weight compounds with a fairly simple chemical structure. The two compounds described in Chap. 2 are part of the same family and can be considered as similar in terms of dynamical behaviour. Both compounds are hydrogen-bonded glass-formers and can be included in the polyalcohol class of glass-formers. One of the two compounds carries polar non-linearly polarisable groups and is used in particular in non-linear optical experiments in Chap. 6.

As confining geometry we adopted thin films (with thicknesses between 10-120 nm). Low-molecular-weight materials have the disadvantage that they cannot form stable free-standing films. They can therefore only be studied as supported films. The presence of a solid wall has been shown to produce opposite effects on the molecular dynamics in thin films. Which effect dominates depends on the strength of the glass-substrate interaction. For weakly interacting systems, the substrate wall plays a role comparable to that of a free interface with an increased mobility in the vicinity of the interface. To confirm the hypothesis that dimensionality affects the dynamics we decided to follow a macroscopic property of the system, namely the volume, as a function of the temperature. In thin films it is equivalent to measure the film thickness. In Chap. 3 we present a study of the films thickness versus temperature for a series of different initial film thicknesses. The main results are a widening of the range in which the glass transition takes place and an increase of the expansivity of the film at temperatures above $T_g$ as the film thickness decreases. The first result is in agreement with the predictions of a simple model for a glassy system in a confined geometry: for a system with decreased dimension one expects an increase of the dynamic inhomogeneity, due to the effect of the interfaces. Molecules
at different positions in the film experience different glass transition temperatures and in the distribution of values of \( T_g \) is wider in thin films than in thick films. The second result on the expansion coefficient confirms the starting hypothesis of a small interaction of the glass-formers with the substrate.

In the second part of the thesis we looked at a different property of the materials, namely the dynamical reorientation after orienting the non-linearly polarisable groups with an external strong DC electric field. The reorienting dynamics can be followed by optical second-harmonic generation. In Chap. 4 we present the basic concept of this non-linear optical technique together with consideration on the symmetry of the second-order susceptibility tensor for a system as ours that changes from a mirror symmetry in the poled state to an isotropic symmetry in the relaxed state. A detailed knowledge of the overall system characteristics allows choosing the most suitable parameters for sample configuration and optical settings.

In studies of the molecular dynamics in the time or in the frequency domain the extend of the covered range of time or frequency becomes very important to describe properly the overall behaviour of the system. For this reason we followed the reorientation dynamics exploring 11 orders of magnitude in time scale. For our experimental setup this approach introduced an experimental challenge when moving to short times (<3 sec). Indeed we had to take into consideration the switching off of the strong applied DC field in the shortest time possible and its synchronisation with the pulse sequence of the incident laser used to measure the second-harmonic signal. To solve this problems we developed a dedicated collection setup and software able to extend measurements down to 1 \( \mu \)sec. In Chap. 5 we report the details of the protocol together with the application of the procedure on a material system having an unsolved dynamic feature in the short time domain. A thin supported film of a supercooled liquid crystal had previously been seen to have two relaxation processes for times \( t > 1 \) sec but an unknown behaviour at shorter time. With our equipment we could resolve two other fast relaxation processes, probably to be associated to molecules having a higher mobility than the rest.

In Chap. 6 we present the reorientational dynamics results on our hydrogen-bonded glass-formers having non-linearly polarisable groups, as a function of temperature and film thickness. The second-harmonic generation decays were fitted with a stretched exponential law. From the fitting parameters we could determine the distribution of the relaxation times inside the films. For all films thicknesses the distribution moves to longer times and becomes broader by decreasing temperature. Comparing different thicknesses we noticed that around the glass transition temperature the distribution of relaxation times becomes wider under confinement. This
result is consistent with the model presented in Chap. 3. On the other hand, for temperatures deep in the glass phase, the confinement does not play any role on the dynamics. This last result implies that the cooperative length $\xi$ over which cooperative motion takes place does not significantly increase as temperature decreases deep into the glass phase. This is contrary to the predictions of Adam and Gibbs and to the general belief.