

## Hypersonic properties as a sensitive probe for the thermal glass transition

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During vitrification of liquids predominantly the mechanical properties are changed. This is especially reflected by specific changes of the static and dynamic hypersonic properties close to the quasi-static freezing temperature. We present the Brillouin-technique as a powerful method for investigating glass formers in order to determine linear and non-linear elastic properties in the hypersonic (GHz) regime. Using these high frequencies, both longitudinal and shear modulus can be measured - even in the liquid phase. Measurements of hypersonic properties of poly-vinyl acetate during glass formation are presented. They will be used in order to discuss the nature of the canonical glass transition.

In the last twenty years of theoretical and experimental work on glasses a tremendous amount of details has been elucidated [1]. Less examinations have been done in the temperature region very close above and below the thermal glass transition temperature (TGT). The reason for this is obvious: Structural relaxation times above the TGT usually follow an Arrhenius or Vogel-Fulcher equation which leads to relaxation times in the range of  $10^4$  to  $10^6$  seconds one or two degrees above TGT. This makes it very time-consuming to realise experiments in thermal equilibrium. Furthermore, structural relaxation is intimately linked with the evolution of viscosity as a function of temperature. Therefore the measurement of structural relaxations should be done by examining mechanical properties of the glass-former in question. We use Brillouin Light Scattering (BLS) as a sensitive probe to investigate the hypersonic properties of several glass-formers near the TGT. Figure 1 shows a typical BLS spectrum of a glass-former with both longitudinal and shear phonons visible.

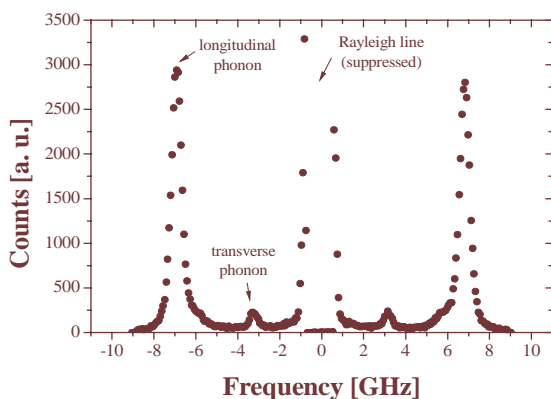


Fig. 1 Typical BLS spectrum of a glass former near the thermal glass transition temperature.

Because of the high probe frequency (GHz), BLS measures so-called clamped mechanical properties up to 30 or 40 degrees above TGT [2]. This means that the probe frequency is high compared to the intrinsic time scales (structural relaxation velocities) of the material.

The dynamic glass transition temperature is far above the TGT. Figure 2 shows the typical temperature dependence of the longitudinal and transverse sound velocity of a glass-former.

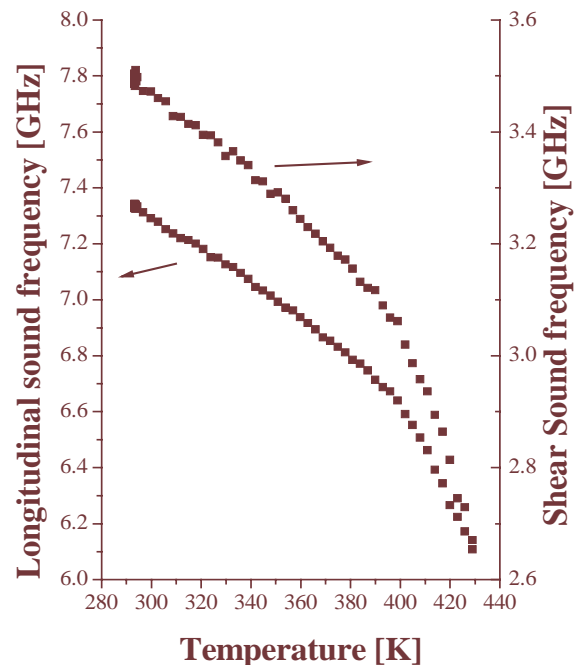


Fig.2 Temperature evolution of the hypersonic velocities of a typical glass former

We used the so-called temperature-step method to investigate the relaxation time behaviour of several glass-formers: Starting in the liquid phase, temperature is decreased step-wise by two or three K per step. After each temperature jump, we measured the longitudinal hypersonic velocity as a function of time. Figure 3 shows the temporal evolution of the longitudinal hypersonic velocity after a temperature change of -2 K in a region above the TGT. Waiting long enough after each temperature step insures that thermal equilibrium could be reached. As expected, relaxation times increase exponentially on approaching the TGT from higher

temperatures. This is shown in the activation plot in figure 4.

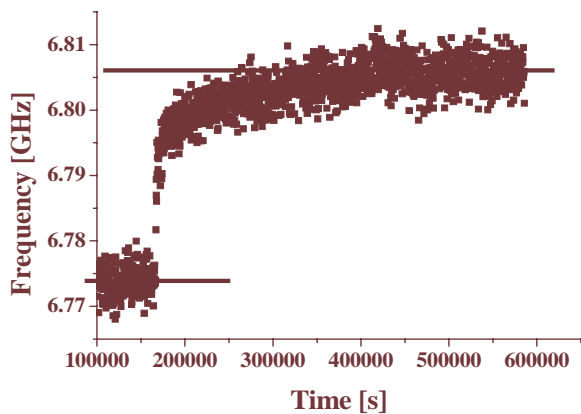


Fig.3 Temporal evolution of the longitudinal hypersound velocity of poly-vinyl acetate after a temperature change of -2 K in the liquid phase.

Above TGT the temporal evolution of the hypersound velocity always looks as shown in figure 3. Having crossed the TGT, the response of the system on changing the temperature by 2 K dramatically changes: no further relaxation can be found. Extrapolating the the activation plot (figure 4) to lower temperatures, one can calculate the expected relaxation times. They clearly are in the time window accessible during our experiments but nevertheless, no further relaxation is observed (see figure 5). Having approached the TGT in small steps starting at higher temperatures and waiting for thermal equilibrium after each temperature change ensures that we did not kinetically freeze our system.

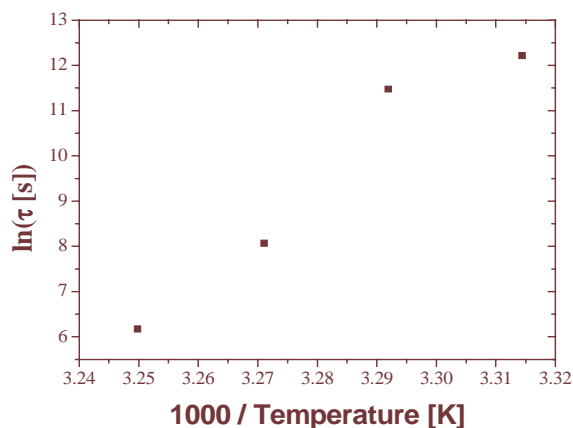


Fig. 4 Activation plot of the relaxation time of the atactic polymer poly-vinyl acetate.

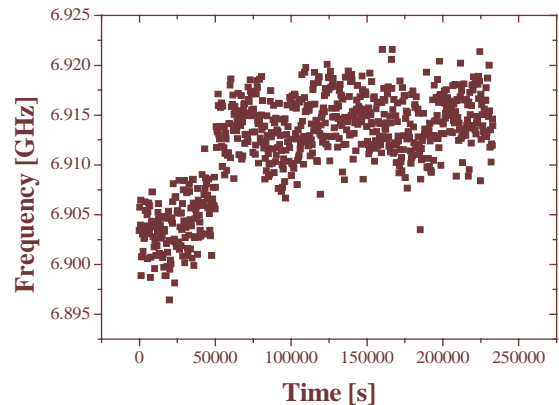


Fig. 5 Temporal evolution of the longitudinal hypersound velocity of poly-vinyl acetate after a temperature change of -2 K just below TGT

This leads us to the conclusion that there exists a temperature below which no relaxation is possible - no matter how slowly an experiment is done. A similar relaxation time behaviour with a clear cut-off at a distinguished temperature was found by Lüty et al. [3] for a different process: the order-disorder transition of CN-molecules.

The presented result indicates that it is not the increase of relaxation times and its cross-over with experimental time scales which leads to the glassy state. Moreover the increase of relaxation times is stopped by the appearance of the glass transition.

#### Literature

- [1] E. Donth, "The glass transition", Springer Berlin (2001)
- [2] J. K. Krüger, J. Baller, T. Britz, A. le Coutre, R. Peter, R. Bactavatchalou, J. Schreiber, Phys. Rev. B (accepted) (2002)
- [3] F. Lüty, J. Ortiz-Lopez, Phys. Rev. Lett. 50, 1289 (1983)