

The hindered glass transition in nanoscaled confinement: relaxation modelling and negative pressure effect

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Spatial confinement is a common tool to study dynamics of phase transitions. Within the last two decades it has especially been used to investigate the nature of the glass transition, and brought enormous insight into this fundamental and still open question. A widespread idea today is growing cooperation of neighbouring molecules and the formation of "collectively rearranging regions", which grow to the size of some nm as the glass transition is approached. Limiting this cooperation in space is accelerating dynamics and shifting the glass transition temperature, which serves as a hint for an inherent length scale underlying this process.

In 2007 it was shown that the rather simple and straight-forward method of dynamic mechanical analysis (DMA) is a useful tool to investigate dynamics in confinement. The dynamic elastic response of a porous host matrix turned out to be very sensitive of the vitrification of a guest filling liquid. Its observation even allows to distinguish between confinement induced acceleration and surface induced slowing down of dynamics. Hence, decoupled relaxation processes were found to take place in nm-sized pores. Different porous matrices (Vycor, Gelsil) with pore sizes ranging from 2.6 to 11.5 nm as well as different glass forming molecular liquids (Salol, o-TP) have been used for investigation. Our theoretical model contains a Cole-Davidson ansatz and the Vogel-Fulcher-Tammann law typical for glass forming liquids, combined with a spatial distribution of relaxors along the pore radius as suggested by recent computer simulations. This results in a downshift of $T_g \propto 1/\text{pore diameter}$ well in line with DSC measurements from literature.

An intensively discussed alternative explanation for this downshift is arising negative pressure upon the liquid due to mismatching thermal expansion of liquid and surrounding porous matrix. Very accurate thermal expansion measurements allowed us to reinterpret this effect and to estimate its maximum contribution to the overall process. Furthermore we were able to measure the linear expansion during wetting of the sponge-like porous samples, which is nicely reproduced by a model from literature, which in fact was developed for drying shrinkage of porous material, but also holds for the reverse process of adsorption swelling.

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[1] W. Schranz, M. R. Puica, J. Koppensteiner, H. Kabelka, and A. V. Kityk, EPL **79**, 36003 (2007).