Thursday,

05th June 2014

at: **5.00 pm**

Hörsaal für
Theoretische
Physik
Linnéstr. 5
04103 Leipzig

*Coffee will be
served from
4.30 pm!*

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Dynamics and thermodynamics of glasses in bulk and under confinement

Glass-forming systems have been the subject of intense research in the last decades. Within this context the following topics have been recently debated: i) the glassy dynamics in nanoscale confinement, with special attention to thin polymer films; and ii) the fate dynamics and thermodynamics below the laboratory glass transition temperature (T_g), namely that obtained at cooling rates of several kelvin per minute. In this seminar, first of all I critically discuss the recent advancements in the understanding of glassy dynamics in confinement. It is emphasized how in several confined glasses – including thin polymer films, nanospheres and nanocomposites – the equilibrium dynamics and thermodynamics are substantially unaltered in comparison to the corresponding bulk glass former. Contrariwise, the out-of-equilibrium dynamics, namely the ability to maintain thermodynamic equilibrium when cooling down from the melt or recover it after the application of perturbations beyond the linear regime, is significantly modified in confined glasses. Such modification is manifested with a depression of the T_g and an acceleration of equilibrium recovery in the glassy state, that is, in the physical aging regime.
In the second part of the seminar, the behavior of the dynamics and thermodynamics of glass-forming systems is discussed. To do so, enthalpy recovery experiments over aging times as large as 10_7-10_8 seconds are presented. The results show a single stage recovery behavior for temperatures larger than about $T_g - 10$ K. Interestingly, a double stage recovery is observed for $T < T_g - 10$ K. In all cases the enthalpy recovered after the two-stage decay approximately equals that extrapolated from the melt, whereas partial enthalpy recovery occurs in the first decay. The presence of a two stage recovery implies that there exist two time scales of equilibration in the glassy state. The equilibration time corresponding to the first stage recovery exhibits relatively low activation energy (several times smaller than that of the segmental relaxation process at T_g). Conversely, the equilibration time of the second decay exhibits activation energy similar to that of the polymer segmental relaxation at $T_g - 10$ K. Finally, I show how the presence of a two stage recovery is evidenced in confinement too, in ways analogous to those of bulk glass formers. This has been observed in thin polymer films. However, as a result of the ability of confined glass forming systems to maintain equilibrium more efficiently than the corresponding bulk glass, the time scale needed to observe the two stage decay decreases with the film thickness. This implies that for sufficiently thin polymer films the two mechanisms of equilibration are observed for those experimental time scales typical of standard calorimetric experiments. As a result, two jumps in the specific heat are detected for freestanding films as thin as 30 nm. This result is discussed within the framework of the debate on the signature of glassy dynamics in thin polymer films. As an obvious consequence of the presence of two equilibration mechanisms in both confined and bulk glass formers, it is argued that the presence of two jumps in the specific heat is not a confinement specific feature. It rather represents a universal feature of glass forming liquids.