Physics of polymers, supercooled liquids and glasses

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Background

The group is mainly interested in the physics of disordered systems with particular reference to polymers and supercooled liquids in proximity of their glass transition.

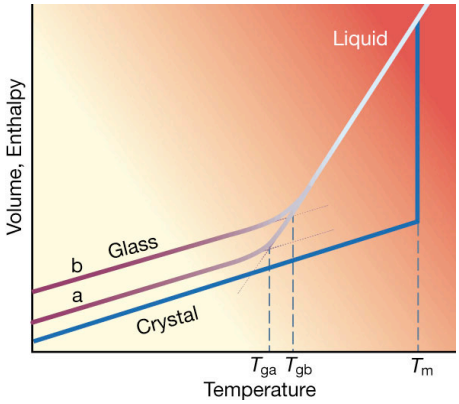

Figure 1 T_m is the melting temperature. A slow cooling rate produces a glass transition at T_{ga}; a faster cooling rate leads to a glass transition at T_{gb}. From ref.2.

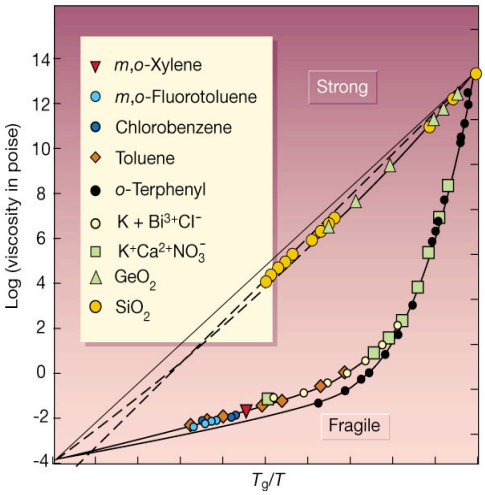

Figure 2 Typical temperature dependencies of the viscosity in supercooled liquids. From ref.2.

Glasses are disordered materials that lack the periodicity of crystals but behave mechanically like solids [1-3]. The most common way of making a glass is by cooling a viscous liquid fast enough to avoid crystallization (Fig.1). Although this route to the vitreous state - supercooling - has been known for millennia, the molecular processes by which liquids increase their viscosity of more than fifteen orders of magnitude (Fig.2) and acquire amorphous rigidity upon cooling are not fully understood. The understanding of the formation of glasses is currently seen as a major intellectual challenge in condensed matter physics. The amorphous products of this slowdown process in polymers, ceramics, and metallic systems provide a variety of important materials which are, in many cases, already in widespread use. In other cases, they

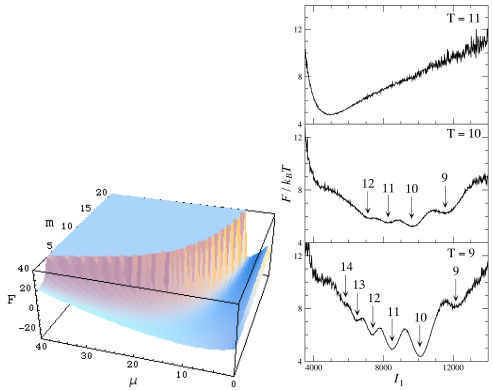

Fig. 3: (left) Free-energy landscape (FEL) of the PE single-molecule crystals. (right) FEL at different temperatures as a function of the largest moment of inertia of the chain. The labels indicate the number of stems of the ordered structures corresponding to the minima.

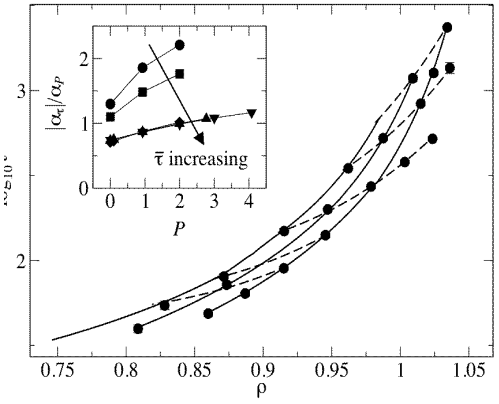

Figure 4 The pressure-temperature dependence of the segmental relaxation time for a linear polymer model. The inset shows the pressure dependence of the ratio between the isobaric and the isochronic expansivities.

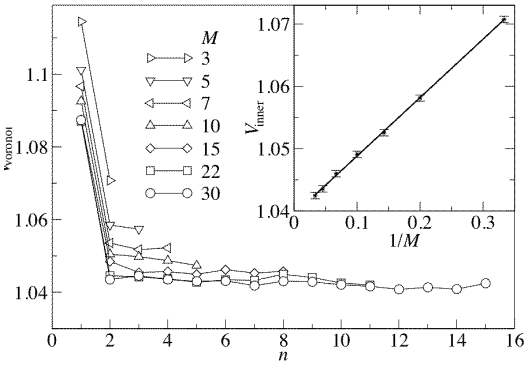

Figure 5 The average volume of the Voronoi polyhedra around the monomers located at the *n* position along the chain with length *M*. Note the larger volume of the polyhedra surrounding the chain-ends (*n=1*).

offer exciting possibilities for the future. Amorphous solids formed by other more exotic routes, and their relation to liquid-formed glasses, are likewise under intense study.

Research Projects

The research projects deal with the characterization of the dynamical and structural properties of polymeric and glassforming systems by using numerical and experimental techniques.

Numerical studies are carried out by using Molecular-Dynamics (MD) and *Monte Carlo* (MC) algorithms [4]. Molecular models of interest are highly coarse-grained or fully atomistic. Recent projects studied the self-assembly and the energy landscape of single-molecule polymer crystals (Fig.3), the influence of molecular packing and the available free volume in setting the relaxation times of polymer melts (Fig.4,5), as well as the static properties of polymeric chains as studied via

their Rouse modes. We were (and are still !) quite interested in the (de)coupling between the viscous flow and the translational / rotational diffusion (breakdown of the Stokes-Einstein and Debye-Stokes-Einstein relations).

Experimental studies are carried out by Electron Paramagnetic Resonance at very high field and frequencies (HF- EPR) [5]. Recent studies addressed the exploration of the energy landscape of glassy polystyrene (Fig.6) and the onset of the fast dynamics in amorphous materials (usually investigated by neutron scattering), the crossover region of molecular and polymeric glassformers, the decoupling between rotational diffusion and the viscosity close to the glass transition.

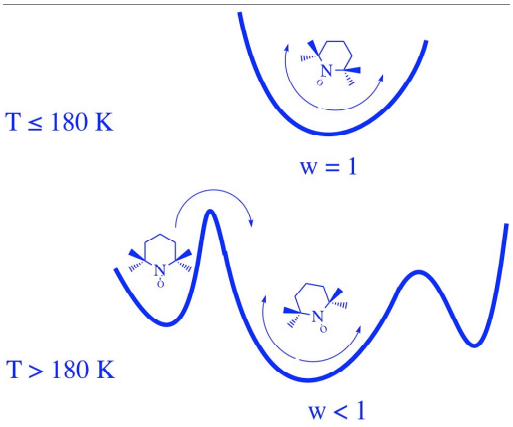

Fig. 6: Schematic view of the detrapping of a molecular probe in the energy landscape of glassy polystyrene due to the onset of the fast dynamics at 180 K.

Further information, current collaborators and the list of recent (downloadable) publications are available on the web (http://www.df.unipi.it/~leporini) .

References

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