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## PhD Thesis: Glass Transition at Interfaces

According to Philip Anderson, the deepest and most interesting unsolved problem in solid-state physics is probably the glass transition. Indeed, glassy materials are ubiquitous in nature, and discussions about glass transition involve many areas of physics, from molecular and spin glasses to hard-sphere jamming. In spite of the intense interest in the dynamical slowing that accompanies glass formation, a single microscopic theory has yet to emerge. Nevertheless, the phenomenological approach of *free volume* and the Doolittle ansatz have been used to support the Vogel-Fulcher-Tammann (VFT) relation, which describes many of the observed behaviors. Fundamental to glass formation are the suggestions that particles are increasingly crowded, and relaxation requires the *cooperative* participation of a growing number of particles. The hypothesis of a cooperatively rearranging region, as introduced by Adam and Gibbs [1], is appealing and has been observed in computational studies.

The suggested existence of a length scale  $\xi$  for cooperative rearrangement has led to tremendous interest in confined glass formers. Perhaps, the most active example of attempts to probe  $\xi$  is the study of glassy polymer films, where fascinating observations have been made. For the most studied case of polystyrene, reductions in the measured glass-transition temperature have been almost uniformly reported as the film thickness is reduced [2], both experimentally and numerically. It has been further suggested that this apparent anomaly is linked to the observed existence of a more mobile interfacial layer [3]. As a consequence, there have been many theoretical attempts to understand the glass transition in confinement, with varying degrees of complexity and success, but as of today the problem remains unsolved and the controversy holds.

Even more intriguing is perhaps the existence of a universal behaviour of those  $T_g$ -reductions for free-standing polystyrene films with large molecular weights [4], that is when the thickness of the sample is comparable to the typical size of one macromolecule – its radius of gyration. This other class of anomalies, most probably related with purely polymeric effects, is still an open question. One qualitative mechanism based on a reptation-like sliding motion has been proposed [5], but it could not describe quantitatively the observations.

The main topic of the thesis will thus be to address such theoretical questions, using a combination of analytical and numerical tools. The team belongs to an international network, including experimentalists that are experts of the field, and the graduate student will interact strongly with them and visit the corresponding laboratories. Finally, other questions related with soft condensed matter and nanofluidics, and emerging from the network, will be addressed in parallel.

### References:

- [1] G. Adam G., J. H. Gibbs, *On the temperature dependence of cooperative relaxation properties in glass-forming liquids*. J. Chem. Phys. **43** 139 (1965).
- [2] J. L. Keddie, R. A. L. Jones, R. A. Cory, *Size-dependent depression of the glass transition temperature in polymer films*, Europhys. Lett. **27** 59 (1994).
- [3] Z. Fakhraai, J. A. Forrest, *Measuring the surface dynamics of glassy polymers*, Science **319** 600 (2008).
- [4] K. Dalnoki-Veress, J. A. Forrest, P.-G. de Gennes, J. R. Dutcher, *Glass Transition Reductions in Thin Freely-standing Polymer Films: a Scaling Analysis of Chain Confinement Effects*, J. de Phys. IV **10** 221 (2000).
- [5] P.-G. de Gennes. *Glass transitions in thin polymer films*. Eur. Phys. J. E, **2** 201, 2000.

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