Stress fluctuations and viscoelastic properties of glass-forming liquids

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Many substances behave as liquids at high temperatures T, but do not crystallize on cooling: rather they show tremendous slowing down of flow behavior at low T. Such mineral or organic glass forming liquids are known from ancient times. It is well-known that amorphous glassy systems are characterized by disordered molecular arrangement. However, the nature of the glass transition is still a subject of an active debate and remains one of the most interesting problems in soft-matter physics. Some theories consider vitrification of liquids as a purely dynamical phenomenon associated with rapidly increasing structural relaxation time and viscosity near some temperature T_g. Other approaches invoke the idea of an equilibrium phase transition underlying the vitrification. Indeed, it was shown that glass transition is normally accompanied by an abrupt change in measured thermodynamic quantities like specific heat, thermal expansion coefficient, or isothermal compressibility [1,2] pointing to a second-order phase transition. On the other hand, a first-order transition is hinted at by the discontinuous behavior of the shear elastic modulus near T_g. The very idea that vitrification in liquids is accompanied by a qualitative structural change (reflected in static, equilibrium properties) proved to be very appealing theoretically [1,3]. Nevertheless, so far there is no definitive evidence, either experimental, or theoretical, or coming from computer simulations, on the existence of such a transition. There are, however, indications that as liquid approaches its glass transition, it shows a growth of some dynamical [4,3] or structural [3,5] length-scales.

Many mechanical properties of liquids and solids (elastic moduli, viscosity) can be obtained by analyzing stress fluctuations in these systems. In particular, the time-correlation function of shear stress C(t) is closely related to the shear relaxation modulus G(t). It was shown recently that such relations in different statistical ensembles can be employed by computer simulations for an accurate determination of shear modulus near the glass transition [6].

It is important that stress fluctuations show qualitatively different length-scale dependencies in liquid and solid states: correlations are long-range in crystals but short-range in liquids. A similar difference is expected between liquids and amorphous solids below T_g. In particular, it is anticipated that a vitrified liquid at T=0 may show stress correlations of infinite range. The aim of the present project is to investigate (both by MD simulations and theoretically) the length-scale dependence of shear stress fluctuations and elastic properties of glass-forming liquids in order to assess their changes through the glass transition region, and to find out whether these changes are possibly related to a structural phase transition associated with vitrification. It will be necessary to analyse both static (equilibrium) and dynamic (time-dependent) stress correlation functions for model systems of polydisperse LJ particles, both in 2 and 3 dimensions. We also plan to analyse systems of polymerized LJ particles.

The candidates must be familiar with statistical physics and have a solid background in computer modelling methods.

[1] W. Kauzmann, Chem.Rev. **43**, 219 (1948). [2] C.A.Angell, PNAS **92**, 6675 (1995).
[3] A. Cavagna, Phys.Rep. **476**, 51 (2009). [4] C. Bennemann, C. Donati, J. Baschnagel, S.C.Glotzer, Nature **399**, 246 (1999). [5] A.N.Semenov, J.Chem.Phys. **143**, 044510 (2015).
[6] J.P.Wittmer, H.Xu, O.Benzerara, J.Baschnagel, Mol.Phys. **113**, 2881 (2015).