Summary & Conclusions

The method of Molecular Dynamics (MD) computer simulations is employed to study ultra thin films of oligomer fluids, confined in spaces comparable to their molecular dimensions and subjected to (very) strong flows. In MD simulations the equations of motion are solved by the computer and the trajectories of the particles are calculated. As MD provides the time evolution of a physical system, relevant static and dynamic properties of sheared confined systems can be obtained from the simulations.

The effect of nanometer confinement

Confinement affects the properties of a fluid in very intricate ways. A fluid near a surface becomes very inhomogeneous, exhibiting large density variations by packing in layers next to the confining wall. This layered structure extends very little—five to six molecular diameters—inside the fluid and in the case of wide films or macroscopic systems it is a very small part of the system; thus its effect is minor as the behaviour of the system is dominated by the behaviour of the vast bulk part of the system away from the surfaces. On the other hand, in very thin films (up to ten molecular diameters) these interfacial regions become a considerable portion of the whole system and affect its behaviour; the thinner the films the stronger the influence.

Inside the wall-fluid interface the properties of the oligomer chains are strongly altered. The relaxation times of the chains become longer and diffusion is hindered. These effects become dramatic near strongly attractive surfaces: if the wall attraction is three times stronger than the fluid cohesion the relaxation times increase more than a thousand times and the diffusion coefficients are also reduced by more than three orders of magnitude.

Furthermore, apart from these sluggish dynamics there is also an increasing ordering inside the interfacial layer with increasing wall affinity. These effects are consequences of the wall induced densification, rather than of the energetic barriers of the wall interactions or mechanisms of epitaxial crystallisation or vitrification. This can be elegantly demonstrated by simulations of systems confined between structureless walls. In these systems there is no wall corrugation but still the same phenomena (sluggish dynamics, enhanced in-plane ordering, "crystalline"-like in-plane motions) are observed which suggests that

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2 this is valid for simple—monomeric—fluids, for oligomer melts it is only two, three monomer diameters
3 this difference in the wall-fluid and the fluid-fluid interaction is realistic and the flexibility of the studied model underestimates the magnitude of this wall induced effect.
this behaviour originates from the geometric constraints and the need of the adsorbed segments to close-pack inside the first layer.

The effect of flow in ultra-thin films

Confinement results in an inhomogeneity, both in the density and the dynamics across an ultra thin pore, this is reflected in the response of these systems to imposed shear. The flow induced across a nanometer wide oligomer film, when the confining surfaces are set in motion, reveals that the adsorbed chains correspond to a more viscous fluid than the free chains in the middle part of the pore. Moreover, shear thinning takes place at much smaller shear rates than in the bulk.

In addition, there is a definite correlation between the velocity profile developed across the film and the variations of the density and local viscosity across the film. Slippage takes place either between the confining wall and the fluid, for weakly physisorbing surfaces, or inside the film—interlayer slip—for systems confined by strongly physisorbing surfaces. The molecular mechanism for the latter case is related to the conformations of the adsorbed chains with respect to the physical connectivity between the adsorbed and the free part of the film.

Flow also affects the confined coils. The adsorbed chains which are already collapsed and stretched on the wall at equilibrium, under flow adopt conformations with many surface contacts, while there is only a slight alignment parallel to flow. This is happening because the segments prefer to be situated so as to facilitate close-packing, rather than orient parallel to the streamlines. Increasing shear rate, causes increasing density inside the solid-oligomer interface that results in a shear enhancement of in-plane ordering inside the first layer. The free chains located in the middle of the pores stretch by shear and align at a preferential angle with respect to the flow direction. These shear induced deformation and orientation are close to what is expected from bulk oligomeric systems. The oligomer molecule architecture is also varied in this study. Although there exist quantitative deviations in the response of different molecules, the qualitative rheological features remain the same.

Finally, shear flow affects the adsorption-desorption process in these nanoscopic conformations. Adsorption and desorption take place simultaneously in a perpetual exchange between adsorbed and free chains, in such a way that density remains dynamically constant. Although shear favours conformations with many contacts at the same time it enhances the mobility of the adsorbed chains thus promoting desorption. The way in which desorption is promoted is not obvious for strongly adsorbing surfaces and under strong enough flow, adsorbed chains remain attached to the surfaces for a long time and suddenly they detach from them following a common kinetic pattern. The desorption, kinetics in the ultimate stages of desorption, involve conformations starting by a desorbed tail and then a correlated, segment-by-segment disengagement from the wall.

The wall induced densification and the shear induced changes of the adsorbed chains conformation are of immense importance to the static and rheological properties of nanoscopic confined films.