

Stick and Slip Behaviour of Confined Oligomer Melts under Shear. A Molecular-Dynamics Study.

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Abstract. – The flow behaviour of melts of short chains, confined in molecularly thin Couette flow geometries, is studied with molecular-dynamics simulations. The effect of wall attraction and confinement on the density and velocity profiles is analysed. In these highly inhomogeneous films, a strong correlation between the density and velocity profile is found. Sticking of the interfacial layer on the wall and slip on the wall and inside the film is manifested by changes in the velocity profile. The location of the slip is determined by the strength of the wall attraction.

Even though the macroscopic phenomena of friction, lubrication and adhesion have been studied for a long time now, their molecular mechanisms have yet to be unveiled. Recent novel experimental techniques such as the surface forces apparatus together with the scanning probe microscopies are capable to give a vast amount of information on the nanometer level; these combined with computer simulations will provide further insight into the nanoscopic dynamics of friction, lubrication and adhesion. The structural and dynamical properties of ultrathin confined films between atomically flat surfaces undergoing shear are studied here with molecular-dynamics simulations.

Simulations are performed on a fluid of short chains in a planar Couette flow geometry realized by confining the polymer system in the z -direction between two parallel planar f.c.c. (111) planes. Periodic boundary conditions are imposed in the other two directions. The Couette flow is introduced by moving the two walls with equal and constant velocities towards opposite directions keeping the wall-to-wall distance constant. In this way, a steady shear rate is introduced with the direction of flow parallel to the x -axis and the velocity gradient parallel to the z -axis, *i.e.* normal to the walls [1].

The chains consist of six segments which are connected in a linear freely joined topology. Of course, the model is not expected to capture the real monomer response and segments correspond to several chemical monomers [2]. The segments of the same chain as well as segments belonging to different chains interact via a pairwise purely repulsive, shifted and

truncated 12-6 Lennard-Jones (LJ) potential:

$$U(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right], & r \leq \sqrt[6]{2} \sigma, \\ 0, & r > \sqrt[6]{2} \sigma, \end{cases}$$

where r is the distance between the centres of the two segments, ε is the LJ energy parameter and σ the LJ length parameter. For successive monomers of the chain a strongly attractive FENE (finite extensibility non elastic) spring potential is added [1-4]:

$$U_{\text{bond}}(r) = -\frac{k}{2} R_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right], \quad r < R_0,$$

where $R_0 = 1.5\sigma$ and $k = 30\varepsilon/\sigma^2$. This choice of parameters has been proven to prevent bond crossing at the temperature used in our simulation [2]. This model has been studied extensively for linear chains both in the bulk [2], confined between walls [1], and under shear [4]. The interaction between walls and segments is modelled by a pairwise Lennard-Jones potential which includes the attractive tail of the potential:

$$U_w(r) = 4\varepsilon_w \left[\left(\frac{\sigma_w}{r} \right)^{12} - \left(\frac{\sigma_w}{r} \right)^6 \right].$$

This potential is truncated at $r_{wc} = 2.5$ to reduce computational effort. In all simulations $\sigma_w = 1.0\sigma$. ε_w , which determines the attraction between the wall and segments, has been varied in order to study the influence of the strength of this interaction.

The temperature was fixed at $k_B T = 1.0\varepsilon$ in all simulations. The kinetic energy imparted from the wall to the chains is dissipated inside the film. The heat generated is removed by a first-order coupling of the temperature to a heat bath. This is accomplished by rescaling the segment velocities at every time step [5]. For systems at equilibrium the scaling of velocities is done in such a way that the centre of mass of the confined film has zero momentum. For systems under shear only the thermal part of the velocities parallel to the direction of the flow velocity are scaled. For the other two directions a first-order coupling to temperature is used.

Newton's equations of motion are integrated by a variant of Verlet's algorithm with a time step of $\Delta t = 0.00462(m\sigma^2/\varepsilon)^{1/2}$. Computational needs are further reduced by the use of lists of nearest neighbours updated every 20 time steps [6]. The results will be presented in reduced

TABLE I. - *Systems simulated.*

Wall attraction $\varepsilon_w(\varepsilon)$	Wall-to-wall distance $h(\sigma)$	Average ^(a) segment density $\rho(\sigma^{-3})$	Wall velocities $v_w(\varepsilon/m)^{1/2}$
1.0	7.0	0.734	0.0 ÷ 0.9
1.0	6.0	0.888	0.0 ÷ 1.5
1.0	4.0	0.935	0.0 ÷ 0.9
2.0	6.0	0.888	0.0 ÷ 5.0
3.0	6.0	0.888	0.0 ÷ 5.0

(a) The average segment density is defined as the number of monomers per unit volume excluding the depletion zones near the walls.

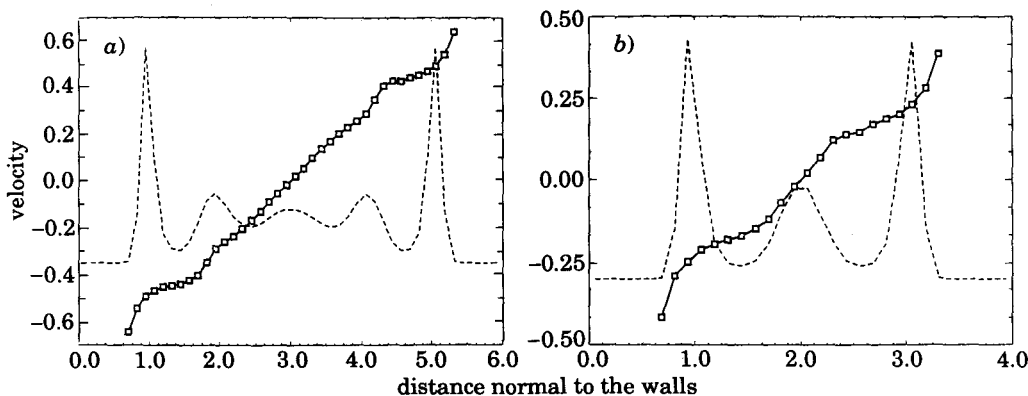


Fig. 1. - Velocity (\square) and density (---) profiles for a wall interaction ($\epsilon_w = 1.0\epsilon$) almost identical imposed shear rates $v_w = 0.7(\epsilon/m)^{1/2}$ (a), $v_w = 0.5(\epsilon/m)^{1/2}$ (b), and different confinements a) $h = 6.0\sigma$ and b) $h = 4.0\sigma$. The slip between wall and system increases and the linear velocity profile in the middle of the film decreases with decreasing h . The inhomogeneity of the confined polymer systems is stronger for smaller wall-to-wall distances (h).

units in which the energy is measured in ϵ , the length in σ (LJ parameters) and the mass in m (monomer mass). The simulation parameters of the systems studied can be found in table I.

Several steps and methods are employed to create initial positions and velocities. Well-equilibrated initial configurations of systems with linear molecules were taken from a lattice Monte Carlo algorithm [7]. Initial velocities from a Maxwell-Boltzmann distribution, with variance equal to the temperature, are subsequently randomly assigned and a constant temperature MD run is made. For systems under Couette flow, a non-equilibrium MD run of 1 to $5 \cdot 10^5$ time steps is used until steady-state flow is reached.

For relatively small wall velocities flow velocities are masked by thermal noise and considerably longer production runs than for the higher shear rates are required. Typically, for wall velocities below 0.2 (table I) runs of $8 \cdot 10^5$ to $1 \cdot 10^6$ time steps are used and for higher shear rates the runs are of $4 \cdot 10^5$ to $6 \cdot 10^5$ time steps. The dimensions of the simulation box in the directions parallel to the surfaces are 8.0σ . This size is large enough to avoid any interaction of a chain with its periodic image, even for chains that are close to the wall. So, for the simulations the volume, the temperature and the number of particles remain fixed (canonical ensemble, NVT MD).

Novel experimental techniques [8, 9] and computer simulations for monomeric [10-15] as well as for polymeric fluids [1], indicate the existence of strong layering in the vicinity of solid surfaces, in the form of oscillations in density. These density variations are caused by the presence of a wall in combination with strongly repulsive excluded-volume interactions between the segments. This is similar to the layering of the pair correlation function of dense fluids.

The normal layering depends on the interaction of the polymer with the wall. For a more attractive wall the density inhomogeneity is enhanced. The monomer density profile depends also on the distance between the two walls. For systems with walls relatively far apart ($h \geq 7.0\sigma$), a region with constant density is present in the middle of the film and the film exhibits bulklike behaviour. As soon as the walls are brought close enough together, the density inhomogeneity extends over the whole film, which then exhibits a strongly layered structure (cf. fig. 1).

As theories that can predict the velocity profile for strongly inhomogeneous media are still developing [16-18], the first question to address concerns the shape of the velocity profile in confined systems under steady shear. Some characteristic examples of velocity profiles as a function of wall-to-wall distance are shown in fig. 1 for systems with the same shear rate and wall-segment interaction. Rather than being linear throughout the slit, as predicted from hydrodynamics of a bulk system under steady shear, the velocity profile normal to the walls exhibits a strong correlation with the density profile. For a higher shear rate and a stronger wall-segment interaction a more detailed picture of the relation between velocity and density profile can be given. In all cases, the velocity profile is linear for the middle part of the system where the density is almost constant. Inside the first layer in contact with the wall the velocity profile is, for the less attractive wall, also almost linear but with a smaller slope. This implies that here the effective viscosity is higher than in the middle of the film. For the more attractive walls, however, this first layer locks on the wall (fig. 2a) and much higher shear rates have to be applied to induce flow inside this interfacial area (fig. 2b)). At these high shear rates the low-density region between the first and second layer is characterized by an abrupt change in the velocity profile (interlayer slip) (fig. 3).

In the simulations carried out for all the systems with the less attractive walls ($\epsilon_w = 1.0\epsilon$) some slip is present between the wall and the first layer. This slip increases with increasing shear rate as expected [19,20]. The slip also increases in narrower confinements for the same wall-segment interactions and shear rates (fig. 1). For the weak attraction, the density profile does not depend markedly on shear rate, not even for the higher shear rates and the smaller wall-to-wall distances, in agreement with earlier simulations for monomer films [12]. Due to slippage between wall and film, there is a limit on the shear rates than can be applied.

For systems with more attractive walls ($\epsilon_w = 2.0\epsilon$) much higher shear rates can be applied since the slip between wall and confined system is negligible even for much higher shear rates. In this more attractive case, for the smaller wall velocities (up to 0.9) almost the complete first layer sticks on the wall and moves with the imposed wall velocity and slip occurs between the first layer and the rest of the system (fig. 2a)). This slip is revealed by a very sharp curve connecting the constant velocity of the first layer with the linear velocity profile in the middle part of the film. The slip increases with shear rate. When higher wall

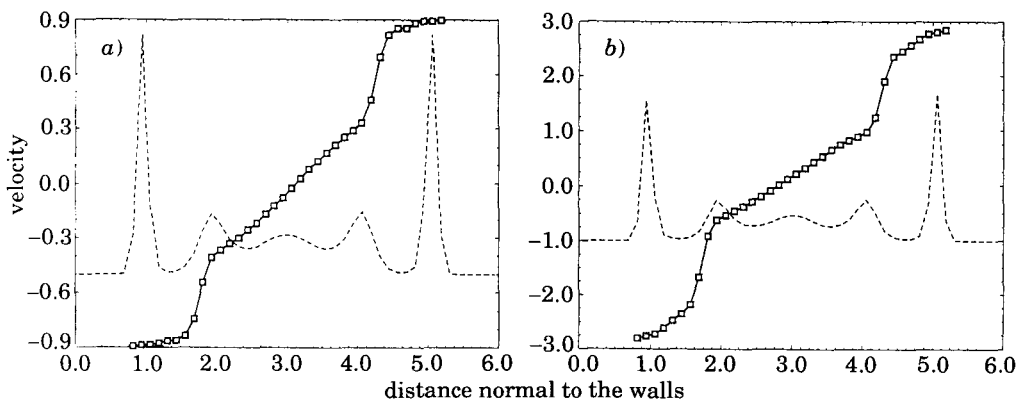


Fig. 2. - Velocity (\square) and density ($---$) profiles for $\epsilon_w = 2.0\epsilon$. For wall velocities smaller than 0.9 the first layer locks on the wall and moves with the imposed v_w (a)). When the shear rate is increased, a linear velocity profile develops inside the first layer and for even higher shear rates a slip starts to appear between the wall and the system (b), $v_w = 3.0$). In all cases there is an interlayer slip between the adsorbed layer and the rest of the system, which increases with shear rate.

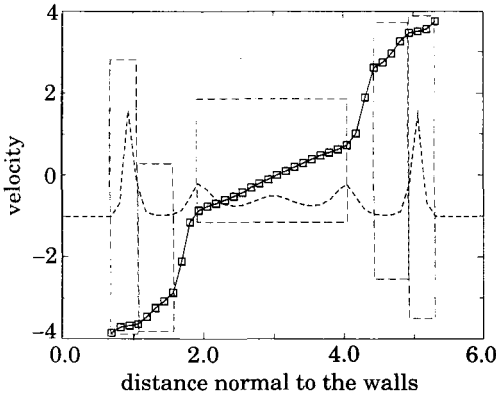


Fig. 3.

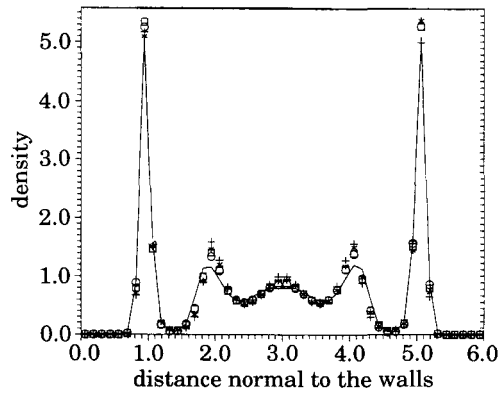


Fig. 4.

Fig. 3. – There is a definite correlation between the density and the velocity profile for highly inhomogeneous confined films. The figure corresponds to $h = 6.0\sigma$, $\epsilon_w = 2.0\epsilon$ and $v_w = 4.0(\epsilon/m)^{1/2}$. The different velocity profile regions correspond to different parts of the density profile.

Fig. 4. – For the less attractive walls ($\epsilon_w = 1.0\epsilon$) the density does not change much with shear rate. But for the most attractive walls the density profile changes systematically with shear rate. In this figure $h = 6.0\sigma$, $\epsilon_w = 2.0\epsilon$ and $v_w = (0.0 \div 4.0)(\epsilon/m)^{1/2}$: \circ 0.9, \square 2.0, $*$ 3.0, $+$ 4.0; — equilibrium.

velocities are applied the interfacial layer is characterized by an almost linear velocity profile and for even higher velocities some slip appears between the wall and this first layer (fig. 2b)). This has been observed before for confined monomeric fluids [15]. The density profiles for these systems ($\epsilon_w = 2.0\epsilon$) change systematically with the imposed shear rate. An increase in density of the first and in particular the second layer is observed, whereas the low-density area between these two layers decreases in density and increases in width (fig. 4). These density changes are due to a tendency for the chains, in contact with the wall, to adopt flat configurations. This is manifested by a significant increase of the fraction of chains with 5 and 6 contacts with the wall when shear is imposed, especially for the more attractive walls. This trend gets stronger with increasing shear rates and greater wall attractions (table II). The adoption of flat configurations enhances the slip in the region between the two layers.

For systems with very attractive walls ($\epsilon_w = 3.0\epsilon$) and high shear rates, as high as those introducing slip between wall and polymers for $\epsilon_w = 2.0\epsilon$, the first layer practically locks on the

TABLE II. – Fractions of chains with n -contacts with the walls (normalized by the total number of chains «touching» the walls). Quantities are in reduced units: $\epsilon_w(\epsilon)$ and $v_w(\epsilon/m)^{1/2}$.

ϵ_w v_w	1.0		2.0		3.0	
	0.0	1.5	0.0	2.0	0.0	2.0
1 cont.	0.11	0.10	0.07	0.05	0.07	0.03
2 cont.	0.17	0.11	0.11	0.05	0.11	0.05
3 cont.	0.19	0.13	0.13	0.06	0.13	0.05
4 cont.	0.18	0.16	0.17	0.07	0.17	0.06
5 cont.	0.18	0.21	0.22	0.13	0.23	0.06
6 cont.	0.17	0.29	0.30	0.64	0.29	0.75

wall. The effect of increasing wall velocity is merely to introduce slip between the first layer and the rest of the polymer system. The behaviour of the density profile is similar to that of the system with $\varepsilon_w = 2.0\varepsilon$; an increase in density is observed for both the first and second layers and the adsorbed chains tend to adopt flat configurations on the wall for higher shear rates.

In summary, non-equilibrium molecular-dynamics simulation studies of confined oligomer melts in a Couette flow geometry were used to investigate the response of nanoscopically confined short-polymer-chain films to shear. Stick conditions of a layer of the confined system on the wall are observed in agreement with experiments [21]. Simultaneously, a definite correlation between the density profile of a highly inhomogeneous confined system and the velocity profile is found. This has been observed before for moderately attractive walls and monomeric systems. Simulation data [12,15] and theoretical analysis [16-18] have shown that the detailed flow behaviour of a fluid near a solid interface is strongly affected, if not deterministically defined, by the equilibrium structure of the fluid in the vicinity of the wall. When more attractive walls are used a correlation between structural changes caused by shear and the change in flow behaviour of the confined system is observed. The slip, both between the wall and the fluid, and the interfacial layer and the middle part within the system, occurs in the low-density areas where different parts of the system meet (*i.e.* wall and polymers, interfacial and middle part).

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