

Inhomogeneities in Sheared Ultrathin Lubricating Films

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Received October 17, 1995. In Final Form: January 19, 1996[⊗]

Nonequilibrium molecular dynamics computer simulations have been used to study nanoscopically confined oligomer films under shear. Beyond the well-known density layering across such films, other structural and dynamical inhomogeneities exist across such films and are discussed here. When these films are subjected to strong shear flows, slip appears at the confining surfaces or inside the pore, depending on the wall interactions. For strong wall affinities interlayer slip develops between the adsorbed layer and the free chains, resulting in a structural discontinuity; a molecular mechanism, involving shear induced conformational changes of the adsorbed chains, is associated with this interlayer slip. Moreover, the resistance to flow (quantified through an effective viscosity) changes considerably across the film, with a dramatic viscosity increase of the adsorbed layer near attractive surfaces. Shear thinning is mainly taking place inside this more viscous interfacial layer, whereas the dynamics in the middle of the film remain bulklike; thus, there also exists strong inhomogeneity in the dynamics of the system. A comparison with SFA experimental and theoretical studies is also made.

Introduction

Although the fundamental and molecular aspects of friction and lubrication are central in major technological and economical problems,^{1,2} there still remain many unanswered questions in the fields of nanotribology and nanorheology.^{3,4} The emergence of advanced techniques, such as the atomic force microscope (AFM)^{5,6} and the surface forces apparatus (SFA), which are capable of probing frictional and rheological properties of nanoscopic well-defined model systems, combined with molecular computer simulations has recently revolutionized the field. The SFA is commonly employed^{7–9} to study molecularly thin films of lubricants confined between atomically smooth surfaces, thus probing only the static and dynamic properties of the lubricant. Complementary AFM experiments can provide information for well-defined geometries that resemble an asperity in contact with a surface. Molecular dynamics (MD) computer simulations modeling both the AFM¹⁰ and the SFA^{11–14} geometries provide insights into the nanometer scale energetics, structure, and dynamics and reveal the molecular mechanisms of

the novel transport and rheological behavior inside nanometer wide confined films.

Recent MD simulations of nanoscopically confined oligomer films report dramatic increases in the relaxation times of oligomers inside a solid–oligomer interface near attractive surfaces, up to three orders of magnitude compared to the bulk,¹³ and a corresponding dramatic reduction of the mobility.¹⁵ Moreover, when shear is imposed on these films, slip can appear between the wall and the fluid or within the fluid (interlayer slip), depending on the wall affinity.¹⁶ In agreement with these findings, recent SFA experiments^{17,18} propose the coexistence within the film of a highly viscous, immobilized, adsorbed layer in contact with a bulklike fluid layer, whilst shearing SFA experiments^{8,19,20} report the existence of interlayer slip. This means that these films exhibit inhomogeneities and discontinuities both in their structure—due to layering and interlayer slippage—and in their behavior—due to the existence of two regions with dramatically different dynamics: relaxation times, transport coefficients, and viscosities.

In this study, an effort is made toward the understanding of the dynamics and the rheology of these nanoscopically confined fluid films, with an emphasis on the above-mentioned inhomogeneities across the films. Finally, since this behavior cannot be explained by conventional bulklike concepts, the molecular dynamics as obtained by our computer simulations are utilized to pin down the molecular mechanisms associated with these phenomena.

Simulation Model and Method

The systems studied are confined films of oligomers with mainly 6 (hexamers) or 10 (decamers) segments per chain. The chains are modeled by an abstract and generic, though well-studied, bead spring model^{21,22} confined between two fcc surfaces normal to \bar{z} and periodic boundary conditions imposed in the

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[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1996.

(1) Singer, I. L.; Pollock, H. M., Eds.; *Fundamentals of friction*; NATO ASI Series; Kluwer Academic: Dordrecht, 1992.

(2) Bhushan, B. *Tribology and mechanics of magnetic storage devices*; Springer: New York, 1990.

(3) Nanotribology. *MRS Bull.* **1993**, 18 (5) May.

(4) Bhushan, B.; Israelachvili, J. N.; Landman, U. *Nature* **1995**, 374, 607.

(5) Binnig, G.; Quate, C. F.; Gerber, Ch. *Phys. Rev. Lett.* **1986**, 56, 930.

(6) Mate, C. M.; McClelland, G. M.; Erlandsson, R.; Chiang, S. *Phys. Rev. Lett.* **1987**, 59, 1942.

(7) Gee, M. L.; McGuiggan, P. M.; Israelachvili, J. N.; Homola, A. M. *J. Chem. Phys.* **1990**, 93, 1895.

(8) Reiter, G.; Demirel, L.; Granick, S. *Science* **1994**, 263, 1741.

(9) Hirz, S. J.; Homola, A. M.; Hadziioannou, G.; Frank, C. W. *Langmuir* **1992**, 8, 328.

(10) For example: Landman, U.; Leudtke, W. D.; Burnham, N.; Colton, R. *Science* **1990**, 248, 454 and references therein.

(11) Thompson, P. A.; Grest, G. S.; Robbins, M. O. *Phys. Rev. Lett.* **1992**, 68, 3448.

(12) Ribasky, M. W.; Landman, U. *J. Chem. Phys.* **1992**, 97, 1937.

(13) Bitsanis, I.; Pan, C. *J. Chem. Phys.* **1993**, 99, 5520.

(14) Manias, E.; Hadziioannou, G.; ten Brinke, G. *J. Chem. Phys.* **1994**, 101, 1721.

(15) Manias, E.; Subbotin, A.; Hadziioannou, G.; ten Brinke, G. *Mol. Phys.* **1995**, 85, 1017.

(16) Manias, E.; Hadziioannou, G.; Bitsanis, I.; ten Brinke, G. *Europhys. Lett.* **1993**, 24, 99.

(17) Montfort, J. P.; Hadziioannou, G. *J. Chem. Phys.* **1988**, 88, 7187.

(18) Granick, S. *Science* **1991**, 253, 1374.

(19) Horn, R. G.; Hirz, S. J.; Hadziioannou, G.; Frank, C. W.; Catala, J. M. *J. Chem. Phys.* **1989**, 90, 6767.

(20) Carson, G.; Hu, H.; Granick, S. *Tribol. Trans.* **1992**, 35, 405.

(21) Grest, G. S.; Kremer, K. *Phys. Rev. A* **1986**, 33, 3628.

(22) Kremer, K.; Grest, G. *J. Chem. Phys.* **1990**, 92, 5057.

other two directions (\bar{x} and \bar{y}). The details of the simulations are presented elsewhere^{14–16} and will only be briefly mentioned here.

Shear is imposed by moving the walls with a constant velocity (v_w) toward opposite directions ($\pm\bar{x}$). The interactions between the particles are modeled by the Lennard-Jones (LJ) potential, truncated at a distance $r_c = \sqrt[3]{2}\sigma$, which is a purely repulsive potential (with ϵ the LJ energy parameter is denoted and σ is the LJ length parameter). Bonding along the chains is ensured by adding a strongly attractive FENE (finite extensibility nonelastic) potential between successive beads along one chain.¹⁵ These potentials have been used before in extensive studies of bulk systems²² under confinement between walls^{13,23} as well as under shear^{11,14–16,24} and reproduce many static and dynamic properties of polymer systems. The interactions between the walls and the segments follow the full Lennard-Jones potential, which includes an attractive part:

$$U_w(r) = 4\epsilon_w \left(\left(\frac{\sigma_w}{r} \right)^{12} - \left(\frac{\sigma_w}{r} \right)^6 \right) \quad (1)$$

By changing the value of ϵ_w the strength of the wall attraction can be varied systematically. In order to reduce the computational effort, this potential is truncated at $r_{wc} = 2.5\sigma$. For wall attractions $\epsilon_w \leq 1.0\epsilon$ there is only a slight slowing down of the molecular motions¹⁵ and a very modest increase of the relaxation times,¹³ characterizing a “weakly physisorbing” surface; whereas for $\epsilon_w = 2.0\epsilon$ and 3.0ϵ the surfaces behave as “strongly physisorbing” by inducing a dramatic increase in the longest relaxation time of the adsorbed oligomers (by a factor of 70 for $\epsilon_w = 2.0$ and 1500 for $\epsilon_w = 3.0$)¹³ and a corresponding slow down of the molecular motions, which is reflected in a decrease of the chain diffusion coefficient (by factors of 40 and 1040 for $\epsilon_w = 2.0\epsilon$ and 3.0ϵ , respectively¹⁵). The classic SFA is furnished with mica surfaces, which are strongly attractive to most of the fluids (simple and polymeric) studied.²⁵ Recently, SFA experiments trying to explore the effect of the wall energetics used bare mica and mica covered by either evaporated metal oxides⁹ or chemically attached self-assembled monolayers of small molecules^{8,26–28} in order to reduce the strong wall affinity of mica. Different SFA machines use metal surfaces which are generally less attractive to polymers than mica.²⁹

At equilibrium care is taken to account for and correct for the system's center of mass accelerations, and under shear only the thermal part of the velocities—after the flow component is subtracted—is thermally stabilized.³⁰ During our simulations we do not allow the solid atoms to undergo any thermal motion around their equilibrium positions, as previous studies show that fixing the substrate atoms does not significantly change the results obtained.³¹

Simulation Results and Discussion

The first SFA experiments already established that confined fluids are strongly inhomogeneous in the vicinity of the confining surfaces, for systems both of small molecules^{32,33} and of long polymers.^{19,34} This inhomogeneity—in the form of strong density variations normal to the walls—results in oscillatory solvation forces with decreasing film thickness.^{19,32–34} This “wall-induced layering” (oscillatory density profile near the confining

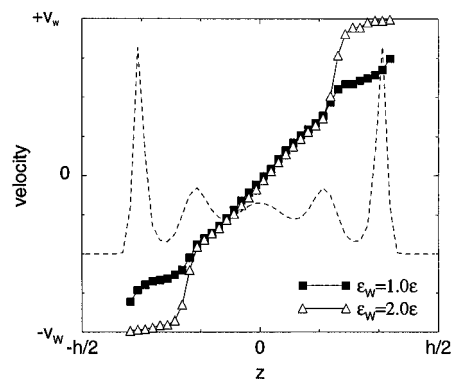


Figure 1. Density profile (---) and steady state velocity profiles for a fluid oligomer lubricant confined between weakly ($\epsilon_w = 1$) and strongly ($\epsilon_w = 2$) physisorbing surfaces. A sufficiently high wall velocity (v_w) is presented for slip to appear near the surfaces ($\epsilon_w = 1$) or inside the film ($\epsilon_w = 2$).

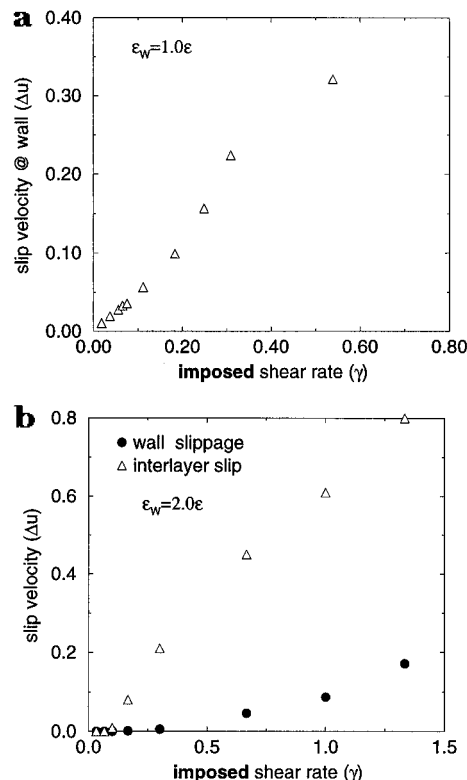


Figure 2. Dependence of the slip magnitude on imposed shear rate; generally slip increases with $\dot{\gamma}$. (a) For weakly adsorbing walls ($\epsilon_w = 1$) the slip plane is located between the surface and the fluid and there is always some slip present. (b) For stronger wall attractions ($\epsilon_w = 2$) and low shear rates there exists no slip throughout the confined film; for higher shear rates interlayer slip develops; and for even higher $\dot{\gamma}$ wall slip also appears, though it is much smaller compared to the interlayer slip.

surfaces) is of the same physical origin as the oscillations in the radial distribution function of simple liquids.²³

The velocity profile developed across the film—at constant shear rate and at steady state flow—changes qualitatively with wall affinity (Figure 1 and ref 16). For weak wall attractions ($\epsilon_w = 1$) the slip plane is located between the surfaces and the first fluid layer (Figure 1), whereas for the stronger wall affinities ($\epsilon_w = 2$ or 3) the slip plane is located inside the film, between the adsorbed chains and the free chains (interlayer slip).¹⁶ Moreover, with increasing shear rate ($\dot{\gamma}$) the magnitude of slip increases (Figure 2). For weakly physisorbing surfaces there exists only slip at the wall—for all the imposed shear rates—which increases with $\dot{\gamma}$ (Figure 2a). For strongly

(23) Bitsanis, I.; Hadziioannou, G. *J. Chem. Phys.* **1990**, *92*, 3827.

(24) Thompson, P. A.; Grest, G. S.; Robbins, M. O. *J. Isr. Chem.* **1995**, *35*, 93.

(25) In our system of units the affinity of mica to most of the substances studied by SFA corresponds to values $\epsilon_w \geq 3.0\epsilon$.¹³

(26) S. Granick and H. Hu *Langmuir* **1994**, *10*, 3857.

(27) Granick, S.; Hu, H.; Carson, G. A. *Langmuir* **1994**, *10*, 3867.

(28) Peanasky, J.; Cai, L.; Granick, S.; Kessel, C. *Langmuir* **1994**, *10*, 3874.

(29) Pelletier, E.; Montfort, J.; Loubet, J.; Tonck, A.; Georges, J. *Macromolecules* **1995**, *28*, 1990.

(30) H. J. C. Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; Di Nola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684.

(31) Cieplak, M.; Smith, E. D.; Robbins, M. O. *Science* **1994**, *265*, 1209.

(32) Horn, R. G.; Israelachvili, J. N. *J. Chem. Phys.* **1981**, *75*, 1400.

(33) Christenson, H. K. *J. Chem. Phys.* **1983**, *78*, 6906.

(34) Horn, R. G.; Israelachvili, J. N. *Macromolecules* **1988**, *21*, 2836.

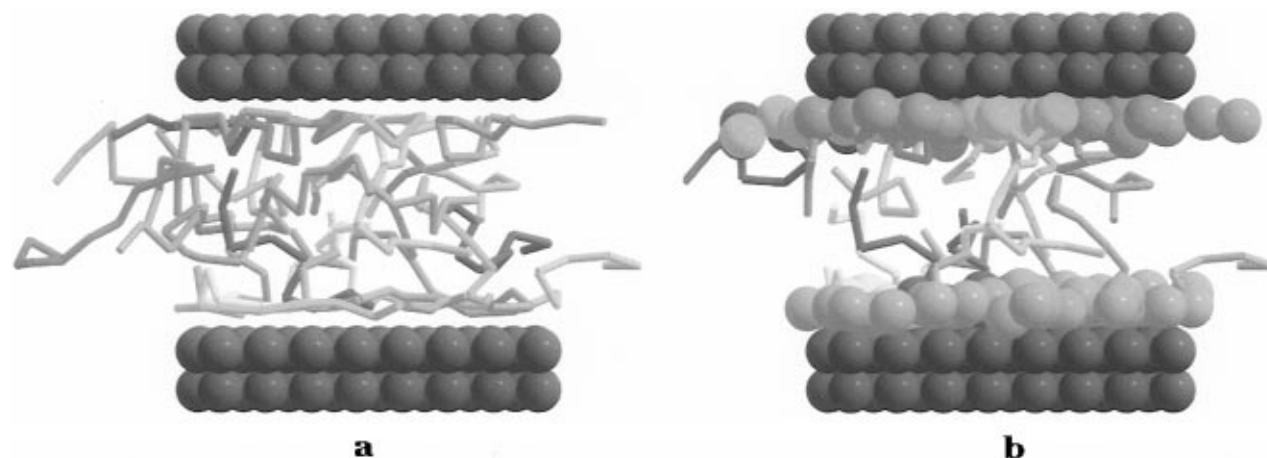


Figure 3. (a) All the confined chains represented by their bonds are visualized. A projection of the system on the xz shear plane is shown. (b) Adsorbed chains on the two confining surfaces (equilibrium, decamers, $\epsilon_w = 1$). The free chains are omitted for clarity. The adsorbed segments are presented by balls ("beads"), and the tails belonging to partly adsorbed chains, by the cylindrical bonds ("springs").

physisorbing surfaces and the lowest shear rates employed in our simulations there exists no slip anywhere in the film (Figure 2b); but with increasing shear rate interlayer slip develops between the adsorbed part of the film and the free chains located in middle part of the pore (Figure 1); for even higher $\dot{\gamma}$, slip at the wall also appears, which, however, is much smaller than the interlayer slip.

The molecular mechanism responsible for the slippage at a surface is well understood and intuitively expected. Slippage at the wall takes place when a smooth and weakly adsorbing surface is moving past a fluid which is characterized by some kind of *physical cohesion*. Under these circumstances³⁵ the fluid in contact with the surfaces cannot follow exactly the motion of the surface but is slowed down due to its physical connectivity with the slower moving fluid located further away from the surfaces; thus, slippage appears at the wall. Even simple LJ fluids exhibit wall slip near a neutral or weakly physisorbing surface.^{36–39} In these systems the connectivity inside the fluid is due to the interparticle attraction of the LJ potential (intrinsic cohesion). In the case of long polymer melts the connectivity is provided by the entanglements between adsorbed and free chains.^{41–43} In our case there is no attraction in the interchain potential used, and even our longer oligomers (10mers) are below the entanglement length (~ 30 monomers²²). But there is a physical connectivity which arises from the existence of partly adsorbed chains, which are partially inside the first layer in contact with the surfaces (adsorbed part) and partially extending inside the middle part of the film (Figure 3). The free tails belonging to partly adsorbed chains bind, physically connect, the adsorbed layers to the slower moving middle part of the film and prevent it from following exactly the motion of the surfaces—i.e. the velocity of the first layer is smaller than the wall velocity—thus giving rise to a slip between the wall and the fluid. At the same time the first

Table 1. Probabilities of Conformations with a Specific Number of Contacts for the Adsorbed Decamers Confined between Weakly ($\epsilon_w = 1$) and strongly ($\epsilon_w = 2, 3$) Physisorbing Walls for Several Imposed Wall Velocities. (v_w in MD units: $(\epsilon/m)^{1/2}$ and $h = 6.0\sigma$)

v_w	number of contacts									
	1	2	3	4	5	6	7	8	9	10
$\epsilon_w = 1.0\epsilon$										
0.00	0.07	0.11	0.12	0.12	0.12	0.12	0.10	0.10	0.09	0.06
0.05	0.07	0.11	0.12	0.12	0.12	0.12	0.11	0.10	0.09	0.05
0.10	0.05	0.11	0.10	0.11	0.13	0.13	0.13	0.10	0.09	0.06
0.20	0.06	0.11	0.10	0.10	0.10	0.11	0.11	0.12	0.11	0.08
0.50	0.08	0.08	0.08	0.08	0.09	0.10	0.12	0.13	0.13	0.11
0.70	0.08	0.08	0.07	0.07	0.08	0.10	0.12	0.14	0.14	0.13
0.90	0.08	0.08	0.07	0.07	0.08	0.09	0.10	0.13	0.16	0.15
1.50	0.08	0.07	0.07	0.07	0.08	0.09	0.11	0.12	0.15	0.16
$\epsilon_w = 2.0\epsilon$										
0.00	0.05	0.06	0.11	0.14	0.14	0.11	0.11	0.09	0.08	0.09
0.10	0.03	0.08	0.08	0.09	0.08	0.10	0.13	0.13	0.13	0.14
0.20	0.05	0.06	0.06	0.04	0.03	0.06	0.09	0.15	0.21	0.24
0.40	0.04	0.04	0.05	0.04	0.04	0.08	0.11	0.14	0.20	0.26
0.50	0.04	0.05	0.05	0.05	0.07	0.07	0.10	0.15	0.19	0.24
0.60	0.04	0.05	0.07	0.08	0.04	0.03	0.05	0.10	0.17	0.38
0.70	0.04	0.04	0.03	0.04	0.04	0.06	0.07	0.13	0.19	0.36
0.90	0.04	0.04	0.04	0.06	0.04	0.04	0.06	0.09	0.16	0.43
1.50	0.05	0.05	0.04	0.03	0.03	0.04	0.04	0.06	0.13	0.52
$\epsilon_w = 3.0\epsilon$										
0.00	0.01	0.04	0.10	0.16	0.11	0.14	0.10	0.11	0.12	0.12
0.10	0.01	0.05	0.07	0.08	0.05	0.15	0.14	0.09	0.10	0.26
0.50	0.01	0.01	0.01	0.05	0.04	0.22	0.09	0.15	0.14	0.28
0.90	0.03	0.006	0.003	0.06	0.001	0.015	0.05	0.03	0.10	0.70
1.50	0.01	0.005	0.005	0.01	0.05	0.08	0.01	0.03	0.06	0.74

layer, which is pushed by the moving surface through a continuous momentum transfer, does not slip past the middle part of the film, since the same tails tie together these two regions. With increasing shear rate the conformations of the adsorbed chains are expected to change¹⁵ (as the coils will align parallel to flow) but, for the weakly adsorbing surfaces ($\epsilon_w \leq 1$) and the densities used in our simulations, there always are many partly adsorbed oligomers to ensure no interlayer slip (Table 1, Figure 4).

The physical connection between the adsorbed chains and the middle part of the film can be quantified using the conformations of the adsorbed chains, e.g. the distribution of probabilities for adsorbed conformations with a certain number of adsorbed segments (Table 1). It becomes clear that the conformations of the adsorbed chains change radically when shear rate is imposed, especially in the vicinity of strongly attractive surfaces. The tendency for the chains in the vicinity of the walls to

(35) The absence of any surface roughness and surface attraction.

(36) Bitsanis, I.; Magda, J. J.; Tirell, M.; Davis, H. T. *J. Chem. Phys.* **1987**, *87*, 1733.

(37) Bitsanis, I.; Somers, S.; Davis, H. T.; Tirell, M. *J. Chem. Phys.* **1990**, *93*, 3427.

(38) Somers, S.; Davis, H. T. *J. Chem. Phys.* **1992**, *96*, 5389.

(39) Heinbuch, J.; Fischer, J. *Phys. Rev. A* **1989**, *40*, 1144.

(40) Manias, E.; Bitsanis, I.; Hadziioannou, G.; ten Brinke, G. On the nature of shear-thinning in nanoscopically confined films. *Europhys. Lett.* **1996**, *33*, 371.

(41) de Gennes, P. G. *C. R. Acad. Sci.* **1979**, *228B*, 219.

(42) Brochard, F.; de Gennes, P. G. *Langmuir* **1992**, *8*, 3033.

(43) Brochard, F.; de Gennes, P. G.; Hervet, H.; Redon, C. *Langmuir* **1994**, *10*, 1566.

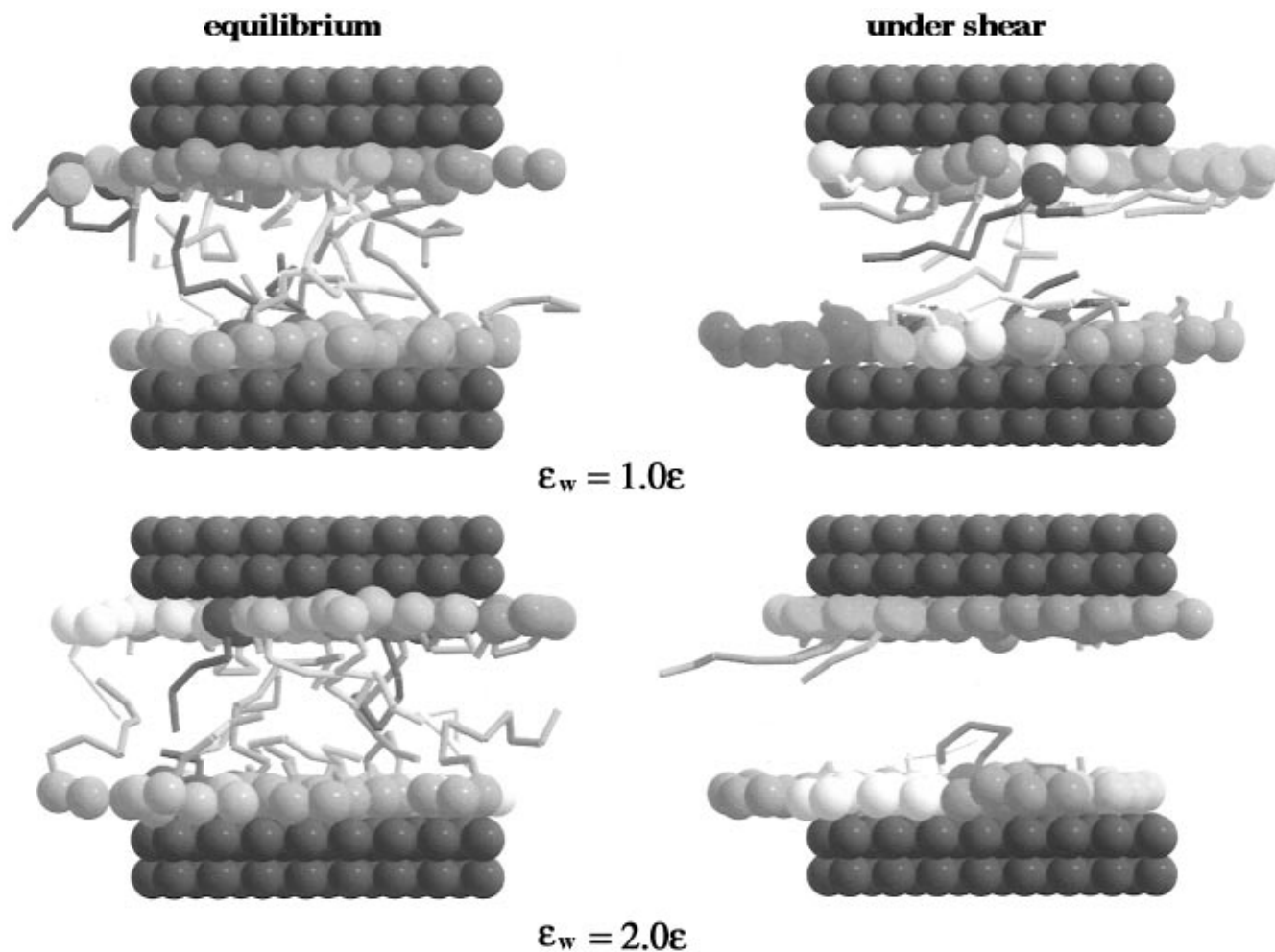


Figure 4. Adsorbed chain conformations on weakly ($\epsilon_w = 1$, top) and strongly ($\epsilon_w = 2$, bottom) physisorbing surfaces for equilibrium and under shear ($v_w = 0.9$). It is obvious that under shear for $\epsilon_w = 1$ there is still a substantial number of adsorbed chains, even at this high shear rate, whereas for $\epsilon_w = 2$ there are almost no partly adsorbed chains to “tie” the adsorbed and the free part of the film (decamers, $h = 6$). See also Table 1.

align parallel to them is enhanced further by flow, since conformations with large z -size⁴⁴ feel a large velocity gradient and frictional forces originating from the velocity gradient try to align the chains parallel to flow.^{45–47} For the weakly adsorbing surfaces there is a sufficient number of partly adsorbed chains, even for the highest shear rates that can⁴⁹ be applied to these systems, to prevent interlayer slip (Figure 4). For the stronger physisorbing surfaces, however, there is a change from no slip, at low shear rates, to considerable interlayer slip at higher $\dot{\gamma}$ (Figure 2).

Inside a film confined and sheared between strongly attractive surfaces (Figure 5): (i) For small shear rates there still exist many partly adsorbing chains (Table 1) acting as connectors between the adsorbed layer and the middle part of the film, thus hindering any interlayer slip (Figure 5, case of $v_w = 0.05$). (ii) With increasing shear rate the adsorbed chains systematically become better

aligned to flow, less partly adsorbed coils exist (Table 1), and the physical connectivity is almost completely lost (Figure 5, case of $v_w = 0.9$). This results in a gradual appearance of a substantial interlayer slip: the location of the slip plane can be clearly seen in the velocity profile of $v_w = 0.9$ in Figure 5 between the adsorbed layer and the free chains. In these systems the adsorbed layer covers the strongly adsorbing surface and locks on it, traveling with the velocity of the wall, so effectively the wall-adsorbed-layer system behaves like an effective neutral wall, which moves with respect to the free chains. So, this interlayer slip is completely analogous to the slip near nonadsorbing walls, as the middle part can be considered as a confined oligomer melt between two neutral ($\epsilon_w = 0$) surfaces, which correspond to the adsorbed layers covering the surface, screening any attraction from the underlying strongly adsorbing wall. The difference is that in this case there is some effective roughness of the surface by means of a perpetual chain exchange between adsorbed chains that desorb and free chains that take their place.¹⁵ This continuous exchange through the desorption-adsorption process sustains a weak physical connectivity between an effectively neutral surface and a melt of free chains, preventing complete slip from taking place, as would be in the case of a neutral smooth surface.⁴¹ Finally, in these sheared films between strongly physisorbing surfaces, for $\epsilon_w = 2$ there appears only a small wall slip for the highest imposed shear rates (Figure 2),

(44) \bar{z} is the direction of the velocity gradient in the simulation geometry.

(45) Subbotin, A.; Semenov, A.; Manias, E.; Hadziioannou, G.; ten Brinke, G. *Macromolecules* **1995**, *28*, 3898.

(46) Subbotin, A.; Semenov, A.; Hadziioannou, G.; ten Brinke, G. *Macromolecules* **1995**, *28*, 3901.

(47) Subbotin, A.; Semenov, A.; Manias, E.; Hadziioannou, G.; ten Brinke, G. *Macromolecules* **1995**, *28*, 1511.

(48) Landau, L. D.; Lifshitz, E. M. *Fluid Mechanics*; Pergamon Press: Oxford, 1982.

(49) As wall slippage increases with $\dot{\gamma}$, after some wall velocity ($v_w = 2.0(\epsilon/m)^{1/2}$ for our densities) the only effect of increasing imposed shear rate is to introduce stronger slip whereas inside the film the induced shear rate remains the same.

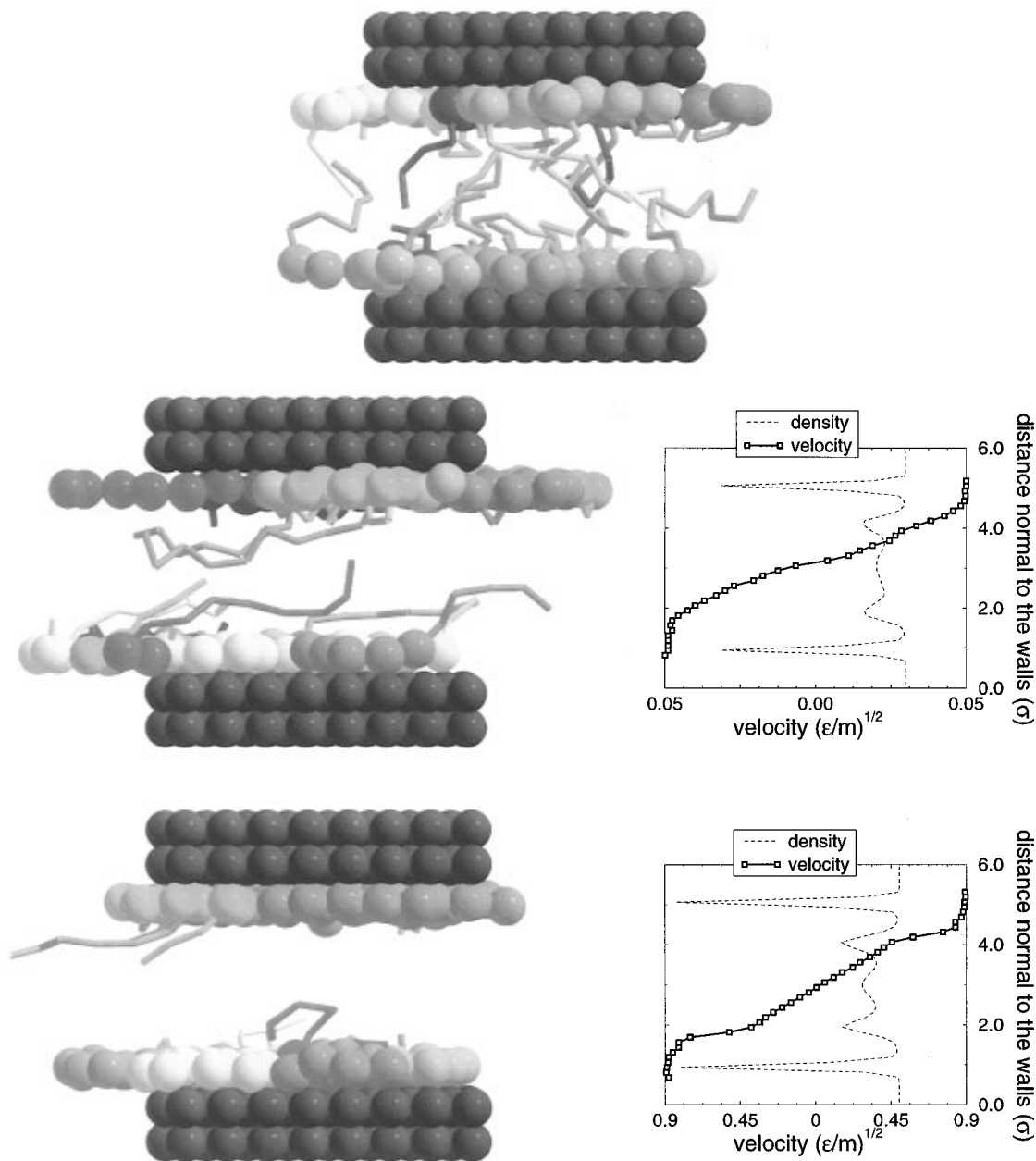


Figure 5. Adsorbed chain conformations (decamers, $h = 6$, $\epsilon_w = 2$) for equilibrium and two shear rates ($v_w = 0.05$ and 0.9). For low shear rates there exists sufficient number of partly adsorbed chains to prevent interlayer slip. For higher shear rates nearly all physical connectivity between the first layer and the middle part is lost and slippage takes place between the adsorbed layer and the free chains. This is the molecular mechanism of interlayer slippage.

which is always very small compared to the interlayer slip, whereas for $\epsilon_w = 3$ slippage at the walls is not observed for any of the shear rates imposed on our films.

Apart from these structural inhomogeneities—density layering and interlayer slip—across these ultrathin oligomer films, there are also other important inhomogeneities with respect to the nature and the dynamics at different parts of the confined systems. As already mentioned, both the relaxation times¹³ and the diffusion coefficients¹⁵ differ dramatically between the chains located inside the interfacial region and those in the middle of the pores (up to three orders of magnitude for wall affinities $\epsilon_w = 3$).^{13,15} Inspired by the SFA experiments,^{7–10,17,20,26–28} an “effective viscosity” can be defined as the mean frictional force per unit area (which is the xz stress component) divided by the induced shear rate ($\eta_{\text{eff}} = \tau_{xz}/\dot{\gamma} = F_{\text{frict}}/S\dot{\gamma}$);¹¹ η_{eff} has dimensions of viscosity and is a measure of the resistance to flow. This quantity characterizes the response of the whole film.¹¹ Taking

into account that in steady state flow the stress tensor components are constant throughout the system,⁴⁸ a *local effective viscosity* can be defined as the stress component divided by the local shear rate (the local shear rate at z_0 can be calculated as $\dot{\gamma}_{\text{local}} = (\partial v_x/\partial z_0)$). From the steady state velocity profiles, developed across these films (Figure 1), it becomes obvious that the local shear rate inside the adsorbed layer is smaller than in the middle and thus the fluid in the wall interface is of higher “viscosity” than further away from the surfaces.

A typical response of a confined film to shear is shown in Figure 6a: the local effective viscosity is plotted for the adsorbed layers and for the middle part of the pore (linear hexamers, $h = 6$, $\epsilon_w = 2$). Although inside the solid-oligomer interface the fluid exhibits strong shear thinning, the middle part of the film behaves almost as a Newtonian fluid, i.e. nearly all the shear thinning takes place inside the adsorbed first layer. Furthermore, as expected from the velocity profile (Δ in Figure 1), the viscosity inside the

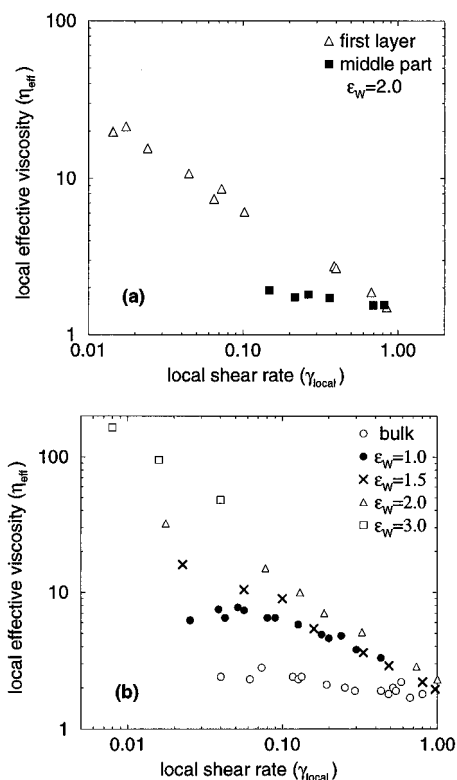


Figure 6. Local effective viscosities inside the interfacial layer and in the middle of the pore: (a) Thin ($h=6\sigma$) film of hexamers between $\epsilon_w = 2$ surfaces; (b) wide ($h=10\sigma$) films between surfaces of various wall affinities.

first layer is higher than that in the middle part (for the smaller shear rates almost an order of magnitude). At the same time, the viscosity in the middle part of the film is only slightly higher than the bulk value. This strong local variation of the effective viscosity was long suspected by experimentalists and proposed as an explanation for their observations^{17–20} but is here clearly demonstrated through the MD simulations. Relevant to many of the experimentally obtained shear thinning power laws is the behavior of the local effective viscosity inside the solid–oligomer interface, presented in Figure 6b. Experiments reporting power laws for shear thinning are usually studying ultrathin films, only a few molecular diameters wide, which implies that they are probing mainly the effective viscosity inside the first layer.²⁰ In Figure 6b the local η_{eff} is shown for oligomers confined in wide films between surfaces of various affinities. The power law shear thinning inside the interfacial area is determined by the wall affinity and is largely insensitive to changes of the film thickness and the molecular architecture.⁴⁰ At the same time, the rheological response of the whole film is the weighted average of these two regions: the “viscous” interfacial layer and the bulklike middle part.⁴⁰ The viscosity increases reported here are not as high as in some experiments,¹⁸ but one has to take into account that the loads used in those experiments are much greater than the ones used by us, and the viscosity is expected to increase exponentially with pressure.^{11,20}

Comparison with Experiments and Theory. Systematic SFA studies, trying to explore the effect of the wall energetics, used either evaporated metal oxides⁹ or chemically attached self-assembled monolayers of small molecules⁸ in order to change the wall affinity of mica. Their findings suggest quantitative and qualitative differences in the sliding and the slip in the steady state in comparison with the classical mica SFA experiments.⁷ A common assumption necessary to account for the devia-

tions between systems with strongly physisorbing surfaces (mica) and less attractive ones (e.g. OTE (octadecyltriethoxysilane) covered mica, which is effectively a CH_3 surface) is that when strongly attractive surfaces are used “slip occurs within the film” and for moderately attractive surfaces “slip is taking place at the solid wall”.⁸ Moreover, in SFA experiments of PDMS (poly(dimethylsiloxane)) between mica,⁵⁰ Horn et al.¹⁹ used an algorithm based on the Chan and Horn method⁵¹ to evaluate the viscous forces, and agreement with their SFA results was obtained only “when stick boundary conditions apply at a distance of 1.5 nm from each surface” and thus “the shear plane is located inside the film approximately one molecular layer from each solid surface”.¹⁹ The above conclusions were derived by fitting equations to experimental data, but the physical justification provided for this assumption is almost identical to what our MD simulations reported herein find as well. What Horn et al. proposed¹⁹ is a “pinning effect” of the adsorbed chains resulting in very slow dynamics and “immobilization” of the adsorbed chains and at the same time a physical connection in the form of “entanglements” between tails and loops of the adsorbed chains and the free chains. These ideas are in very good agreement with the results presented in this paragraph and other proposed models of previous studies studying the nature of confined PDMS.¹⁷

Furthermore, some theoretical and experimental studies dealing mainly with longer chains—sometimes even with entangled melts—do have similarities with our simulations and moreover are in surprisingly good agreement as far as the molecular mechanisms of wall and interlayer slippage are concerned. Brochard and de Gennes (BG) have recently developed a theory^{42,43} describing the response to flow of a melt near a strongly adsorbing surface. To briefly recapitulate their conclusions, strong slip is expected near smooth nonadsorbing or weakly adsorbing surfaces. For stronger wall affinities BG expect that some chains will bind strongly to the surface creating a “fluffy carpet”, and by extending into the melt, they offer a link with the chemically identical melt, suppressing any slippage. With increasing shear rates there is a nonslippage to slippage transition. The mechanism that they propose is that “the adsorbed chains undergo a coil stretch and disentangle from the melt”. The adsorbed chains lie on the wall, and thus the surface is covered by a neutral layer of polymer which allows slip to take place. These ideas were also exploited by Bruinsma,⁵² who proposed a “two-fluid model” for a melt of chemical identical chains in the vicinity of a surface, with an immobilized, glassy, adsorbed layer and a bulk melt slipping over it, placing the slip plane exactly between the adsorbed layer and the free chains. A method developed recently by Leger et al.,⁵³ enabling direct observation of the velocity profile for extremely small distances near a surface, was employed to study polymer melts in the vicinity of very strongly physisorbing surfaces (PDMS on silica) and weakly physisorbing surfaces (PDMS on silica covered by a monolayer of OTS (octadecyltrichlorosilane)).⁵³ These experiments reveal the existence of an immobilized adsorbed layer near the strongly attractive walls, and slip is suppressed for low shear rates by means of a physical connectivity between the free bulk through the tails of the adsorbed chains extending in it. Slippage

(50) There is very strong adhesion between PDMS and mica; in our reduced units the energy of interaction would correspond to values of ϵ_w higher than 3.¹³

(51) Chan, D. Y. C.; Horn, R. G. *J. Chem. Phys.* **1985**, *83*, 5311.

(52) Bruinsma R. *Macromolecules* **1990**, *23*, 276.

(53) Migler, K. B.; Hervet, H.; Leger, L. *Phys. Rev. Lett.* **1993**, *70*, 287.

comes into play after strong enough flows are imposed, as predicted by the BG theory, and is located inside the film.

Finally, we should point out that we focus on confined systems for which the interfacial chains are in a "glassy", disordered state.¹³ Under different conditions—temperature, pressure, and wall symmetry—other MD simulations⁵⁴ found that confinement may lead to "solidification" near the surface, manifested by the existence of domains with crystalline ordering. In these systems shear may affect the structure of these domains resulting, in a destruction of their crystallinity, thus causing the shear melting of these "nanocrystallites", which can result in the appearance of slippage.⁵⁴

Summarizing. Nonequilibrium molecular dynamics simulations have been carried out in order to gain some insight into the nature of nanoscopically confined films

under shear. These films exhibit structural (density fluctuations, interlayer slip) and dynamical (relaxation times, transport coefficients, viscosity) inhomogeneities on the molecular scale across the film. A molecular mechanism—involving shear-induced conformational changes of the adsorbed chains—is proposed to account for slippage taking place inside the fluid films, observed in SFA and other experiments. Moreover, an increased effective viscosity is found inside the solid-oligomer interface (i.e. the adsorbed layer) compared with the viscosity in the middle of the pores and/or the bulk. Thus, for the pressures employed in these studies, regions of molecular dimensions with different viscosities develop across the film: a bulklike middle part and two highly viscous adsorbed layers on each surface. Almost all the shear thinning takes place inside these adsorbed layers.

(54) Thompson, P. A.; Robbins, M. O. *Science* **1990**, *250*, 792.