Effect of shear on the desorption of oligomers in nanoscopically confined films

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Bitsanis *et al.* J. Chem. Phys. **99**, 5520 (1993) found that in nanoscopically confined films between strongly physisorbing surfaces *chains with many contacts with the walls are irreversibly adsorbed.* When shear is imposed to these systems molecular dynamics (MD) simulations show that the majority of the adsorbed oligomers adopts flat conformations on top of the walls. Although these conformations are characterized by high molecular adsorption energies, the same MD simulations show that desorption is strongly promoted by shear. The underlying mechanism is discussed.

Recent experimental studies of ultra thin films by the Surface Forces Apparatus (SFA) reveal striking behavior of lubricating films when confined in dimensions comparable to the molecular size. Such films become inhomogeneous[1,2] and their effective viscosity increases dramatically when reducing the film thickness.[3] This implies that the mobility of the confined molecules decreases as the confinement becomes narrower (although characterized by liquidlike behavior for separations down to 6 atomic diameters[2,4,5]) and under further compression a solidlike behavior is observed.[6] The molecular mechanism responsible for this behavior is the vast slowing down of molecular motions inside the adsorbed layer due to the surface induced densification.[7]

These macroscopic experimental observations can be complemented by atomistic computer simulations[7,8] to obtain detailed information about the microscopic/molecular processes underlying the macroscopic behavior. Recently, Bitsanis and Pan published an equilibrium simulation study[7] providing explanation for the *origin of the "glassy" dynamics at the solid-oligomer interface* and discussing the desorption of oligomers from *weak* and *strong physisorbing* surfaces. The present work is motivated by this study and demonstrates how shear affects the desorption of oligomers.

The system studied here is a film of oligomers (hexamers) at liquid densities confined between two double layered (111) fcc surfaces. The chains are modeled by a well studied bead spring model[7–9] and shear is imposed by moving the walls with a constant velocity (v_w) towards opposite directions ($\pm x$). The force field describing the interactions consists of a pairwise purely repulsive, shifted and truncated 12–6 Lennard–Jones (LJ) potential between all segments:

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

where ϵ is the LJ energy parameter and σ the LJ length parameter. For successive monomers in a chain a strongly attractive potential is added:

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

where $R_0 = 1.5\ \epsilon$ and $k = 30.0\ \sigma/\epsilon^2$. These parameters have been proven to prevent bond crossing at the temperature used in our simulation.[9] The interactions between the walls and the segments are also modeled by a pairwise Lennard–Jones potential, which now includes the attractive tail of the potential

$$U_w(r) = 4\epsilon_w\left(\left(\frac{\sigma_w}{r}\right)^{12} - \left(\frac{\sigma_w}{r}\right)^{6}\right). \quad (3)$$

The SFA setup developed in our laboratory[10] is equipped with a feedback system which keeps the separation of the two mica plates constant; in order to mimic this geometry the distance between the two walls (h) is constant in our MD simulations. This means that the simulations are done under constant temperature (T), number of particles (N), and volume. Despite the brevity of this paper, one simulation detail that is worth mentioning is the thermostat used for a confined system under shear. We fixed the temperature at $kT = 1.0\epsilon$ by rescaling the velocities[11] in two different ways: (i) scaling only the components of the velocities normal to the direction of the flow and (ii) scaling also the thermal part of the velocity component parallel to flow. For the second method the film is divided in slices and the flow velocity is defined in each slice by averaging and scaling self consistently.[12] For these chain molecules and for slices containing on average 15 particles, the two methods give the same results (velocity profiles and local temperatures) within the simulation accuracy. A variant of Verlet's method was used to integrate the differential equations of motion with a time step of 0.004 62 MD units.

Usually chains are grouped according to their center of mass distance from the walls. However recent studies[7] show that a more physically justified grouping is based on the number of contacts with the confining surface. "Adsorbed" chains are those with at least one segment inside the first layer (Fig. 1) of the density profile of either wall, while "free" chains have all segments outside the first layers. For chains up to decamers (10 segments per chain) and film thicknesses down to six segment diameters ($h = 6\sigma$) no chains form "bridges" between the two walls, thus all adsorbed chains are in contact with a single surface. It has been found[7] that under equilibrium conditions "almost the entire population of adsorbed chains relaxes with the same time
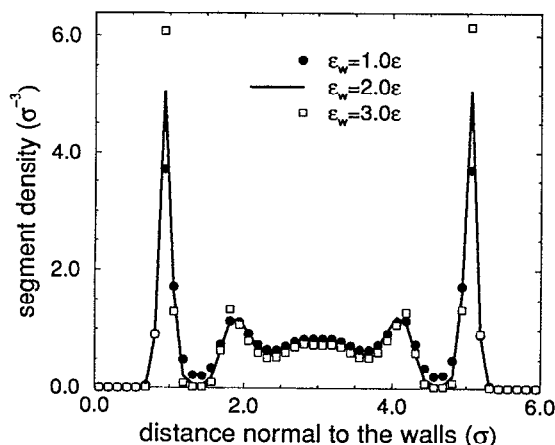
FIG. 1. The inhomogeneity of nanoscopically confined liquids is enchanced by the increase of the wall attraction. All the adsorbed segments are located inside the two peaks close to the walls.

constant in a manner remarkably insensitive to the number of surface-segment contacts." Moreover, for wall attractions $\epsilon_w < 1.0\epsilon$ there is only a slight slowing down of the molecular motions characterizing a "weakly physisorbing" surface, whereas for $\epsilon_w = 2.0\epsilon$ and 3.0ϵ the surfaces behave as "strongly physisorbing" by inducing an increase in the longest relaxation time of the adsorbed pentamer chains by a factor of 70 (for $\epsilon_w = 2.0$) to 1500 (for $\epsilon_w = 3.0$).[7]

We will focus on the desorption of these *adsorbed* chains as a function of the number of surface contacts. In Figs. 2 and 3 the mean square displacement normal to the walls (z msd) vs the time is plotted, for chains that have 1–6 (adsorbed) contacts with the confining surfaces. The z msd are calculated on time domains of $64*10^3$ time steps and averaged over 137 time origins. In order to be directly comparable with Ref. 7 the z msd are scaled with the radius of gyration in the bulk (Rg) and time is scaled by the bulk end-to-end vector relaxation time of the hexamers ($\tau_1 = 16 \pm 2$ MD units). Under equilibrium (no flow) for weakly physisorbing surfaces ($\epsilon_w = 1.0$) all chains manage to escape from the surface relatively fast. But for $\epsilon_w = 2.0$ only those chains that have one or two contacts with the walls manage to desorb in the time scale presented. Chains with more than 3 contacts with the $\epsilon_w = 2.0$ surface and all adsorbed chains for the case of $\epsilon_w = 3.0$ remain adsorbed for the total time of the simulation, which is more than five times longer than the time scale presented in Fig. 2. This is in excellent agreement with previous findings for much wider films of pentamers.[7]

When shear is imposed the chains tend to adopt flatter conformations on top of the walls and this tendency is enhanced for increasing shear rates and higher ϵ_w (Table I). For an imposed shear rate $\gamma = 0.5$ $(\epsilon/m\sigma^2)^{1/2}$, which is much higher than the typical shear rates used in SFA experiments, $(v_w = 0.9$ $(\epsilon/m)^{1/2})$ 28% of the adsorbed chains have 6 surface contacts for $\epsilon_w = 1.0$, 57% for $\epsilon_w = 2.0$, and 67% for $\epsilon_w = 3.0$. This implies that the average energy of adsorption per chain increases considerably for higher shear rates. In the case of strongly physisorbing surfaces more than 75% of the
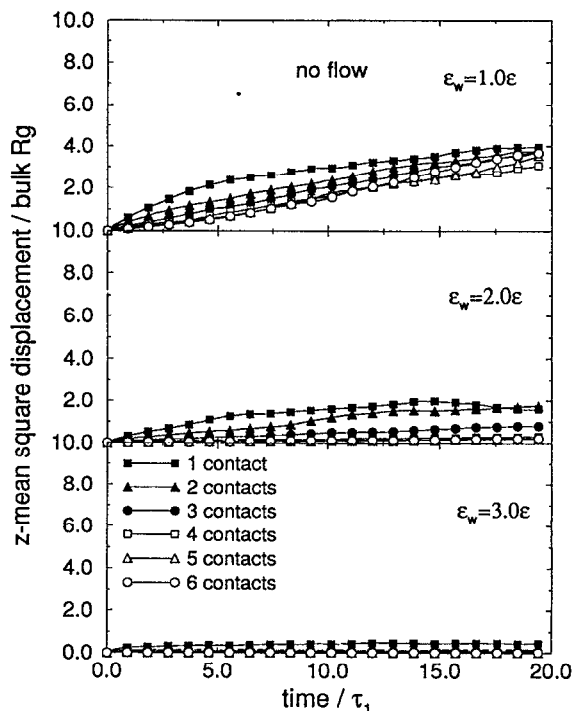

FIG. 2. Center-of-mass mean square displacements normal to the walls (z msd) vs time for chains with 1–6 contacts with the surfaces, under equilibrium (no flow). For comparison reasons the same scale is used.

adsorbed chains have an adsorption energy exceeding 10 kT ($\epsilon_w = 2.0$, 5–6 contacts), whereas for $\epsilon_w = 3.0$ more than 75% of the adsorbed chains have an adsorption energy exceeding 15 kT (5–6 contacts). At first sight this suggests that the desorption will be much smaller under flow, however this is not at all the case.

For a reduced shear rate $\gamma \approx 0.5$ the mean square displacements normal to the walls increase dramatically in comparison with the equilibrium situation (Fig. 3). For $\epsilon_w = 1.0$ the z msd of all adsorbed chains (1–6 contacts) almost doubles; for $\epsilon_w = 2.0$ even chains with 6 contacts (≈ 12kT) desorb relatively fast, whereas in equilibrium even chains with 2 or 3 contacts were irreversibly adsorbed. Finally for $\epsilon_w = 3.0$ chains with less than 4 contacts desorb in the time scales shown in Fig. 3 whereas adsorbed chains with more contacts escape from the surface in longer times than probed with our MD simulations.[12]

It is known that the self diffusion in a nonNewtonian fluid increases under shear. For example MD studies of a bulk LJ fluid at the triple point show that for the same shear rate as in Fig. 3 the diffusion coefficient parallel to the velocity gradient increases almost twofold in comparison with equilibrium.[13] This is in good agreement with our results for $\epsilon_w = 1.0$ for short times where the msd is almost linear with time. For longer times the confinement forces the msd to increase more slowly as the space in the z direction that the chains can travel is restricted by the two walls. But for the stronger physisorbing surfaces self diffusion alone is not sufficient to cause such a dramatic effect as shown in Fig. 3. The molecular mechanism behind this is believed to be the
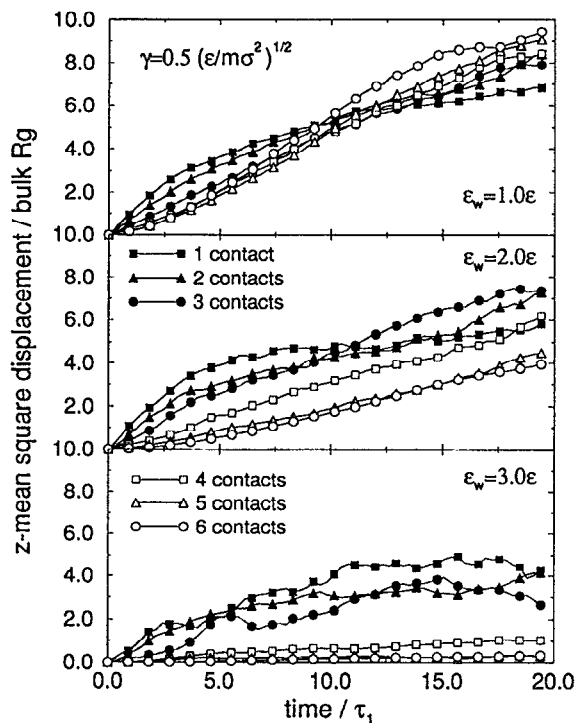
FIG. 3. Center-of-mass mean square displacements normal to the walls (z msd) vs time for chains with 1–6 contacts with the surfaces, under shear.

following. Adsorbed segments jump off from the wall due to diffusion. Under equilibrium the connectivity along the chain is the only variable which biases the direction of the diffusional motion, which explains why chains with some free segments (1–3 contacts) desorb fast. On the other hand, under flow when a segment diffusionally desorbs, it feels a force due to the velocity gradient which is a driving force to peel off the rest of the adsorbed segments of the same chain. Of course, this means that the phenomenon should be enhanced by higher shear rates.

The shear rate (γ) employed to obtain the result presented in Fig. 3 is extremely high in comparison with the SFA experiments, although similar shear rates can be found in magnetic storage devices. Molecular dynamics is capable of handling shear rates of these magnitudes only,[8,13] as for smaller γ the flow velocities are masked by the thermal motions and averages over extremely long runs are needed. Nevertheless, if the center of mass z msd is plotted vs the shear rate an almost linear relation is found for the free and

TABLE I. Fraction of the adsorbed chains with one to six contacts with the surfaces. ($h = 6.0\sigma$)

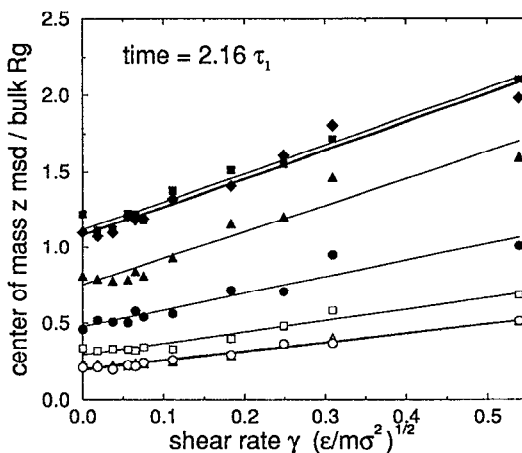| ϵ_w	1.0 ϵ			2.0 ϵ			3.0 ϵ		
Wall velocity	.00	.90	1.5	.00	.90	2.0	.00	.90	2.0
1 contact	.12	.10	.11	.07	.05	.05	.07	.01	.03
2 contacts	.17	.11	.10	.10	.06	.05	.11	.08	.05
3 contacts	.19	.13	.12	.14	.06	.06	.13	.11	.05
4 contacts	.18	.17	.16	.17	.08	.07	.17	.04	.06
5 contacts	.18	.21	.21	.22	.18	.12	.23	.09	.06
6 contacts	.16	.28	.30	.30	.57	.65	.29	.67	.75

FIG. 4. Center-of-mass mean square displacements normal to the walls (z msd) for time $t = 2.16\tau_1$ vs shear rate for chains with 0–6 contacts, where τ_1 is the Rouse bulk relaxation time. The symbols are the same as in Figs. 2 and 3 ($\blacklozenge$:0 contacts); $\epsilon_w = 1.0\epsilon$.

adsorbed chains (Fig. 4). This implies that if the film is subjected to a lower shear rate the desorption will still be enhanced by flow but to a lesser extent. Moreover, concentrating on chains with 6 contacts, which exhibit the smallest slope in Fig. 4, we see in Fig. 5 that for reduced times of 19 τ_1 [which correspond to real time in the order of 0.6 to 15 nsec for PDMS or PI at room temperature, or for PS or PTHF at about 430 K (Ref. 9)] even smaller shear rates have a substantial effect on the desorption (manifested by increasing slope of line). Finally, we should point out that we focus on confined systems for which the interfacial chains are in a "glassy," disordered state.[7] Under different conditions—temperature, pressure, and wall symmetry—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 melting of these "microcrystallites."
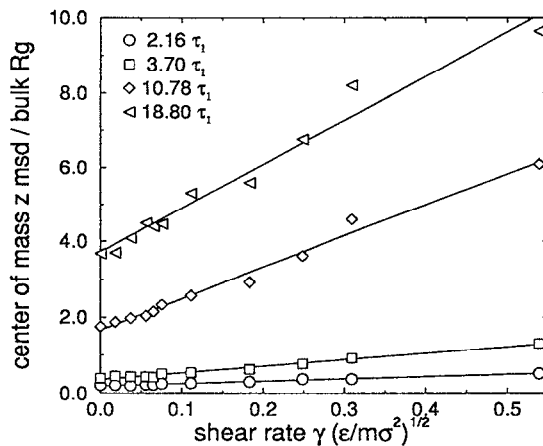

FIG. 5. Center-of-mass mean square displacements normal to the walls (msd) for several times vs shear rate for chains with 6 contacts; $\epsilon_w = 1.0\epsilon$.

In summary, it has been demonstrated that shear favors flat conformations of adsorbed molecules—characterized by high molecular adsorption energies. At the same time shear promotes considerably their desorption even from strongly physisorbing surfaces, on which short chains get immobilized under equilibrium conditions.

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