

THE NATURE OF NANOMETER-THICK LUBRICATING FILMS

Evangelos Manias and Emmanuel P. Giannelis

*Department of Materials Science and Engineering,
Cornell University, Bard Hall, Ithaca NY 14853.*

Abstract

Molecular Dynamics simulations have been used to investigate the rheological properties and dynamics of nanoscopically confined lubricating films. Comparative experimental studies of 10 to 20 Å thin polymer films confined between mica-type layers explore the dynamics of similar systems, and confirm the computer simulation predictions. The use of model systems of *polymers intercalated in layered mica-type silicates* facilitates the study of SFA-like geometries with a variety of common analytical techniques, thus dramatically expanding the horizons of studying nanometer wide confined polymer films.

Introduction & aim of this work

The rheological and tribological behavior of thin confined lubricating films is becoming dramatically different when the dimensions of the systems approach the nanometer level. The emergence of advanced techniques, such as the atomic force microscope (AFM) and the surface forces apparatus (SFA) which are capable of probing frictional and rheological properties of well-defined nanoscopic systems, combined with atomistic computer simulations have recently revolutionized the field [1].

The most important difference between bulk lubricants and their ultra-thin confined films is a strong inhomogeneity that develops across such films. Recent Non Equilibrium Molecular Dynamics simulations [2] have revealed that beyond the well known density layering across nanometer-thin lubricant films, other structural and dynamical inhomogeneities exist across them. Namely, when these films are subjected to strong shear flows slip appears at the wall for weakly attractive surfaces; or inside the lubricant film –interlayer slip– for strongly physisorbing walls and high shear rates [2, 3]. Moreover, the 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 first, more viscous, interfacial layer, whereas the response of the polymer beyond this layer –i.e. 3 to 7 Å away from the walls– remains bulk-like in value, and exhibits an almost Newtonian behaviour [4].

The aim of this work

The most striking fact of all these computer simulation findings is *the length scale over which these dramatic changes take place*. The simulation findings [2] suggest that the dynamics of the polymers change as much as 3 orders of magnitude between the adsorbed layer and the second layer away from the wall; i.e. dynamics are extremely slow in the immediate vicinity of the surface (within one monomer from the wall), whereas they are bulk-like 3-7 Å away from it. In order to unveil the origins of these dynamic inhomogeneities, we *explore experimentally the predictions of the computer simulations*. In this endeavor, we use *polymer/silicate intercalated nanocomposite systems* (figure 1). These systems are structured in alternation of 10 Å mica-type crystalline layers and 10-20 Å thick polymer films, that self-assemble in a very parallel manner [5]. These intercalated nanocomposite systems offer the same geometry as an SFA (i.e. nanoscopically confined polymer films confined between parallel atomically smooth mica-type crystalline surfaces), but by virtue of their structure at much high concentration in a macroscopic sample (figure 1); this allows for the use

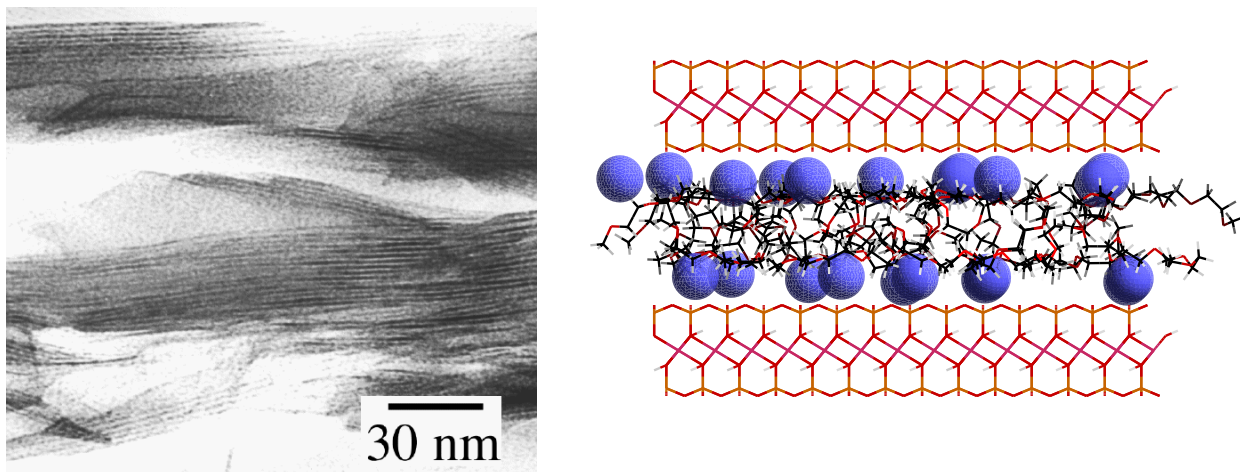


Figure 1 A TEM image of an intercalated nanocomposite (PS/fluorohectorite) and a simulation snapshot of a PEO/silicate intercalated system. Details on nanocomposites in [5].

of common analytical techniques (such as for example FTIR/Raman, SANS, DSC, NMR, parallel plate rheometer and so on) to probe the properties of 2nm thin polymer films, thus dramatically expanding the horizons of studying nanoscopically confined polymer films.

Results & Discussion

The most striking predictions of the computer simulations, for the nanoscopically confined lubricant films, are the dramatically different dynamics between the polymer located within the first monomer diameter (within $\sim 3\text{-}7 \text{ \AA}$ from the confining surfaces) and the second layer (just beyond $\sim 3\text{-}7 \text{ \AA}$ from the surfaces). The polymer dynamics can be studied in two ways, through: (i) relaxation times, and (ii) diffusion coefficients.

The **relaxation times** of chain molecules are studied in our computer simulations through the time correlation function of the end-to-end vector in the case of the oligomer [6, 7] and the corresponding relaxation time is the relaxation time of the first Rouse mode [7]. The behaviour of this relaxation is shown in figure 2a and discussed in detail elsewhere [6, 7]. With increasing polymer-surface affinity there exists across the film a coexistence of a fast (almost bulk-like) and a slower relaxation process. The latter becomes dramatically slow with stronger attractions (up to 3 orders of magnitude slower than the corresponding bulk for $\epsilon_W = 3.0\epsilon$, table I). From the simulations it is revealed that the adsorbed chains are the slow relaxing species, whereas the chains without adsorbed monomers have relaxation times comparable to those of the bulk, even when they are located inside the second layer from the surface [7], or are confined in slits of just 3 monomer diameters wide [6], thus even in the strongest geometric confines possible.

In order to validate experimentally this prediction we carried out $^2\text{H-NMR}$ experiments in perdeuterated-PEO/silicate nanocomposites (figure 2b). In these geometries PEO is confined between two atomically smooth mica-type silicate surfaces, separated by 9 \AA almost 3 times the monomer diameter of the PEO polymer chain. For the lowest temperatures where the local segmental motion of the polymer is quiescent, the NMR signal possesses well-formed singularities and sharp step-edges characteristic of the solid/glassy dynamics. With increasing temperature the “sharp” spectral features gradually broaden with a simultaneous build-up of the intensity at the center of the powder pattern, indicative of the onset of fast, isotropic, liquid-like dynamics. This central peak results from increased segmental motion which causes temporal averaging of the signal. Unlike the bulk sample, the interca-

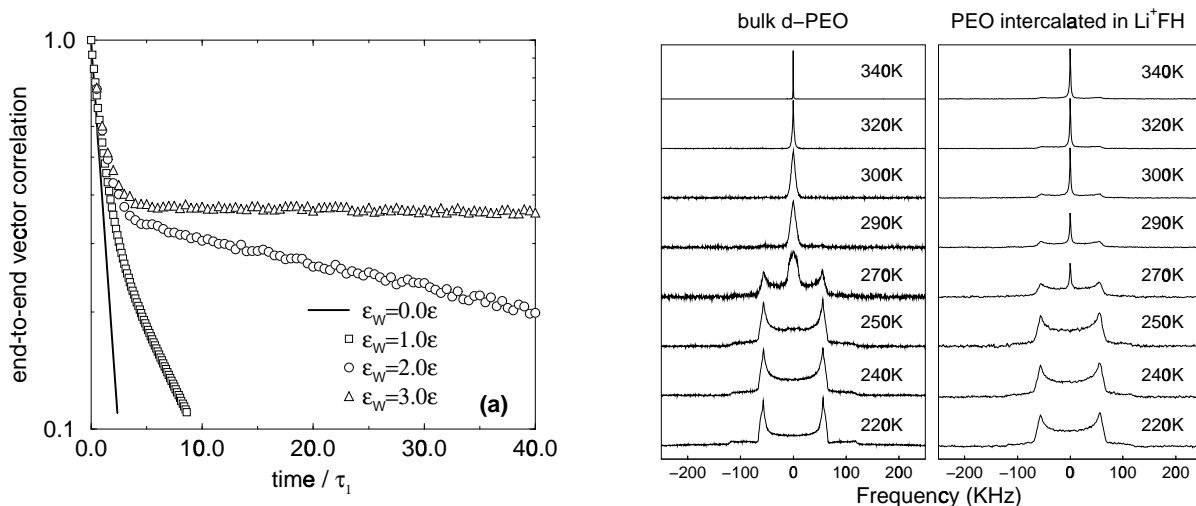


Figure 2 Local dynamics of confined polymers. (a) A coexistence of fast (due to free chains) and slow (due to adsorbed coils) relaxations is predicted by MD simulations for lubricant films confined to films even as thin as 3 monomer diameters [6]. The relaxation time of the slow species increases dramatically with wall affinity (ϵ_w). (b) Temperature dependence of ^2H NMR spectra, for bulk and confined PEO (9Å thin film) [8]. For a wide range of T (260-340K) the confined –intercalated– polymer shows a coexistence of fast and slow modes.

lated/confined polymer displays significant spectral features both for the slow, anisotropic solid-like and the fast, isotropic, liquid-like rate of C-D bond reorientations over a wide range of temperatures [8]. Thus, there exists a coexistence of slow restricted motions and fast liquid like reorientations within the 9Å of confined PEO film.

The same coexistence of fast and slow modes we also observe in spin-echo NMR of 21Å intercalated film of polystyrene, and dielectric spectroscopy of 23Å film polysiloxanes [9].

The **diffusion coefficients** is the second way to study the polymer dynamics in confined spaces. MD simulations [10] have shown a dramatic slow down of chain molecule diffusion with increasing wall affinities (table I). In order to experimentally study the effect of surface-polymer affinity on the diffusion of polymers near surfaces, we investigated the intercalation –insertion– kinetics of polystyrene (PS) into atomically smooth silicates. These experimental system offers many advantages beyond an exceptionally well defined confined geometry: $5 \times 5 \mu\text{m}$ silicate layers separated by $21 \pm 0.5 \text{Å}$ of organic film. The surfaces can be modified by end-grafting alkyl-ammonium, with the grafting density being a characteristic constant of the silicate. The surface energetics can be systematically strengthened in two ways: (i) by increasing the exposed surface to the polymer with the use of shorter alkyl-ammonium surfactants; (ii) by attaching larger amounts of strongly physisorbing groups along the polymer chain. In our case, Br groups are ideal, since they interact strongly with silicon-oxide surfaces (like the 2:1 silicates), and can be easily attached to the phenyl rings of the PS at a predefined monomer percentage.

Table I (Left) MD simulation results: the slow relaxation times and diffusion coefficients in confines [6, 10]. (Right) D of PBrS divided by D of neat PS[11], experiments done in a 21Å slit. Half of the silicate is covered by dodecyl- NH_3^+ .

ϵ_w	τ_1/τ_{bulk}	D_{bulk}/D_{conf}	Br	D_{conf}
0.0 kT	1	0.9	0%	1.0
1.0 kT	3	1.2	3%	1.3
2.0 kT	102	46.	9%	76.
3.0 kT	1500	1040.	15%	193.

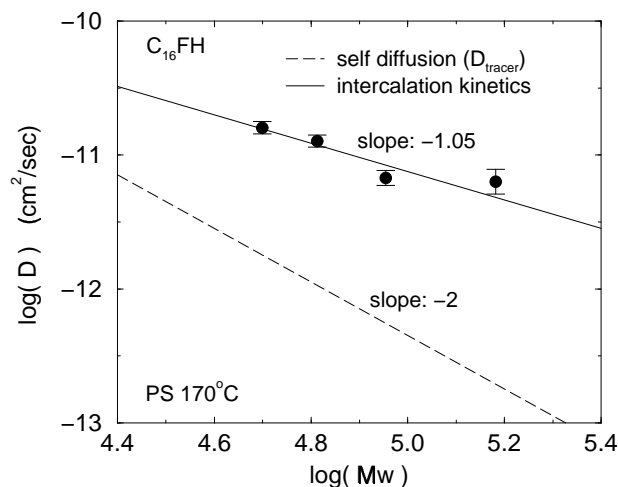


Figure 3 The diffusion coefficients of PS as measured in 21Å confines between mica-type silicates. Since the intercalation process is taking place under a strong density gradient these D are quite faster than the tracer D of PS at 170°C. Although the PS M_W are well into the entangled regime, there is a $D \sim M_W^{-1}$ dependence reflecting the pseudo-two-dimensional geometry. In all cases, D decreases with increasing wall affinity (i.e. increasing PS bromination level or decreasing surfactant length) [11].

The diffusion coefficient of the polymers inside the galleries determines the intercalation rate. This rate of polymer insertion in the silicates can be measured either through monitoring the silicate gallery expansion by X-Ray Diffraction, or through following the population of stretched polymers by SANS. Both give identical results and since XRD is more readily available, it was much more exploited in our study.

In all cases, we observe a strong decrease of the polymer diffusion coefficient with increasing silicate-polymer attraction, both when strengthening the attraction by decreasing wall coverage, with surfactant length going from C_{18} to C_{12} , or by increasing polymer bromination (table I). Actually, if one considers that only half of the surface is exposed to the PBrS and only 15% of the monomers are brominated at most, effective ϵ_w increase is $\sim 0.5kT/\text{monomer}$ and D is reduced by 193 times; thus experimentally the decrease in D for long polymers is *even more dramatic* with surface attraction than the simulations predict [11].

In conclusion, utilizing intercalated polymer/silicate nanocomposites we studied experimentally the dynamics of nanoconfined polymers. In very good agreement with our previous simulation work, we have observed a coexistence of fast and slow relaxations across polymer films as thin as 9Å, and moreover the mobility of the polymers decreases dramatically when strengthening the surface interactions.

References

- [1] B. Bhushan, J. N. Israelachvili and U. Landman, *Nature* **374**, 607 (1995).
- [2] E. Manias, G. Hadziioannou, and G. ten Brinke, *Langmuir* **12**, 4587 (1996).
- [3] E. Manias, G. Hadziioannou, I. Bitsanis, G. ten Brinke, *Europhys. Lett.* **24**, 99 (1993).
- [4] E. Manias, I. Bitsanis, G. Hadziioannou, G. ten Brinke, *Europhys. Lett.* **33**, 371 (1996).
- [5] E.P. Giannelis, *Advanced Materials* **8**, 29 (1996), also *Chem. Materials* **8**, 1728 (1996).
- [6] E. Manias, *Ph.D. thesis*, (ISBN 90-367-0545-2) University of Groningen 1995.
- [7] I. Bitsanis and C. Pan, *J. Chem. Phys.* **99**, 5520 (1993).
- [8] S.Wong, S.Vasudevan, R.Vaia, E.Giannelis, D.Zax, *J. Am. Chem. Soc.* **117**, 7568 (1995).
- [9] K. Karatasos, G. Vlachos, S.H. Anastasiadis, E. Manias, E.P. Giannelis *in preparation*.
- [10] E. Manias, G. Hadziioannou, G. ten Brinke, *Molecular Physics* **85**, 1017 (1995).
- [11] E. Manias, H. Chen, R. Krishnamoorti, J. Genzer, E.P. Giannelis *in preparation*.