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Entropic interactions: neutral and end-functionalized chains in confined geometries

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Abstract. The abrupt liquid-to-solid transition experienced by simple non-polar liquids with quasi-spherical molecules when compressed to a few molecular layers between smooth, solid surfaces can be drastically modified by the presence of polymeric chains end-attached to the surfaces (polymer brushes). The origin of this is the weak interpenetration of the brushes, which can be strongly compressed and yet have a very fluid interfacial region when sheared past each other, resulting in very low friction. The use of telechelic brushes, which are functionalized at both ends and could form loops rather than tails, should result in an even lower interpenetration, and thus in a better lubrication effect. A simple calculation, however, shows that brush-like dimer or multimer-structures might be more favourable energetically than simple loops in the case where the telechelic end-groups attract each other, leading to a very different form of interactions. Recent measurements of the normal and shear forces between surfaces bearing layers of telechelic brushes are in line with these expectations.

1. Introduction

When simple fluids such as cyclohexane or the cyclic siloxane octamethylcyclotetrasiloxane (OMCTS), which have been widely used as model liquids [1, 2], are confined to a few monolayers between smooth solid surfaces, they undergo an abrupt liquid-to-solid transition [3, 4]. This can be readily seen in experiments using the surface force balance (SFB), where the normal and the shear forces between two atomically smooth mica sheets across the confined liquid are measured directly. Figure 1 shows the effective viscosity of OMCTS, deduced from such shear measurements [3, 4], as it is progressively squeezed to thinner films.

The OMCTS film remains fluid from large thicknesses down to a few molecular layers, but abruptly becomes like a solid (in the sense of being able to sustain a shear stress for macroscopic times) when its thickness is reduced from seven to six monolayers. Its effective viscosity increases by at least seven orders of magnitude at the transition at this critical thickness, as seen in figure 1. Other liquids exhibit similar behaviour (though at somewhat different values of the critical thickness) [4]. This has been qualitatively interpreted [4] in terms of a transition from a layered but fluid configuration to one that is layered and solid, as indicated in figure 2.

The physical origin of such a transition may lie in the progressively reduced space that is available to the confined molecules in the gap. One might expect the entropic gain associated with disordered motion of the molecules—which leads in the bulk to their liquid-like state—to be reduced by this confinement until at some point it is insufficient to overcome the enthalpic (van der Waals) attraction between the molecules which tends to order them. This would be the point of the liquid-to-solid transition. It is of interest that a recent computer study [5] simulating

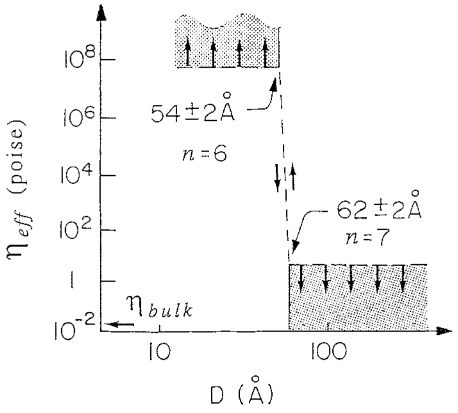

Figure 1. The effective viscosity η_{eff} of OMCTS confined between two smooth mica surfaces as a function of the film thickness. An abrupt transition by at least seven orders of magnitude occurs as the film is thinned from seven to six monolayers of the confined liquid (adapted from [4]).

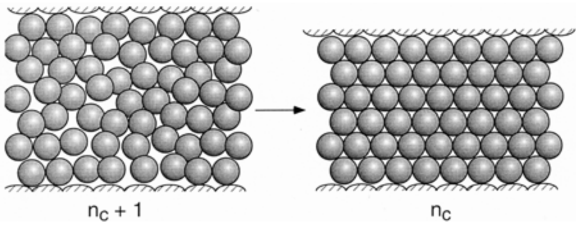

Figure 2. Schematic illustration of the possible structural transformation that takes place at the transition indicated in figure 1. A layered but fluid conformation of the molecules becomes ordered and like a solid as the film thickness is reduced from a value $n_c + 1$ monolayers to the critical thickness n_c monolayers (adapted from [4]).

the mechanical properties of confined OMCTS also revealed that at film thicknesses of less than six monolayers (but not for thicker films) the confined material exhibited a yield stress on shear, i.e. a solid-like behaviour setting on abruptly at a confinement very similar to that shown in the experiments [3]. The transition to a solid-like state can have important implications for the lubricating behaviour of thin films of simple liquids (the behaviour of highly confined simple liquids has been studied extensively by several groups using different analytical and computer simulation methods, see for example [6]), as there is a high frictional spike when such a solidified film is initially sheared. Thus in machinery that has been left unused for a period, the sliding parts may come together to squeeze out any lubricating films (such as oil) to the last few monolayers, whereon they become like a solid and their high initial friction on being slid results in high wear [7]. The attachment of polymers to the sliding surfaces may help to overcome this effect. The presence of solvated polymer brushes on sliding surfaces has been shown to result in extremely low frictional forces [8], as shown in figure 3.

This shows the normal and shear forces between two solid surfaces bearing polystyrene brushes as they are compressed and slid past each other. The origin of this effect is well understood [9], and is illustrated in figure 4.

The opposing brush layers resist interpenetration on being compressed, and as a result the sheared interfacial region between them, of thickness d (figure 4(a)), remains rather fluid when the two brush layers are made to slide past each other, resulting in a very low friction coefficient. The reason for the resistance to mutual interpenetration of the brushes has to do

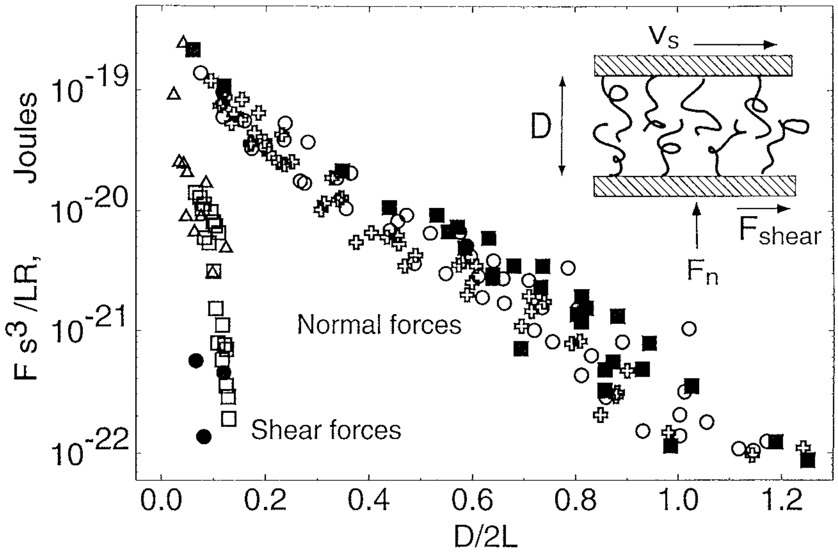

Figure 3. The variation of normal forces (F_n) and shear (or frictional) forces with separation between two mica surfaces bearing end-tethered polystyrene brushes across toluene, for several brush lengths. The separation axis is normalized with respect to the interaction onset distance $2L$, and the force axis is normalized with respect to the inter-anchor spacing s and the mica curvature R to create a master curve for the normal force profiles. F_n increases by some orders of magnitude while F_{shear} is lower than the measuring sensitivity of the apparatus until the brushes have been compressed to about an eighth of their unperturbed configuration ($D/2L$ <~ 0.15). The effective friction coefficient at that point is ~0.001. (adapted from [8]).

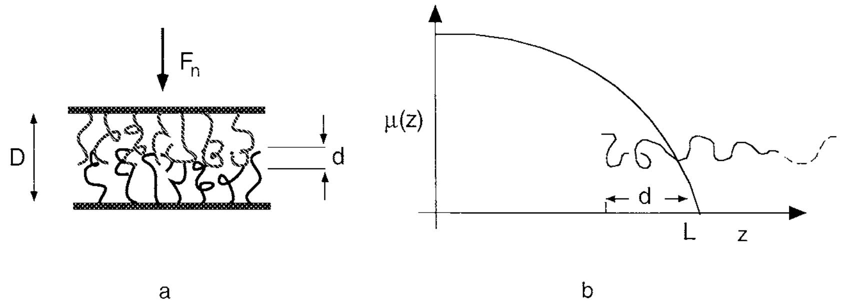

Figure 4. (a) Illustrating the compression of two brushes to a surface separation D. The region of mutual overlap is of thickness d, and is the region sheared when the brush-bearing surfaces slide past each other. The extent of overlap increases only slowly with compression, as indicated in (b): this shows the parabolic potential μ resisting the penetration of a polymer chain into the existing brush layer of unperturbed thickness L. A more detailed consideration [9, 24] reveals that the extent of interpenetration varies with the compression as $d \propto D^{-1/3}$; that is, an eightfold compression say will only double the extent of the region of mutual interpenetration. As a result the effective viscosity within the overlap zone remains low even at high compressive loads, resulting in low friction coefficients (adapted from [9]).

with the energy barrier that a polymer brush chain has to overcome in order to penetrate the potential field associated with the opposing brush, as illustrated in figure 4(b). This arises from the excluded volume repulsion experienced by the chain segments in the good-solvent conditions of the solvated brushes.

2. Polymer loops compared with polymer brushes as efficient lubricating layers

A possible route to improving the lubricating efficiency of surface-attached polymer layers even further might be to replace the dangling chains extending and stretching out from the solid substrate—see figure 4—by polymer *loops*. The penetration of a polymer loop into an existing polymer layer is expected to be even less favourable than that of a single chain end. This is because for penetration to occur, there is a topological necessity for such a loop to double up on itself, as indicated in figure 5.

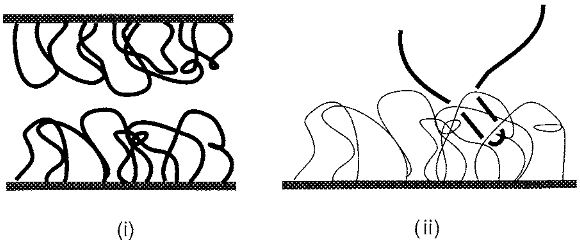

Figure 5. The mutual interpenetration of two interacting loop layers (i) is resisted not only by their potential fields (as for linear chains, figure 4), but also by the topological requirement of doubling-up of the interpenetrating loops, as schematically indicated in (ii). This should result, for a given load, in even weaker interpenetration than between regular brushes, and thus in very low friction coefficients between two sliding, compressed loop-bearing layers.

The likelihood of such a doubling-up has been considered in detail in the case of translational diffusion of entangled branched [10] or ring polymers [11], where doubling-up of the ring or side-arm is necessary (‘hairpin configuration’) for reptation of the molecules to take place in the entangled surroundings. For a loop to penetrate into an adsorbed entangled polymer layer a hairpin configuration is also necessary [12], as indicated in figure 5(b). The probability of such hair-pin formation—and thus the likelihood of interpenetration—becomes exponentially small with the length of the doubled-up portion. Thus if the single-chain tails of a regular brush (figure 4) could be replaced by a brush of loops (figure 5), compression of two such loop-brushes would be expected to result in even less mutual interpenetration and a consequent lower friction when the interfacial region is sheared.

Telechelic chains—polymer molecules where both ends are functionalized with end-groups or moities that adhere to the adsorbing substrate while the central part of the chain is non-adsorbing—could be suitable candidates for the creation of a loop layer by self-assembly from solution. The issue of loop formation from telechelics has been discussed in detail by Milner and Witten [13], and others. (For a recent treatment and review see, e.g. [14].) In their model [13] the functional groups at both chain ends experience an adhesive interaction with the surface, but do not attract each other, and the resulting structure of the telechelic layers is predominantly one of loops, with some dangling ends. On approach of the two telechelic-bearing surfaces, some of the chains penetrate through the opposing layers to form bridges across the inter-surface gap, with one functional end adhering to one of the surfaces, and the other functional end adhering to the opposing surface. Some support for this mostly-loops-and-some-bridges picture has been obtained in studies by Dai *et al* [15, 16] of interactions between surfaces bearing telechelic chains of the sort treated by Milner and Witten [13], while a predominantly loop structure is indicated in studies of surface-attached triblock telechelics [17].

In an investigation related to the issue of loop formation, Kumacheva *et al* [18] studied brush formation from a mixture of long and short polystyrene (PS) chains functionalized at one end by a given zwitterionic group (–X, identical for both chain lengths), immersed in the good solvent toluene, with a zwitterion/substrate adhesion energy $-\gamma_1 k_B T$. They found that for any significant difference in the chain lengths the short chains had a greater propensity than the long ones to self-assemble into brushes on the surface. Indeed, when a small concentration of such short end-functionalized chains (N_{short}-mers say) was added to a solution in contact with a brush of longer N-mers on a substrate, the shorter chains would very readily displace the longer ones to form an N_{short}-mer brush [18, 19]. This is directly related to the Milner–Witten prediction of the predominance of loops rather than dangling tails [13], because one may view a layer of loops as closely equivalent to a regular brush consisting of chains of length one half that of the tails, as indicated in figure 6.

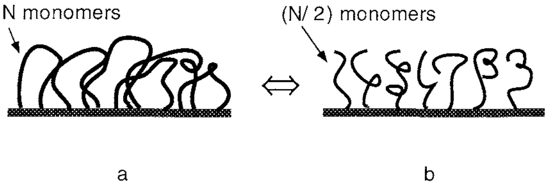

Figure 6. A layer of N-mer loops (left) has a similar free energy to that of a regular $(N/2)$-mer brush (right) with identical surface density (as can be seen by 'cutting' the loops on the left at their midpoint).

3. Self-associating and non-self-associating telechelics

It is of interest to examine the expected structure of surface attached telechelics not just for the case where there is attraction only between the ends and the surface, so that loops form (as discussed above), but also where there is an attraction between the ends themselves. Such telechelic chains would be self-associating in bulk solution, and can form extended networks through association of their ends [20]. For this common class of telechelics, where the functionalized ends attract each in solution with an energy $-\gamma_2 k_B T$, we proceed as follows, extending the approach used by Kumacheva *et al* [18].

As evaluated in [18], for a *single*-end-functionalized brush of degree of polymerization N and an end/substrate attractive energy $-\gamma_1 k_B T$, the free energy per unit area of the interface is given at equilibrium by $\Delta F(N, \gamma_1)$, where

$$\Delta F(N, \gamma_1) \equiv \frac{\gamma_1 + \ln[\phi_b/\sigma]}{(\frac{11}{6}N)^{6/5}}(k_B T/a^2)\ln\phi_b. \tag{1}$$

Here ϕ_b is the bulk solution volume fraction of the telechelics, $\sigma = a^2/s^2$ is the surface density of chains (a is the monomer size and s the mean interchain spacing on the surfaces), and k_B and T are Boltzmann's constant and the temperature. In general for the PS–X systems studied [21], $\gamma_1 \approx 7$, ϕ_b takes values in the range 10^{-4}–10^{-5}, and σ is in the range 10^{-2}–10^{-3}. From (1) we see at once that (since $\Delta F(N, \gamma_1) < 0$) the shorter brushes have lower free energy per unit area, in line with the observations of Kumacheva *et al* [18] that short PS–X chains displace the longer PS–X brush from the surface.

In our model the telechelics, with functionalized end-groups at both ends, have a degree of polymerization N, and they can take two basic configurations on the surface as shown in figure 7, that of tails (figure 7(a)) or that of loops (figure 7(b)).

We make the approximation that the end-attached chains have the form of an Alexander brush, i.e. that they are uniformly stretched and that their ends terminate near the brush edge as indicated (rather than a parabolic profile). As discussed above (see figure 6), the configuration

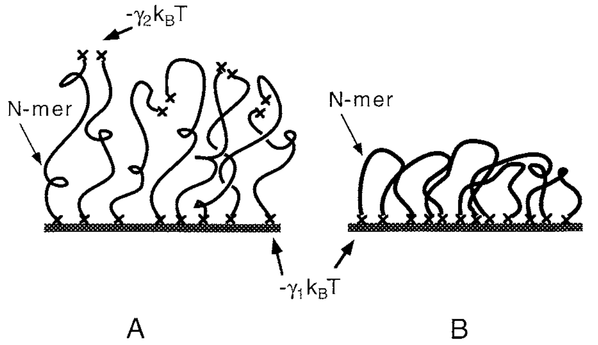

Figure 7. Telechelic N-mers with functional groups –X at either end can adopt either of the configurations shown in (A) and (B). In (A), pairs of dangling ends (dimers) have an interaction energy $-\gamma_2 k_B T$, while in both (A) and (B) the chain-end/substrate interaction energy is $-\gamma_1 k_B T$.

of figure 7(b) is equivalent in terms of its energy to a regular (single-end functionalized brush) of degree of polymerization ($N/2$). It is also straightforward to show that in the case of an N-mer brush where the ends interact with an energy $-\gamma_2 k_B T$, and dimer-loops form as shown in figure 7(a), the free energy per unit area of the interface is given at equilibrium by $\Delta F(N, \gamma_1, \gamma_2)$, where

$$\Delta F(N, \gamma_1, \gamma_2) \equiv \frac{\gamma_1 + \frac{1}{2}\gamma_2 + \ln[\phi_b/\sigma]}{(\frac{11}{6}N)^{6/5}}(k_B T/a^2)\ln\phi_b. \tag{2}$$

Thus the competition between the two forms represented by figures 7(A) and 7(B) depends on the relative values of $\Delta F(N/2, \gamma_1)$ and $\Delta F(N, \gamma_1, \gamma_2)$ from (1) and (2), respectively. Now the interaction energy $-\gamma_1 k_B T$ of the PS–X zwitterioic end-groups (–X) with the (mica) substrate surface is due to dipole–dipole interactions, and has the magnitude of typical hydrogen bond interaction energies. It is reasonable therefore to expect, since the zwitterion–zwitterion interaction is also a dipole–dipole one, that γ_2 is comparable with γ_1 (it is likely to be somewhat larger). σ is also a function of the chain length N for the case of self-assembly of the PS–X brushes from solution. From (1) and (2) we have

$$\frac{\Delta F(N, \gamma_1, \gamma_2)}{\Delta F(N/2, \gamma_1)} = \frac{\gamma_1 + \frac{1}{2}\gamma_2 + \ln[\phi_b/\sigma(N)]}{2^{6/5}(\gamma_1 + \ln[\phi_b/\sigma(N/2)])}. \tag{3}$$

For typical values used in the X–PS–X telechelic experiments (following section), where the molecular weight of the X–PS–X chains is 70 000 ($N \equiv 700$), we have $\phi_b = 10^{-4}$, $\sigma(N) = 10^{-2}$, $\sigma(N/2) = 1.6 \times 10^{-2}$, and we set $\gamma_2 = \gamma_1 = 7$. Setting these values in (1) and (2) we find: (a) that both $\Delta F(N/2, \gamma_1)$, $\Delta F(N, \gamma_1, \gamma_2) < 0$ (as expected since brush formation is known to occur); and (b) $|\Delta F(N, \gamma_1, \gamma_2)| > |\Delta F(N/2, \gamma_1)|$ (for the values above, $\Delta F(N, \gamma_1, \gamma_2)/\Delta F(N/2, \gamma_1) \approx 1.35$). That is, the free energy per unit area for the configuration shown in figure 7(A) is appreciably lower than that of figure 7(B), and dimer formation (figure 7(A)) rather than the simple loop formation (figure 7(B)) would be expected to dominate. We make three remarks: (1) this conclusion is likely to be quite general for situations where the end/end attraction is comparable with or larger than the end/surface attraction; (2) it is likely that multi-mer formation (and not just dimer formation as in figure 7(A)) would also be energetically favoured over the simple loop formation (see, e.g. [22]); (3) our simple model is based on the Alexander brush, but it is likely that the conclusions would also be valid for the parabolic brush.

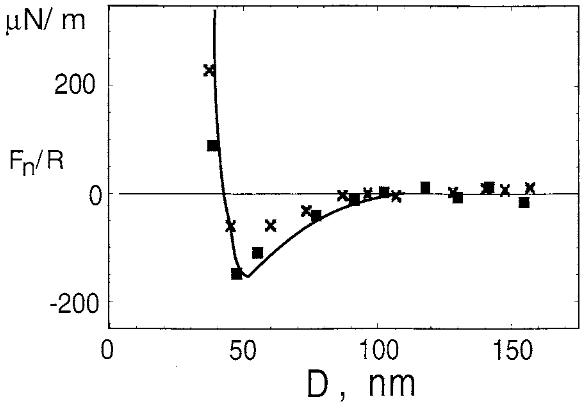

Figure 8. Force–distance profiles on the approach of two mica surfaces bearing X–PS–X telechelics across the good solvent toluene. A clear attractive well is observed, in contrast to what would be expected for interacting loops (adapted from [23]).

4. Interactions between telechelic-bearing surfaces [23]

Very recently Eiser *et al* studied [23] the normal and shear interactions between mica surfaces bearing layers of X–PS–X telechelics immersed in toluene, a good solvent for the PS chains. Following a transient long-ranged interaction attributed to loosely-aggregated surface-layers of free telechelics, a limiting force–distance profile showing an attractive well between the approaching surfaces was reached, as shown in figure 8.

Such an attraction is qualitatively very different to the repulsion that might be expected from two interacting loop layers. Moreover, on sliding the surfaces at different separations, a marked shear or frictional force was required to maintain the sliding motion as soon as the two telechelic layers came into overlap (as determined from the onset of the attractive well), again in contrast to the efficient lubrication expected from two rubbing loop layers. The behaviour is summarized in figure 9.

Such a behaviour is, however, consistent with the formation of dimers or multimers on the opposing surfaces, rather than loops, as predicted by the calculations in the previous section, and their mutual interaction. When two dimers or multimers interact one might expect some entropic advantage to the formation of double-bridges, as shown in figure 10. This is because the formation of such double-bridges enables the end-segments of the dangling chains to explore a larger region of space, and thereby increases their entropy. It is also possible, as suggested by S Safran (private communication), that there is an enthalpic attraction between opposing dimer or multimer zwitterionic end-groups due to their propensity to associate in solution. S Millner (private communication) has pointed out that the magnitude of quadrapole–quadrapole interaction associated with the interaction of two opposing dimers (as in figure 7(A)) might be comparable to a dipole–dipole interaction for the case of bulky zwitterions.

A more detailed analysis of the profiles, given in [23], shows that the range of the attractive well on approach of the surfaces (figures 8 and 9) does indeed correspond to the height of PS–X brushes of molecular weight equal to that of the X–PS–X chains, rather than half of the X–PS–X chains as would be expected if loops such as in figure 4 were to form. This again supports the representation in figure 10.

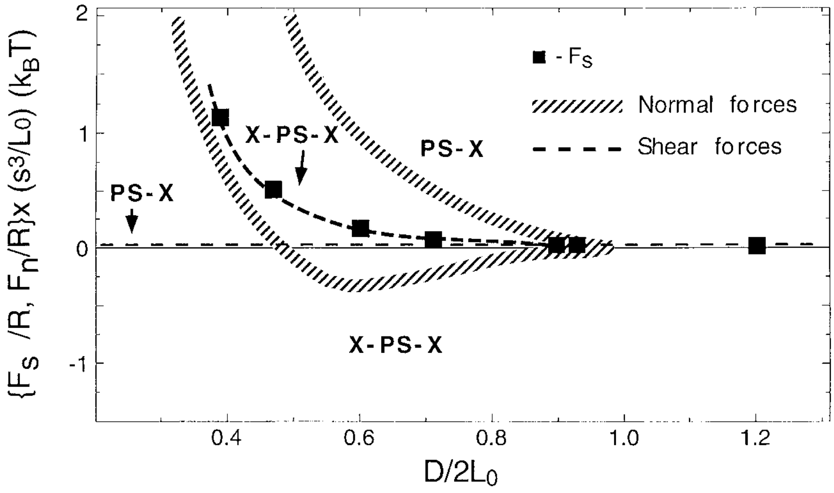

Figure 9. Summary of normal (F_n) and shear (F_s) forces between PS–X and X–PS–X layers as a function of normalized surface separation $D/2L_0$. (L_0 is the unperturbed height of the respective brushes), highlighting the contrast between them. The force axis is normalized with respect to the curvature of the interacting surfaces and L_0, and with respect to the polymer surface density. The PS–X layers (see also figure 3) show a monotonic repulsion and very weak shear forces on sliding even at high compression, whereas the X–PS–X layers manifest an attractive well and appreciable frictional or shear forces as soon as they overlap.

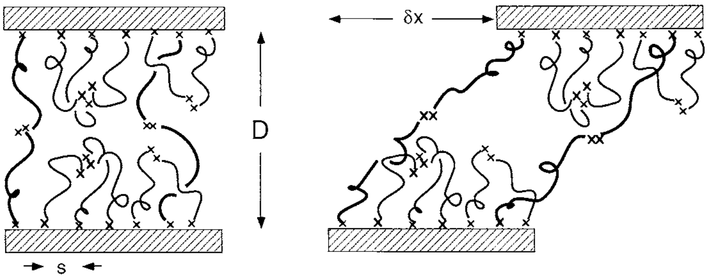

Figure 10. Schematic illustration of the interactions of the X–PS–X telechelic layers (shown in figure 9) on approach and on shear. The double-bridges shown (in bold) are thought to form due to entropic favourability associated with greater configurational freedom of the end segments. The attractive well (figure 8) and the appreciable shear forces on sliding result from the interaction and stretching of the double-bridges (adapted from [23]).

5. Summary and conclusions

We describe three systems of fluids confined to molecular dimensions by smooth, hard impermeable walls, and their mechanical response to normal and shear distortion. Confined simple liquids may undergo a liquid-to-solid transition induced by progressive confinement, due probably to the reduced contribution of entropy (tending to keep the molecules randomized and thus liquid) relative to enthalpic interactions (tending to order the molecules and thus solidify the confined films).

The presence of neutral polymer brushes extending into the solution in good solvent conditions changes this behaviour in several ways. Such brushes lead to large repulsive interactions between the surfaces when they are compressed, and to little mutual interpenetration of the brushes, due to the effect of excluded volume on the chain conformational entropy. The consequence is very low friction when two such brush-bearing surfaces slide past each other under compression.

Functionalizing the chains at both ends may lead to loop formation, which should enhance even further the friction reduction effect. However, if the chain-ends attract each other as well as the substrate, this may result in brushes consisting of surface-micelle like structures. Interactions between two surfaces bearing such structures can be attractive rather than repulsive, due to the entropic advantage associated with forming bridges across the gap, and lead also to substantial resistance to lateral motion (i.e. to significant frictional forces) when the surfaces slide past each other under compression. Entropy thus enters in very different ways in determining the behaviour of these highly confined liquids.

Acknowledgments

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