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Aqueous boundary lubrication: Molecular mechanisms, design strategy, and *terra incognita*

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ABSTRACT

The molecular mechanisms for aqueous boundary lubrication are very different from those in the classic boundary lubrication, originating from the fluidity of the hydration shells surrounding the surfactant and lipid headgroups. We discuss the important molecular and structural criteria for effective aqueous boundary lubricants, and highlight the strategy for reinforcing the interfacial structure for aqueous boundary lubrication *via* synergistic interactions between amphiphilic polymers and lipids/surfactants. It is proposed that the energetic considerations of different molecular elastic deformations in the *stalk model of cell membrane fusion* can be applied to guide our design of molecular architectures for surfactants and lipids to implement structural integrity in aqueous boundary lubrication. We discuss a controversy associated with the *quiescent bilayer* structure, in the context of boundary lubricant interfacial structures. We also highlight other effective aqueous boundary lubrication systems, including hydrated ions and biomimetic hierarchical constructs inspired by the enigmatic and extremely efficient biological lubrication. Finally, we suggest that the *Stribeck curve* might be re-considered in light of recent advances in aqueous boundary lubrication, although the exact scope of this new aqueous boundary lubrication regime remains *terra incognita*.

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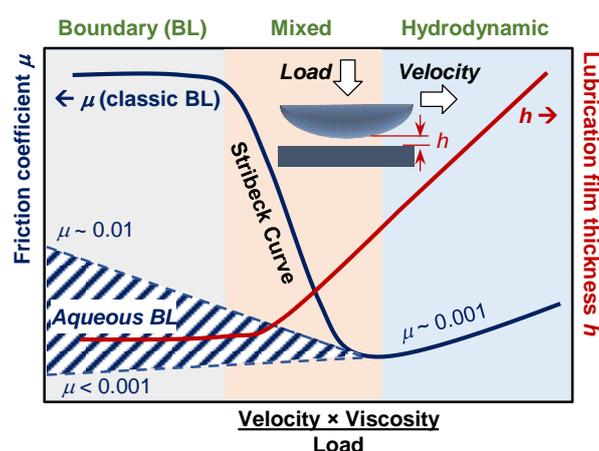


Figure 1: The *Stribeck curve* plots the friction coefficient μ vs the dimensionless entity $(Velocity \times Viscosity / Load)$ in three different regimes, and the corresponding lubrication film thickness h . Recent experimental advances show that μ for aqueous boundary lubrication (BL) could be as low as that in the hydrodynamic lubrication regime or even lower. It is thus tempting to suggest a modified *Stribeck curve* with a hatched *Aqueous Boundary Lubrication* region – its exact scope remains *terra incognita*.

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1. Introduction

In classic *boundary lubrication* (BL) in air or oil, as first coined by Hardy in 1925 [1], rubbing surfaces are coated with a thin molecular layer (*e.g.* surfactants or self-assembled monolayers (SAMs)), and the plane of shear is shifted from the underlying surface to the interface between the molecular boundary layers [2], effectively reducing friction and wear. *Aqueous boundary lubrication* by simple ions, surfactants, lipids, macromolecules, and their synergistic assemblies, as we now appreciate, is as widespread and versatile as it is

glycoproteins can form a molecular film called the salivary pellicle on all the tissues in the oral cavity [4, 5], and the aqueous BL the film mediates, *e.g.* between the tongue and the palate, is related to the sensory perceptions of textural attributes during food consumption [6] and plays a role in mouthfeel/astringency [7-9]. When the eyelid blinks over a hydrogel contact lens, the sliding between the lens and the cornea also falls in to the BL regime [10], as mediated by the mucus and lipid layer at the cornea surface. It has long been recognised that synovial joints, which display remarkably low friction coefficients ($\mu < 0.001$), are lubricated in the BL regime at least at certain stages of a walking cycle [11] by a

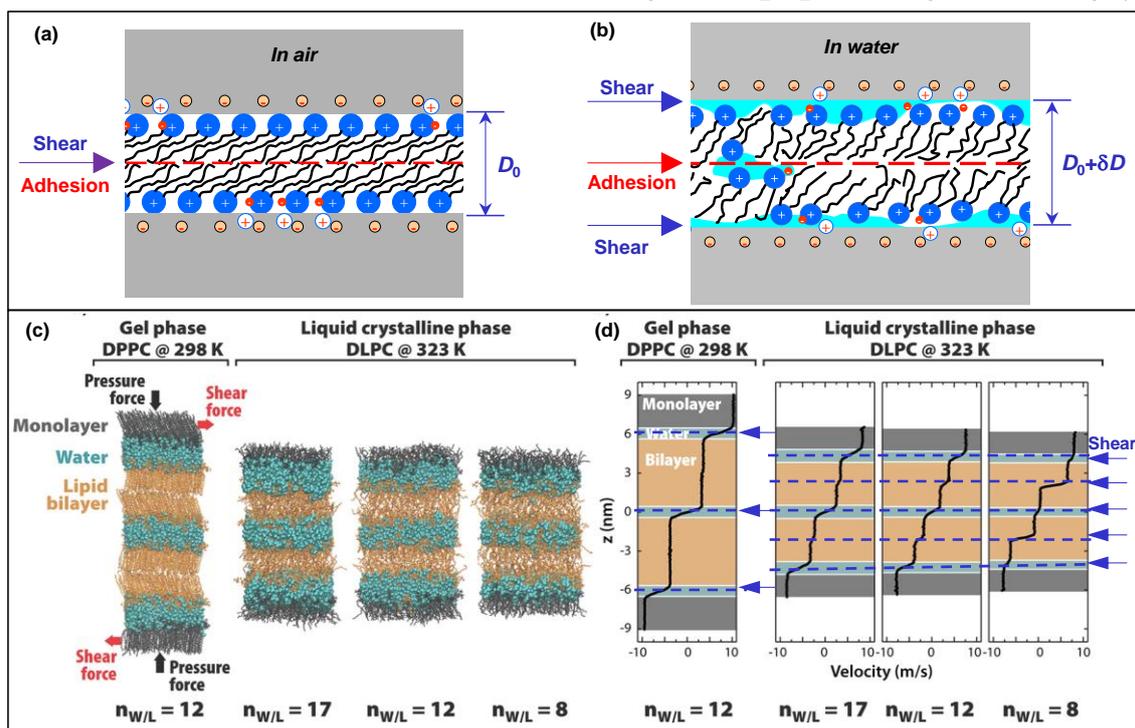


Figure 2: (a) In classic boundary lubrication (BL), the plane of adhesion and shear lies at the interface between the tails. (b) Upon immersion in water, the surfactant headgroups become hydrated, giving rise to a small swelling of $\delta D \sim 2.5 \text{ \AA}$ and greatly enhancing surfactant lateral mobility. Some surfactant molecules could also undergo the flip-flop motion in which the molecules would turn over. In this case, the plane of adhesion is at the mid-plane, giving rise to adhesion comparable to that in air (a). However, shear sliding would take place at either of the interfaces between the headgroups and the substrates decorated with molecular water puddles. (c) Bilayer stacks in an MD simulation at different hydration levels (with $n_{W/L}$ water molecules per lipid). From left to right: DPPC L_{β} gel phase at 293 K $n_{W/L} = 12$, and DLPC L_{α} fluid lamellar phase at 323 K, with $n_{W/L} = 17, 12$, and 8 , respectively. Two shear forces are applied to the outer monolayers at constant normal pressure. (d) Vertical profiles (black lines) of the steady-state average particle velocity along the shear direction, as a function of the height of the bilayers in (c). The planes of shear are indicated by the blue dashed lines and blue arrows. For the DPPC L_{β} gel phase, shear occurs only in the water layers, and for DLPC L_{α} fluid phase, shear occurs within the water layers and, increasingly so for lower hydrations levels, within the bilayers (*i.e.* between monolayers). For (c): Adapted with permission from (Botan A, Joly L, Fillot N, Loison C. Mixed Mechanism of Lubrication by Lipid Bilayer Stacks. *Langmuir*. 2015;31:12197-202). Copyright (2015) American Chemical Society.

important and complex.

Surfactants and polymers are ubiquitous in industrial formulation and processes, *e.g.* as dispersants or functional additives, and they readily self-assemble at the solid-liquid interface for form various structures, thereby playing a key role in aqueous BL. For example, in hydraulics and metal working, aqueous lubricants are considered potentially more environmentally friendly and fire resistant as compared to oil based lubricants [3]. It is also relevant to biological processes and biomedical applications. For instance, saliva proteins and

hierarchical boundary layer of phospholipids, hyaluronic acid (HA), and glycoproteins, although the exact mechanisms remain enigmatic [12].

Intensive research on aqueous BL has been undertaken in the past decade or so, with the focus on evaluating the efficacy of different molecular systems as aqueous boundary lubricants, and especially on solving the mysteries of extreme lubrication in biological living systems. In the engineering *Stribeck curve* plot [13], the friction coefficient μ in the BL regime would increase quite sharply compared to that in the hydrodynamic

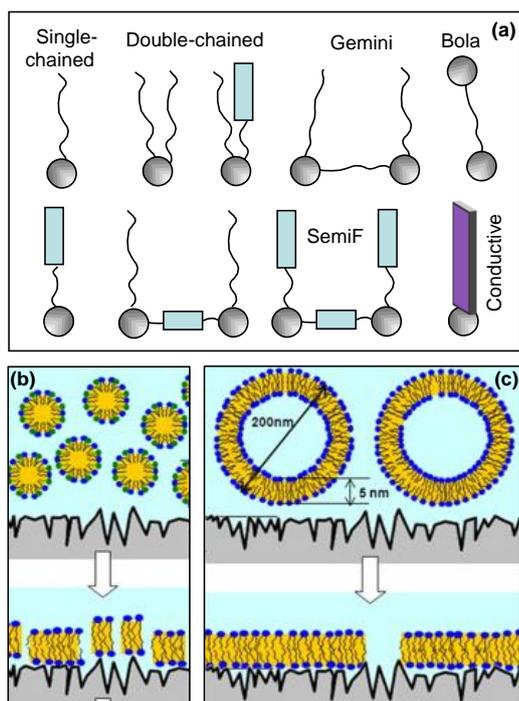


Figure 3: (a) Different molecular architectures of surfactants and lipids, including fluorinated (SemiF) or conductive segments that could be incorporated in the tails, whilst the headgroups could be cationic, anionic, zwitterionic, and neutral. Surface bilayers could be formed by self-assembly from a micellar solution (b) or from surface induced rupture of liposomes or vesicles in the case of lipids (c). For (b) and (c): Adapted from Tribol Int. 2011, 44, Corneci MC, Dekkiche F, Trunfio-Sfarghiu AM, Meurisse MH, Berthier Y, Rieu JP. Tribological properties of fluid phase phospholipid bilayers, 1959-68, Copyright (2011), with permission from Elsevier.

regime where the surfaces are fully separated by a thin lubrication film. Recent experimental advances have shown that the μ values achievable by biomimetic boundary lubrication systems can reach that in the hydrodynamic regime ($\mu \sim 0.001$) or even lower [12], with $\mu \sim 2 \times 10^{-5}$ reported between surfaces coated with liposomes [14]. As we now realise, aqueous BL operates *via* a mechanism rather different from that in air.

2. Molecular mechanisms for aqueous boundary lubrication – shift in the shear plane

Wright and Dowson already noted in their 1976 study that aqueous solutions of sodium lauryl sulphate (SDS) and cetyltrimethylammonium bromide (C_{16} TAB) could lubricate cartilage surfaces as effectively as the synovial fluid [11]. Richards and Roberts studied friction between rubber and glass in an SDS solution [15], albeit attributing the lack of surfactant film stability to insufficient electric double layer repulsion between the surfaces. Lubricating properties of aqueous solutions of four types of anionic surfactants (sodium olefin sulfonate, sodium oleate, sodium octanoate and sodium dodecylbenzene sulfonate) on the steel-glass contact were evaluated using a macrotribometer under different pH and salt conditions, and it was suggested that a 2–4 nm boundary layer was formed on the surfaces [3]. Friction results using the surface force apparatus (SFA) between surfactant monolayers formed upon rupture of their bilayers showed shear

characteristics not dissimilar to those in classic boundary lubrication by surfactant monolayers in air [16]. The effect of pH, ionic strength, and surfactant concentration on friction between a colloidal silica probe and a silica surface in C_{12} TAB and C_{16} TAB solutions was also investigated by lateral force microscopy (LFM) [17]. Up to that point, the mechanisms for aqueous boundary lubrication, particularly the role of water, were unclear, and the interpretations were largely derived from the knowledge of BL in air, focusing on the role of surfactant tails and sliding at the tail-tail interface. This is perhaps best illustrated by then widely accepted mechanism proposed by Hills [18] which conjectured that phospholipids formed multilayers on cartilage surfaces and tail-tail sliding between the layers facilitated effective biolubrication, just like that in classic BL. Hills' conjecture is still revisited quite frequently in the literature, although as we now know that it is not correct.

Briscoe *et al.* [19, 20] made an unexpected observation that, when a pair of mica surfaces bearing a monolayer of a double-chained cationic surfactant *N,N*-dimethyl-*N,N*-diundecylammonium bromide (DDunAB) were immersed in water, friction was reduced to $\sim 1\%$ of that in air, whilst adhesion remained comparable to that in air. It was proposed that, as shown schematically in Figure 2(a) and (b), the quaternary ammonium headgroups became hydrated – consistent with a layer swelling of $\delta D \sim 2.5 \text{ \AA}$, greatly enhancing the lateral molecular mobility, with molecular flip-flop also possibly taking place. The plane of adhesion in water remained at the mid-plane, *i.e.* at the interface between the monolayers. However upon shear, sliding would take place at the hydrated substrates, where the resistance to shear was the weakest. The essence of this mechanism is that the hydrated ionic surfactant headgroup is highly lubricious, underpinned by the fluidity of the water molecules in its hydration sheath [21], facilitating the marked friction reduction observed. As such, if indeed lipid multilayers do exist on cartilage surfaces as Hills suggested [18], the lubrication mechanism would not be due to the tail-sliding; instead, sliding should take place between the hydrated lipid headgroups.

A recent molecular dynamics (MD) simulation study [22] has confirmed that, upon shear, sliding in the L_{β} gel phase dipamitoylphosphatidylcholine (DPPC) bilayer stacks occurs in the water layers (Figure 2(c) and (d)). However, for the L_{α} bilayer stacks of dilaurylphosphatidylcholine (DLPC), the relatively more fluid tails compete with the water layers. Sliding takes place both within the water layers, and increasingly so for the reduced hydration levels, within the bilayers, *i.e.* between the monolayers, as indicated by the blue dashed lines and blue arrows in Figure 2(d). This simulation result casts some doubts over the above hydration lubrication mechanism that shear sliding in aqueous boundary lubrication universally takes place at the fluid hydration layer. This discrepancy however could be readily resolved, as the simulation systems of the lipid multilayers can be realized experimentally, *e.g.* by Langmuir-Blodgett deposition, drop-casting from an organic solvent [23] or an aqueous medium [24], or spin-coating [25] with the hydration levels tunable by careful control of the relative humidity in an SFA.

3. Design strategy for effective aqueous boundary lubricants – tailoring molecular architecture

Conceptually, the mechanism in Figure 2(b) clarifies the roles of the surfactant headgroups and tails in aqueous BL. That is, the cohesion between the tails can provide the structural

integrity to facilitate hydration lubrication *via* the hydrated headgroups in an aqueous medium. A key challenge for an effective aqueous boundary lubricant is thus to maintain the outer leaflet of the bilayer under high compression and pressure, so that it is not squeezed out (*i.e.* to suppress the hemifusion process). Such structural integrity is most readily tuned by varying the surfactant concentration or solution condition, and the tail length. Richards and Roberts noted that the collapse of the boundary layer in their early rubber-glass friction in an SDS solution was related to the SDS concentration [15]. Ratoi and Spikes suggested that the bilayers formed by anionic surfactants on glass and steel collapsed to form monolayers under low shear velocities and under high load [3]. Vakarelski *et al.* noted that the squeeze-out pressure of their C₁₂TAB and C₁₆TAB surface layers was affected by the solution pH [17]. Silbert *et al.* reported that the pressure for the break-down of alkyltrimethylammonium chloride (C_nTAC; *n* = 14, 16, and 18) surface layers on mica was higher for the surfactant with a longer tail, which could retain its extremely effective lubrication ($\mu \sim 0.001$) under a higher load [26]. From these studies, it is clear that the collapse of the bilayer structure on the surface would lead to an increase in friction due to the loss of the hydration lubrication mechanism mediated by the headgroups on the outer leaflets. Indeed, when such structural collapse occurs, the shear characteristics between the monolayers under water are complex, resembling those of BL in air, such as the high friction and the stick-slip behavior [16, 27].

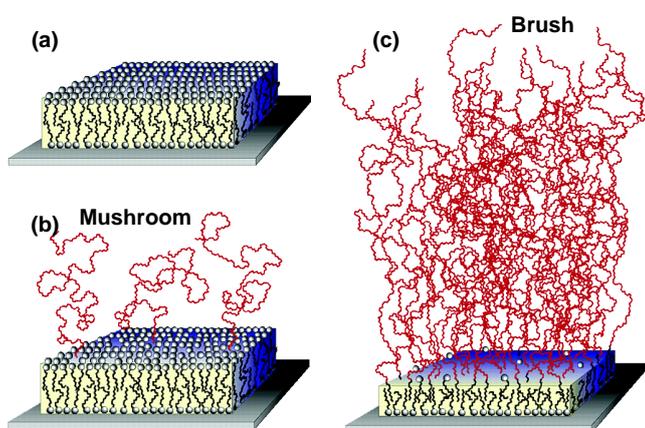


Figure 4: Reinforcing lipid bilayers (a) with hydrophilic polymers (in this case end-functionalised with a short hydrophobic segment) as a strategy to improve the structural integrity. (b) At low density, the polymers adopt a mushroom conformation, compromising the bilayer structural integrity. (c) At high density, the polymer chains adopt a brush conformation, providing a steric barrier and strengthening the bilayer. Adapted with permission from (Blom A, Drummond C, Wanless EJ, Richetti P, Warr GG. Surfactant boundary lubricant film modified by an amphiphilic diblock copolymer. *Langmuir*. 2005;21:2779-88). Copyright (2005) American Chemical Society.

The structural integrity of the surfactant boundary lubricant layer also depends intimately on the surfactant molecular architecture. The double-chained surfactants seem to provide more robust surface layers against pressure and shear as compared to the single-chained counterparts, due to the enhanced hydrophobic interactions between their tails and also their innate molecular shape as characterized by a packing parameter close to 1, with a low spontaneous curvature that matches more closely to the flat substrates. This has been

demonstrated by the resistance of di-chained didodecyldimethylammonium bromide (DDAB) bilayers against hemifusion (*i.e.* the removal of the outer monolayer leaflet) [28]. It is also consistent with the observation of very effective lubrication and load bearing properties of phospholipid bilayers (DPPC, DOPC, and DLPC) [29, 30].

Accordingly, the design strategy for effective aqueous boundary lubricants can be developed by tailoring the surfactant molecular architecture to specific applications and also surface curvature. Figure 3(a) illustrates a number of different surfactant tail architectures, including Gemini [31, 32], bola [33, 34], single-tailed double-tailed surfactants [19, 28] and phospholipids [29]. Conducting [35-37] and fluorinated segments [38] can also be judiciously incorporated in the molecular architecture, including in the Gemini spacer and tails [39] or asymmetrically in one of the two tails of a di-chained surfactant [40]. The spatial and chemical varieties in these architectures offer an effective molecular tool box to tailor the boundary lubricant. A feature is that the boundary layers can be readily self-assembled from solution, *e.g.* *via* adsorption of monomers and micelles, or rupture of vesicles/liposomes in the case of phospholipids, as illustrated in Figure 3(b) and (c) respectively [29]. This provides a convenient route to forming the boundary layers, although some controversies persist regarding the exact structural details of the surfactant and lipid layers at the solid-liquid interface [41], as discussed below.

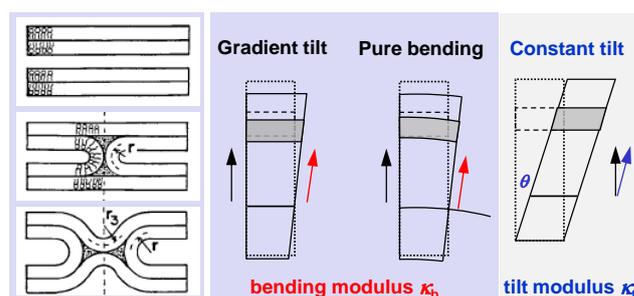


Figure 5: Left: The stalk model of membrane fusion. Adapted from Siegel DP, Epanand RM. The mechanism of lamellar-to-inverted hexagonal phase transitions in phosphatidylethanolamine: Implications for membrane fusion mechanisms. *Biophys J*. 1997;73:3089-111, Copyright (1997), with permission from Elsevier. A stalk (left middle) with the shape of an hour glass forms between the proximal monolayers in contact. The distal monolayers then nibble in to form a transmembrane contact (TMC, left bottom), and its subsequent expansion leads to the full membrane fusion. The elastic energy cost associated with the local curvature r and r_3 as denoted originates from the molecular deformation in the process, and is characterised by a bending modulus κ_b for gradient tilt and pure bending (Middle), and a tilt modulus κ_t for constant tilt (Right).

4. Reinforcing lipid bilayers with polymers – exploring synergistic interfacial self-assembly

Another strategy to reinforce the structural integrity of the surfactant boundary layer is to incorporate polymers with specific functionality that can interact synergistically with the surfactant. Blom *et al.* studied boundary lubrication by surface structures self-assembled from co-adsorption of a mixture of a di-chained DDAB surfactant and poly(ethylene oxide) (PEO) containing 100 EO units and end-functionalised with a short hydrophobic octadecyl block [28]. As schematically shown in

Figure 4, it was suggested that a DDAB underlying bilayer formed on mica, and that the hydrophobic block could be incorporated in the bilayer, thus anchoring the polymer. At low grafting density, the PEO polymer chains adopted a mushroom conformation and their insertion into the DDAB bilayer compromised the bilayer integrity, inducing hemifusion and associated high friction and stick-slip shear instabilities. However, at high grafting density (Figure 4(c)), the PEO chains adopted a brush conformation evident from the Alexander-de Gennes type interactions mediated by polymer brushes [42-44] between the PEO layers. This structural reinforcement was further demonstrated by Drummond *et al.* [45], where hemifusion between bilayers of a 12-3-12-3-12-trimeric surfactant (methyl dodecylbis[3-(dimethyldodecylammonio) propyl]ammonium tribromide), a cationic oligomeric surfactant with dodecyl ammonium moieties connected at the ammonium groups by propyl chains, was suppressed by co-adsorption with a poly(acrylic acid)-poly(acrylamide) (PAA-PAM). It was postulated that the negatively charged PAA block adsorbed atop the underlying cationic bilayers, shielding them sterically and preventing hemifusion and sustaining low friction. The synergistic nature of this process should be appreciated, as conversely it can provide a self-assembly mechanism to anchor polymer chains to the surface. It should be noted that such a lubrication synergy is not always observed. For instance, adsorption of negatively charged hyaluronic acid (HA) atop a cationic bilayer led to possible bridging between the surfaces, resulting in an increased friction [46]. Overall, aqueous BL mediated by the boundary layers formed by co-assembly or complexation of polymers (particularly polyelectrolytes) – surfactants at the solid-water interface [47] remains under explored. Dedinaitė *et al.* observed low friction mediated by polyelectrolyte-surfactant layers, but also reporting intricate structural rearrangement in the layer upon loading [48]. A number of parameters could be tuned to control and optimise the boundary layer structure, such as the polymer molecular weight, architecture, charge density, concentration, as well as the parameters that characterise surfactants (Figure. 3(a)). A further promising boundary layer system that could present structural synergy (*i.e.* producing hydrated and load bearing layers) involves lipid bilayers cushioned by underlying polyelectrolyte multilayers (PEM) [49], a system of which the lubrication properties also remain to be fully explored.

5. Insights from membrane fusion

Membrane fusion is fundamental to biology and considerable effort has been made to improve our understanding of this process. A widely accepted framework is *the stalk model* (Figure 5; Left panel) [50-56], which idealises the fusion process, in essence, as follows (which has been observed using an SFA [57]). The contact proximal monolayers could overcome the headgroup hydration repulsion and merge to

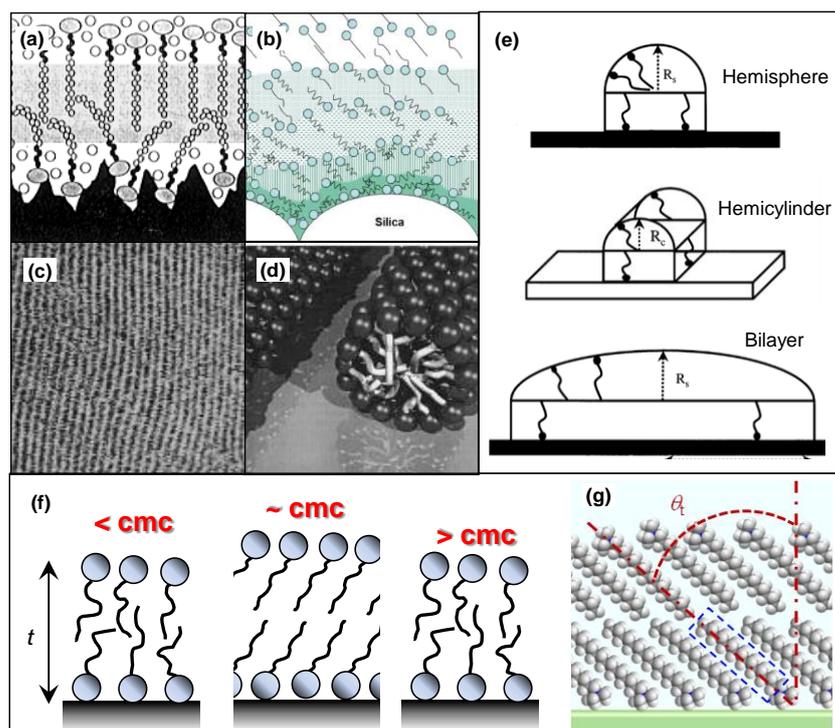


Figure 6: The structure and morphology of surfactants self-assembled at the solid-liquid interface remain controversial. Some different structures proposed include: (a) C_{16} TAB bilayer on rough silica by neutron reflectivity (NR); (b) Multilayers of C_{16} TAB on 12-14 nm silica nanoparticles from TMDSC, TGA and FTIR measurements; (c) and (d) Full C_{16} TAB cylinders of diameter ~ 7 nm on mica as revealed by contact mode AFM imaging; (e) Energetically favourable conformations of surface aggregates (hemisphere, hemicylinder, and bilayer) from computer simulations; (f) The “Quiescent” bilayer structure (without being perturbed by an AFM scanning tip) showing a bilayer thickness t maximum at \sim cmc surfactant bulk concentration as revealed by XRR and NR; and (g) The tilted conformation of the quiescent C_n TAB bilayer at the cmc. *Acknowledgement:* (a) Adapted with permission from (Fragneto G, Thomas RK, Rennie AR, Penfold J. Neutron reflection from hexadecyltrimethylammonium bromide adsorbed on smooth and rough silicon surfaces. *Langmuir*. 1996;12:6036-43.) Copyright (1996) American Chemical Society. (b) Adapted with permission from (Zhang T, Xu G, Puckette J, Blum FD. Effect of Silica on the Structure of Cetyltrimethylammonium Bromide. *J Phys Chem C*. 2012;116:11626-34). Copyright (1996) American Chemical Society. (c) and (d) Adapted with permission from (Ducker WA, Wanless EJ. Adsorption of Hexadecyltrimethylammonium Bromide to Mica: Nanometer-Scale Study of Binding-Site Competition Effects. *Langmuir*. 1999;15:160-8). Copyright (1999) American Chemical Society. (e) Adapted from *Colloids Surf A*, 2000, 167(1-2), 37-46, R.A. Johnson and R. Nagarajan, Modeling self-assembly of surfactants at solid-liquid interfaces. II. hydrophilic surfaces, Copyright (2000), with permission from Elsevier.

form a stalk which is concentrically symmetric with the shape of an hour glass. The stalk then expands radially, as the distal monolayers nibble in to form the transmembrane contact (TMC) before proceeding to pore formation and full fusion. In the context of aqueous BL, the molecular deformations involved in hemifusion (*i.e.* removal of the outer leaflet in the supported bilayer) and full fusion (*i.e.* removal of the final monolayers) are energetically analogous to those in the biological membrane fusion process [58]. Thus, we could gain valuable insights from the energetic considerations in the stalk model of membrane fusion, when we pursue our molecular architecture design of the aqueous boundary layers to achieve stupendous structural integrity for load bearing capacity by effective lubricants.

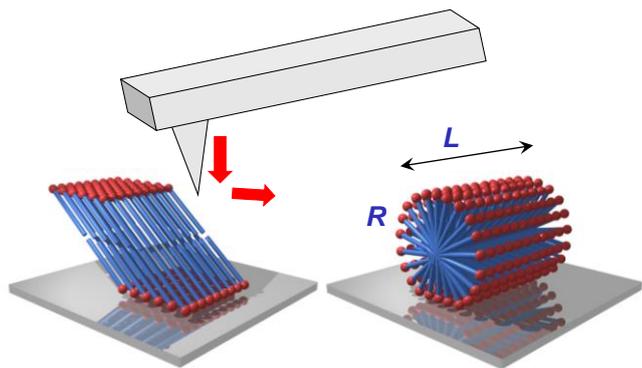


Figure 7: A *quiescent* bilayer can be induced to transform into a cylinder by a scanning AFM nano-tip. The force required is estimated as low as 20 pN, which is much lower than that exerted on the surface structure by an AFM tip in imaging (see the text for details).

This structural integrity originates from the membrane bending, which in turn derives from molecular deformations, as schematically shown in the middle and right panels in Figure 5. That is, it costs elastic energy for the molecules to deform in the fusion process, as characterised by a bending modulus κ_b and a tilt modulus κ_t . κ_b describes the molecular deformations of gradient tilt and pure bending, in which the cross-section of the lipid molecule is under shear. κ_t is associated with the molecular deformations of constant tilt, in which the lipid molecule is stretched along its length with its cross-section area unaltered. These deformations all lead to configurational entropic loss, and thus are unfavourable – which is the origin of the energetic cost for membrane fusion.

Both the bending modulus κ_b and the tilt modulus κ_t are intimately related to the lipid molecular architecture, *i.e.* any chemical and spatial incompatibilities in the varied architectures (Figure 3(a)) could be evaluated in terms of these elastic constants, thus guiding the molecular architectural design for effective aqueous boundary lubricants.

6. Quiescent bilayers vs. surface aggregates

Understanding the characteristics of adsorbed surfactant structures at the solid-liquid interface and their properties is important to interpretation of the molecular mechanisms underpinning aqueous BL and to designing robust molecular boundary layers. However, despite intensive research in the past decade, the morphology and structure of the self-assembled surfactant aggregates at the solid-water interface remain controversial. We will refer to one of the most extensively studied surfactants, C_n TABs, to illustrate this issue. The C_n TAB adsorption at solid-liquid interface has been characterized with a number of different experimental techniques, including AFM [59-73], SFA [74-80], neutron reflectivity (NR) [73, 81-84], optical reflectivity (OR) [72, 85], ellipsometry [86, 87], calorimetry [88, 89], Fourier transform infrared (FTIR) spectroscopy [90, 91], sum frequency generation spectroscopy (SFG) [92], X-ray photoelectron spectroscopy (XPS) [93], X-ray reflectivity (XRR on mica) [41, 94], and simulation studies [95-99]. Some example structures proposed from these studies are shown in Figure 6 for comparison.

Earlier SFA measurements assumed a bilayer or bilayer-like structure formed by the surfactant at the mica-water interface

[74-80]. Comprehensive NR results suggest similar bilayer or bilayer-like structures at the silica-water interface, and a C_{16} TAB bilayer on rough silica is schematically shown in Figure 6(a) [81]. Such a bilayer structure has also been confirmed at the mica-water interface using NR [100]. Using a “*bending mica*” method [94, 101] and employing XRR, Speranza *et al.* [41] reported recently that the C_n TAB ($n = 10, 12, 14,$ and 16) bilayer thickness experienced a maximum at \sim cmc (Figure 6(f)), corresponding to a densely packed, tilted surfactant conformation (Figure 6(g)). Above the cmc, the surfactant would desorb and the layer would become more fluid. This bilayer thickness maximum has also been confirmed by NR on silica for several other types of surfactants [102]. This general finding is significant in terms of its implication to the boundary lubricant layer, as it contradicts with the convention wisdom that the surface layer would become more densely packed as the surfactant concentration is increased above cmc.

It is interesting to note that C_{16} TAB multilayer structures have also been suggested on fumed silica nanoparticles of 12–14 nm in diameter from temperature-modulated differential scanning calorimetry (TMDSC), thermogravimetric analysis (TGA) and FTIR analysis [103] (Figure 6(b)), pointing to the possible role of both the substrate surface chemistry and curvature on the boundary layer structure, although similar findings are yet to emerge verify this.

In contrast, AFM imaging suggests a variety of surface morphologies (*e.g.* spheres and cylinders) which are dependent on a wide range of experimental parameters (*e.g.* concentration, time and pH) on both mica and silica. Figure 6(c) and (d) show full C_{16} TAB cylinders of diameter \sim 7 nm on mica as an example [61]. We refer to Ref. [41] for a more detailed discussion on this structural discrepancy between from AFM imaging and other techniques.

Recent computer simulation studies have also examined the molecular organization of soft matter structures adsorbed on hydrophilic surfaces. Johnson and Nagarajan [96] modelled the self-assembly of the cationic C_{12} TAB at the solid-liquid interface. They suggested the formation of composite surface structures, with a monolayer in contact with the hydrophilic surface. On top of this monolayer, hemispheres, hemicylinders or another monolayer with opposite molecular orientation were observed (Figure 6(e)). The energies required for the formation of such composite structures were lower than the energies for the full cylinders or full spheres. These simulation studies are in agreement with the XRR, NR and OR studies, but contrast with the organization of surfactant aggregates observed from AFM imaging.

Speranza *et al.* [41] suggested that this discrepancy might be explained by AFM scanning inducing aggregate formation, as supported by a recent AFM study of hexadecyltrimethylammonium chloride (C_{16} TAC) surfactants on gold surfaces [104]. The essence of this suggestion is that the normal force F_n and lateral force F_s exerted at the surfactant layers by the scanning nano-tip, could induce the formation of surface aggregates (*e.g.* cylinders of radius R and length L ; Figure 7) from flat bilayers. Speranza *et al.* estimated the bending energy E_b required for bilayer-to-cylinder transformation as [105] $E_b \sim \pi k_c L/R$, where k_c is the elastic bending constant of a lipid bilayer of order 10^{-20} J [105]. This bending energy E_b is approximated to the work done ΔW by the application of a force f over the length L , and thus the force required to

facilitate this bilayer-to-cylinder transformation is $f = d(\Delta W)/dL \sim \pi k_c/R$. Assuming $R \sim 2$ nm, this gives $f \sim 20$ pN or of that order, well below the typical values of the forces (F_n and F_c) experienced in the application of AFM imaging which are in the range of 100 pN or above. Thus, it is feasible that the scanning AFM tip would “perturb” the conformation of the surfactant surface layers.

This suggestion that the bilayer structure observed by XRR and NR is the intrinsic, unperturbed – thus “quiescent” – bilayer, whilst the surface aggregates observed by AFM imaging are induced, is controversial but important. Not only it raises the question on how we control the molecular packing and structural integrity in the boundary lubricant layer (Figure 6(e) and (f)), but also invites further input from the AFM community, which is heavily relied upon to characterize the morphology and structure of the boundary lubricant layers.

7. Future outlook – ions, nanofluids, hierarchical boundary layers, enigma of biolubrication, and *terra incognita*

With enlightened understanding of the molecular mechanisms for aqueous boundary lubrication [19, 20], it is clear that there are two criteria for an effective aqueous lubricant. First, it should be endowed with a water loving moiety, as effective lubrication under water originates from the fluidity of the hydration layer associated with the hydrophilic groups, *e.g.* the headgroups in the case of surfactants and lipids. Second, it should promote the structural integrity that is essential for loading bearing, preventing the hydrophilic groups from being squeezed out. We have focused our discussions on lipids and surfactants here – which can be readily self-assembled at the solid-liquid interface, and the how their molecular architecture could be tailored to meet the above criteria. We have also discussed reinforcement of lipid boundary layers *via* synergistic interactions with amphiphilic polymers. We have noted the areas that present opportunities for further investigations, including lubrication by lipid multilayers and PEM-cushioned bilayers; lubrication by surfactants and lipids between hydrophobic surfaces also remains under explored. The stalk model of membrane fusion is recommended as a framework to guide energetic considerations in implementing different surfactant and lipid molecular architectural designs. We have also discussed a controversy relating to the morphology and characteristics of self-assembled interfacial structures by surfactants – pertinent to considerations of these interfacial constructs as effective boundary lubricants, suggesting that unperturbed quiescent bilayers might be induced to transform into aggregates as observed in AFM imaging. Along with an observed structural transformation at \sim cmc [41, 102], it demonstrates the richness of the surfactant self-assembly behavior at the solid-liquid interface – and it is likely to remain controversial and thus invites future input from experimentalists, theorists and simulators.

Can other hydrated interfacial constructs or moieties serve as effective aqueous boundary lubricants? Klein has estimated that a hydrated monovalent ion might well support a pressure up to 1 GPa [106], and identified the viscous loss mechanism in the subnanometre hydration shells of confined monovalent ions [107]. Nanotribology measurements using LFM showed that the lubrication efficacy of hydrated monovalent cations could be related to their hydration tendency: smaller ions could accommodate more water molecules and thus lubricate better [108]. However, this correlation did not hold for divalent

cations; instead, it was the fast exchange dynamics of water molecules in the hydration shell of a divalent cation with the bulk water that could give a clue to its lubrication efficacy [109]. For anions, a possible correlation was found between the anion friction reduction and the Hofmeister series [8] – which itself remains unexplained. Lubrication by ions thus remains an important and open area, as it is intricately related to the fluidity of the hydration shell around hydrophilic moieties, which underpins the mechanism of aqueous boundary lubrication [19, 20] and is fundamentally connected with the fluidity of highly confined water – a topic that excites and polarises colleagues in equal measure (*e.g.* [21] vs [110]).

Nanoparticles and their dispersions (called *nanofluids* [111]) have been increasingly incorporated in modern formulations, although we remain uncomfortable with the lack of the understanding of their biological and environmental impact [58]. It is known that the size, shape, and surface chemistry of the nanoparticles dispersed in both aqueous and non-aqueous media can be readily tailored to mediate desired surface forces [111, 112], and they can also be deposited or incorporated at the surface to endow well-defined nanotextures to control friction (*e.g.* [113-115] and references therein). However, how nanofluids can be synergistically combined with polymers and surfaces/lipids to mediate effective aqueous boundary lubrication remains to be fully explored.

In the macromolecular domain, boundary lubrication operates very handsomely indeed [12, 116]. In fact, the extremely efficient boundary lubrication in biological living systems ($\mu < 0.001$) has long puzzled us, and it has also inspired several biomimetic polymeric aqueous boundary lubricants, notably polyzwitterionic brushes [44] and bottle-brush block-copolymers (*e.g.* [117-119]) which resemble the macromolecular architecture of mucin or lubricin, a glycoprotein implicated in biolubrication [120]. However, it is becoming increasingly appreciated that it is the *supramolecular synergy* [121, 122] between several of the biolubricants previously implicated, such as phospholipids [123], HA, lubricin or mucin [124], superficial zone protein (SZP), and aggrecan, rather than their heroic individuals that is responsible [125, 126]. It is important to point out that the physiology of the outermost cartilage layer – the *lamina splendens* – remains unclear [116, 127]. Progress must be made so that our conceptual design to understand, mimic, and sometimes repair and replace this ingenious biological construct is *au fait*, rather than *ignotum per æque ignotum*. It is thus fair to comment that the intimate details of the wet and slippery mechanisms in biolubrication remain enigmatic, and will continue to whet our scientific appetite.

As a closure, we return to the century old Stribeck curve in Figure 1 which has summed up our previous conventional wisdom on different lubrication regimes and which continues to guide us in engineering and tribological designs. In light of the recent advances in aqueous boundary lubrication, exhibiting a friction coefficient in the range of $\mu \sim 0.01 - 0.001$ or below when in full operation, it is tempting to re-scope the aqueous boundary lubrication regime (the hatched region in Figure 1), although its exact shape and scope is yet to be fully established – thus indeed still *terra incognita*.

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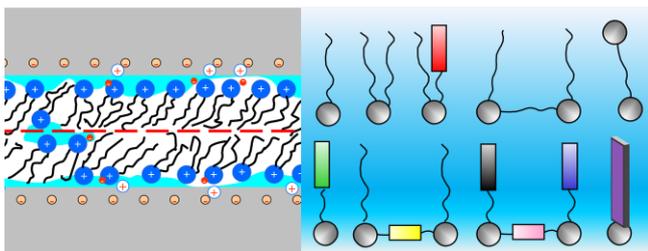
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Graphical abstract

ACCEPTED MANUSCRIPT

Highlights

- Molecular mechanisms of aqueous boundary lubrication lie in hydration lubrication
- Supermolecular synergy an area for further investigations
- The stalk model of membrane fusion may guide molecular designs for boundary layers
- Structure and morphology of self-assembled surfactant layers remains controversial
- A new aqueous boundary lubrication regime proposed for the *Stribeck curve*