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Molecular adsorption, self-assembly, and friction in lubricants

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Abstract

Lubricants are complex fluids consisting of a base oil and many different additives, and are used to control friction and wear between solid inorganic surfaces in relative motion. A review of recent work on molecular simulations of lubricants is given. It is shown that simulations can be used to uncover a lot of interesting behaviour, including additive adsorption, additive self-assembly, and a competition between the two. The specific examples to be discussed are: the adsorption of stearic acid and oleic acid in squalane on iron-oxide surfaces; the self-assembly of glycerol monooleate in bulk *n*-heptane; the adsorption and friction of glycerol monooleate in squalane on iron-oxide surfaces; and the conformations of functionalised copolymers in bulk *n*-heptane. The structures adopted by the additives can be correlated with the observed frictional properties, opening up the possibility of molecular-level design of new lubricants.

Keywords: adsorption; self-assembly; friction; lubricants; molecular dynamics simulations

1. Introduction

Engine lubricants are complex solutions of additives in a base-oil solvent. The base oil is a polydisperse mixture of aliphatic and aromatic hydrocarbons, and constitutes approximately 80 wt% of the lubricant. The remaining components include viscosity modifiers (typically polymers), dispersants (to keep

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soot in the oil rather than being deposited on engine components), detergents (inorganic compounds that react with sludge precursors and neutralise acids), organic friction modifiers (OFMs), inorganic friction modifiers, and corrosion inhibitors. (Note that the use of the term ‘detergent’ here is different from the
10 conventional definition of a water-soluble surfactant.) The complete formulation lubricates moving parts in the engine, which can be assumed to be metal or metal-oxide surfaces. Although passenger cars will crossover from internal combustion engines (ICEs) to electric power trains within the next few decades, there is still an urgent need to mitigate the effects of fuel consumption, CO₂ pro-
15 duction, and engine-component wear during the transition period. Moreover, there is a move towards lower-viscosity base oils to improve fuel economy, and this places additional burdens on additives to reduce friction and wear within the engine. Friction accounts for approximately 10% of energy losses from the engine, and even a modest decrease in the frictional losses $\sim 1\%$ would translate
20 to substantial reductions in emissions and CO₂, and financial savings to vehicle owners. An equally important market for fuels and lubricants is in marine shipping, which will rely on ICEs for the foreseeable future. A lot of work remains to be done to improve the longevity of marine engines, and hence reduce costs associated with servicing and replacement, and to mitigate the pollution arising
25 from them [1].

This contribution focuses on the physical chemistry of OFMs, which encompasses a broad range of structural and dynamic phenomena at the solid-oil interface. OFMs are often surfactant-like molecules which are assumed to adsorb at interfaces, and provide soft layers which reduce friction between two solid
30 surfaces brought together under load and sheared relative to one another. Some of the basic physical parameters are the (transient) loads on engine components (up to 10^9 Pa), the surface roughness and average surface separation (L) of engine components ($\sim \mu\text{m}$), and the relative sliding velocity ($v_s = 0.1\text{--}10\text{ m s}^{-1}$). These parameters give corresponding shear rates of $\dot{\gamma} = v_s/L = 10^5\text{--}10^7\text{ s}^{-1}$.

35 Typical OFMs can form surface layers of around 2 nm thickness, so how do they control friction? The answer is that the load is supported at asperity

contacts, where the peaks on one solid surface are in very close contact with the peaks on the other surface. At these contacts, the local separation is smaller, and the shear rate is higher, than the engineering parameters given above, but
40 these are the conditions under which the OFMs operate. To put this in context, the relationship between the OFM layer and the surface roughness is similar to that between a blade of tall grass (1 m) and the height of a mountain (1000 m).

The classical picture of lubrication is that the OFMs adsorb on a surface to form a monolayer [2, 3, 4] driven by the attraction of the polar head groups
45 with the inorganic surface, and the favorable interactions between the non-polar tails and the base oil. This is shown schematically in Fig. 1(a). This is thought to increase the degree of slip between two surfaces, the adsorbed layers, and any confined liquid. Experimental investigations of strongly confined liquids under extremes of pressure and shear are difficult to carry out. Although the
50 structures and adsorbed films can be investigated under quiescent conditions using techniques such as X-ray or neutron reflectometry, and sum frequency generation (SFG) spectroscopy, carrying out these experiments *in situ* is extremely challenging. Molecular simulations provide valuable insights into the structure and dynamics on length scales appropriate to the asperity contact
55 (0.1–10 nm), and can be used to correlate molecular structure with tribological properties. Equilibrium and non-equilibrium molecular dynamics (MD) simulations have been used extensively to examine the structure, dynamics, and tribological properties of lubricants [5, 6]. Examples include pure polymer melts and hydrocarbons [7, 8, 9, 10, 11, 12, 13, 14], silanes [15], fatty acids and
60 amines [16, 17, 18, 19, 20, 21], glycerin [22], glycerides [23], zinc dialkyldithiophosphates [24], MoS₂ [25, 26], room-temperature ionic liquids [27, 28], and carbon nanoparticles [29].

For both experiment and simulation, one of the major problems is the sheer complexity of lubricants, and the evolving chemical and physical characteristics
65 of the surfaces. In both types of research, simple model systems are required to start building up an understanding of how lubricants work. To this end, the main message of this contribution is that, on the basis of molecular simulations,

there are well-known OFMs that do not form simple monolayer structures, and that self-assembly in bulk and at interfaces can compete with surface adsorption and have substantial effects on the resulting friction. Some competing structures are shown in Fig. 1(b). A hemi-micelle can be adsorbed on the surface, whereby the polar head groups are attracted to each other and the inorganic surface, and the non-polar tail groups are solvated by the base oil. Alternatively, the surfactant can remain in the liquid layer as a complete reverse micelle, with the polar head groups forming a core, and the non-polar tail groups immersed in the base oil. Any water in the system will prefer to be at the inorganic surfaces and/or in the cores of reverse micelles [30, 31].

Figure 1: Schematic diagrams of (a) monolayer adsorption at planar interfaces, (b) adsorption and self-assembly between planar interfaces, and (c) monolayer adsorption at a curved interface. Surfactant molecules are shown as polar head groups (circles) with non-polar tails. Solid surfaces are shown as hatched areas.

In this article, a short review of recent molecular-simulation work on the properties of OFMs is given. The rest of the article is arranged as follows. A brief overview of the relevant MD simulation methods is given in Sec. 2. In Sec. 3, the conventional case of monolayer adsorption is discussed with respect to the effects of surface curvature, and the dependence of the adsorbed-film properties on molecular details. Section 4 is dedicated to the occurrence of self-assembly in bulk non-aqueous liquids. The competition between adsorption and self-assembly in confined liquids is illustrated in Sec. 5, along with the effects on friction.

2. Simulation methods

Standard equilibrium MD simulations in the NVT and NPT ensembles can be applied to the study of adsorption and self-assembly in both bulk and confined-liquid systems [32, 33]. Simulations are carried out with periodic boundary conditions applied, either in all three directions (bulk systems) or in two directions (systems in a slit pore). Temperature and pressure are controlled with a standard method, such as the Nosé-Hoover thermostat/barostat. Typically, self-assembly of surfactant-type additives can be observed on the ten-nanosecond time scale, while sampling the full range of conformations of polymeric additives may require simulations of several hundred nanoseconds (see Sec. 4).

The full range of non-equilibrium molecular-simulation methods for studying lubrication phenomena has been reviewed recently [6]. For the study of liquid properties under confinement and shear, a thermostat is required to remove the excess heat energy arising from work being done on the system against viscous and friction forces. There are several methods for doing this, but in the work reviewed here, temperature is controlled by thermostating the system only in the y direction, while the system is sheared in the xz plane. This ensures that the velocity profile $v_x(z)$ is not strongly influenced by the thermostat, at least for the liquid layers described here, which are typically around 10 nm thick. For thin liquid layers – on the order of several molecular diameters – the observed properties can depend sensitively on the method of temperature control [34, 35]. Of particular importance is the conduction of heat from the liquid layer in to the solid surfaces, and hence rigid walls are not appropriate for such simulations. The load on a confined liquid can be controlled directly by applying forces to the outermost layers of atoms in the solid surfaces, without having to apply an extended-Hamiltonian barostat. Non-equilibrium MD simulations can routinely be carried out on the 10–100 ns time scale. Steady-state velocity profiles in the liquid layer are established quite quickly (~ 10 ns), but long runs may be necessary to gather sufficient statistics for observables. For example, the kinetic

friction coefficient μ can be calculated by averaging the total instantaneous lateral friction force (F_L) and normal load (F_N) acting on the surface atoms under shear conditions. Each of these properties fluctuates significantly, and must be averaged over long simulations in order that the ratio $\mu = -F_L/F_N$ can be calculated reliably.

As with all molecular simulations, the choice of force field is an important factor. The DREIDING force field [36] and OPLS force field (in both all-atom and united-atom formulations) [37, 38] have been used in the work reviewed here. For model base oils, checks are made against experimental measurements of properties such as the density or viscosity, and deviations under ambient conditions are typically no more than 5% [31]. As will be shown in Sec. 4, the self-assembly of polar additives in bulk oil is described very accurately with standard force fields. The interactions between lubricants and surfaces are more complicated. For some minerals, such as mica, force fields specifically designed to describe interactions between inorganic and organic species are used, such as the INTERFACE-PCFF force field [39, 40, 41, 42]. Force fields are available for other commonly studied inorganic surfaces, such as iron oxide (α -Fe₂O₃) [24]. Of course, such force fields can only describe physisorption of surfactant-type molecules onto the substrate. Viable alternatives include reactive force fields such as ReaxFF [43], and *ab initio* MD methods, but the application to large-scale simulations is difficult. A proper account of chemisorption in MD simulations [44, 45], and the description of tribochemistry [46, 47] are ongoing problems.

3. Adsorption at the metal-oil interface

A good illustration of the ‘classical’ picture of lubrication is provided by the examples of stearic acid and oleic acid in squalane base oil [19]. The molecular structures of these molecules are shown in Fig. 2(a)–(c). Squalane is a convenient model of base oil, in that it has average molecular weight and viscometric properties. Fig. 2(d) shows an atomistic MD snapshot of stearic acid adsorbed

on parallel iron-oxide ($\alpha\text{-Fe}_2\text{O}_3$) (100) surfaces at temperature $T = 298$ K and pressure $P = 10^8$ Pa. Clearly, the molecules form well-defined monolayers, although the surface coverage is somewhat less than the maximum values determined from adsorption-isotherm experiments (from dodecane) [48]. A recent
150 computational and experimental study of stearic acid on iron oxide provides an explanation for this, on the basis of a random sequential adsorption model [49]. Note that the MD simulations are carried out with a classical force field, and so the additive molecules are physisorbed onto the surface.

Figure 2: (a)–(c) Molecular structures of (a) stearic acid, (b) oleic acid, and (c) squalane. (d) Snapshot from a MD simulation of stearic acid adsorbed on iron-oxide (100) surfaces from squalane at $T = 298$ K and $P = 10^8$ Pa (adapted from Reference 19). The central simulation cell and two of its periodic replicas are shown. The stearic acid molecules are shown in blue and white, the squalane molecules are shown in gold, and the oxygen and iron atoms are shown in red and brown, respectively.

The frictional properties of these films were examined at $T = 298$ K and a
155 load equivalent to $P = 10^8$ Pa by shearing the two parallel walls with relative velocity v_s , and measuring the ratio of the lateral and normal forces F_L and F_N , respectively. The extended Amontons-Coulomb law is $F_L = F_0 + \mu F_N$, where F_0 is a weak adhesive force known as the Derjaguin offset, and μ is the kinetic friction coefficient. Because the load is so high, $F_L \gg F_0$ [20], and so the friction
160 coefficient is simply $\mu \simeq F_L/F_N$. It was found that μ increases first linearly with shear rate, and then logarithmically at high shear rates. The data can be fitted

extremely well with an Eyring-type model [50, 51, 19] given by

$$\mu = \mu_0 \ln \left[\left(\frac{\dot{\gamma}}{2\dot{\gamma}_0} \right) + \sqrt{1 + \left(\frac{\dot{\gamma}}{2\dot{\gamma}_0} \right)^2} \right] \quad (1)$$

where μ_0 and $\dot{\gamma}_0$ are fitting parameters. (An example is discussed in Sec. 5.)

For a given surface coverage, it was observed that at all shear rates, the friction
 165 coefficient of stearic acid was higher than that of oleic acid. This was put down
 to more solid-like clustering of the saturated stearic acid molecules, arising from
 better packing. Films of unsaturated oleic acid molecules were more disordered,
 and therefore provided a less rigid layer on the iron-oxide surface. The difference
 between stearic acid and oleic acid decreased with increasing surface coverage,
 170 as the films resemble each other more when the molecules are packed together
 densely. These results on the effects of saturation are not immediately applicable
 to lubricants, however, because the surface coverage is not controlled in an
 engine. Instead, it is the bulk concentration of additive that is controlled, and
 stearic acid has a stronger adsorption than oleic acid; fits to the Langmuir
 175 isotherm show that the maximum surface coverage is $\Gamma_{\max} = 6.2 \times 10^{-6} \text{ mol m}^{-2}$
 for stearic acid and $\Gamma_{\max} = 3.7 \times 10^{-6} \text{ mol m}^{-2}$ for oleic acid [48]. This may go
 some way to explaining why, experimentally, stearic acid has better anti-friction
 properties than oleic acid [52].

In some cases, the detailed structures of the adsorbed films can be compared
 180 directly with experiment. For example, SFG spectroscopy and polarised neutron
 reflectometry experiments on hexadecylamine adsorbed from dodecane on to α -
 Fe_2O_3 at $T = 298 \text{ K}$ and $P = 10^5 \text{ Pa}$ show that the monolayer thickness is
 1.6–2.0 nm, and the average molecular tilt angle is 48° with respect to the
 surface [53]. Atomistic MD simulations show that the monolayer is 1.5–2.0 nm
 185 thick, and the average molecular tilt angle is 40° [20].

Finally, it should be noted that in simulations, the surfaces are often modeled
 as being perfectly smooth and parallel, but not always [54, 55]. In experimental
 investigations of adsorbed-film structures, the surfaces should be as flat as pos-
 sible, and a small degree of roughness should be taken into account. One inter-

190 esting problem is how the adsorption of molecules depends on surface curvature,
 with all other parameters being held equal (specifically, bulk concentration and
 adsorption energy). This situation was studied using a coarse-grained model of
 surfactant molecules in an implicit solvent, adsorbing on to structureless spher-
 ical surfaces with a fixed radius of curvature R [56]. It was found that, for a
 195 given bulk concentration of surfactant, the adsorption decreases with increasing
 particle radius. As an example, for a bulk concentration corresponding to about
 $1 \times 10^{-3} \text{ mol L}^{-1}$, the adsorption on a particle with $R = 0.8 \text{ nm}$ was about 80%
 higher than that on a particle with $R = 4.0 \text{ nm}$ ($\Gamma = 4.5 \times 10^{-6} \text{ mol m}^{-2}$
 versus $\Gamma = 2.5 \times 10^{-6} \text{ mol m}^{-2}$). An analysis of the various contributions to
 200 the adsorption free energy shows that the positive entropic component, arising
 from packing of the surfactant tail groups, is less for the small particle than for
 the large particle. (Note that the energetic component, representing binding of
 the head group to the surface, is the same in both cases.) For the small par-
 ticle, the tail groups splay out radially from the surface, whereas for the large
 205 particle – and planar surfaces – the tail groups are (on average) parallel with
 one another. This is shown schematically in Fig. 1(a) and (c). Hence, the steric
 interactions are greater on flat surfaces than on highly curved surfaces. Not only
 does this reduce the adsorption on flat surfaces, but it also introduces a larger
 barrier in the free-energy profile along the ‘reaction coordinate’ defined by the
 210 distance between the polar head group and the surface. This barrier affects the
 adsorption and desorption kinetics.

4. Self-assembly in non-aqueous solution

OFMs are often surfactant-like molecules with polar head groups and non-
 polar tail groups. A classic example of an OFM is glycerol monooleate (GMO),
 215 the molecular structure of which is shown in Fig. 3(a). Remarkably, GMO and
 related molecules form reverse micelles in bulk solution [57, 58, 59, 60, 30, 31, 61].
 A snapshot from an atomistic MD simulation of 5 wt% GMO in *n*-heptane is
 shown in Fig. 3(b). The choice of *n*-heptane as a base oil is important, because it

is readily available in deuterated form, which can be used in small-angle neutron
 scattering (SANS) experiments to improve contrast between solute and solvent.
 Such experiments have been done to determine the radius of gyration of the
 GMO reverse micelles. Fig. 3(c) shows the form factor $P(q)$ of GMO reverse
 micelles in *n*-heptane as determined from SANS and MD simulations [30]. q is
 the scattering wave vector. Fitting the data to a Gaussian model

$$\frac{P(q)}{P(0)} = \exp(-q^2 R_g^2 / 3) \quad (2)$$

gives $R_g = (1.663 \pm 0.007)$ nm (SANS) and $R_g = (1.552 \pm 0.004)$ nm (MD),
 which shows remarkable consistency. In *n*-heptane, the aggregation number
 in the reverse micelle is about 30 molecules, while in toluene, the number is
 about 20 molecules. Nonetheless, the radius of gyration is roughly the same in
 both solvents, which reflects the different levels of solvation of the non-polar tail
 groups by the solvents [30].

Figure 3: (a) Molecular structure of glycerol monooleate (GMO). (b) MD snapshot of GMO in *n*-heptane at $P = 10^5$ Pa and $T = 298$ K (adapted from Reference 30). The solvent is shown in a stick representation. The atoms in GMO are shown in red (oxygen), black (carbon), and white (hydrogen). (c) Form factor of reverse micelles in GMO from SANS (filled black points) and MD simulations (open red points) (data taken from Reference [30]). The solid black and dashed red lines are fits of Eq. (2) to the SANS and MD data, respectively, in the range $q \leq 1 \text{ nm}^{-1}$.

Another aspect of self-assembly in bulk-solution conditions involves functionalised polymeric additives, which can be used as viscosity modifiers, friction modifiers, anti-wear agents, etc. The central question is whether the distribution of functional groups along a polymer backbone can affect the size of the polymer, as measured by either the radius of gyration R_g , or the end-to-end distance R_{ee} [62]. Fig. 4 shows simulation snapshots of one unfunctionalised polyethylene-polypropylene copolymer, and five functionalised polymers with the same composition (approximately 10 kDa, 240 monomer units and 8 functional groups per molecule), dissolved in *n*-heptane at $T = 298$ K and $P = 10^5$ Pa. The chemical details of the functional groups are proprietary, but the essential point is that they are solvophobic and are expected to associate reversibly in the solution. The molecules are very flexible, and the sizes undergo substantial thermal fluctuations, but the average values depend sensitively on the functional-group distribution, as shown in Fig. 4. Moreover, the shear viscosity η of the polymer solution (as measured in the MD simulations) is strongly correlated with the polymer size. η was measured in equilibrium MD simulations using the Einstein relation

$$\eta = \frac{V}{20k_B T} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \sum_{\alpha\beta} [G_{\alpha\beta}(t) - G_{\alpha\beta}(0)]^2 \right\rangle \quad (3)$$

where V is the system volume, $G_{\alpha\beta} = \int_0^t P_{\alpha\beta}(t') dt'$, $P_{\alpha\beta}$ is an element of the symmetrised traceless portion of the stress tensor, and $\alpha, \beta = x, y, z$ [63, 64, 65]. The results show that η increases with increasing R_g .

These two examples show that lubricant additives in bulk solution can undergo self-assembly. Hence, self-assembly may compete with adsorption and friction reduction, and this is discussed in Sec. 5.

5. Competition between adsorption and self-assembly

Fig. 5(a)–(c) shows simulation snapshots of 10 wt% GMO in squalane confined between α -Fe₂O₃ (100) surfaces at $T = 353$ K and loads of (a) $P = 10^5$ Pa, (b) $P = 10^8$ Pa, and (c) $P = 10^9$ Pa. The surfaces were in relative motion with $v_s = 10$ m s^{−1} and shear rate $\dot{\gamma} \sim 10^9$ s^{−1}. At low pressure, the GMO is mostly

Figure 4: Snapshots from MD simulations of polymers in *n*-heptane at $T = 298 \text{ K}$ and $P = 10^5 \text{ Pa}$ (new snapshots adapted from Reference 62): (a) unfunctionalised polyethylene-polypropylene copolymer backbone; (b) even distribution of functional groups; (c) random distribution of functional groups; (d) all of the functional groups in the middle; (e) all of the functional groups at one end; (f) functional groups split evenly between both ends. The solvent is shown in a transparent representation, the polymer backbone atoms are shown in dark gray, and the functional group atoms are shown in orange. Also shown is the radius of gyration R_g (data taken from Reference 62) and the shear viscosity η (new data).

aggregated in to a reverse micelles, even under shear conditions. As the pressure is increased, the degree of aggregation decreases, and the adsorption on the surfaces increases. This shows that, under engine conditions, additive molecules may show a competition between adsorption and self-assembly.

The impact on friction can be assessed by measuring the friction coefficient μ in MD simulations. Fig. 5(d) shows μ as a function of $\dot{\gamma}$ for the same GMO system, from MD simulations and a fit according to Eq. (1). The quality of the fit is excellent, and in this case $\mu_0 = 0.110 \pm 0.009$ and $\dot{\gamma}_0 = (2.3 \pm 0.3) \times 10^8 \text{ s}^{-1}$. $\dot{\gamma}_0$ gives a rough indication of where μ switches over from a linear dependence on low shear rates ($\mu \approx \mu_0 \dot{\gamma} / 2 \dot{\gamma}_0$), and a logarithmic dependence on high shear rates [$\mu \approx \mu_0 \ln(\dot{\gamma} / \dot{\gamma}_0)$].

There are at least two interesting effects concerning the impact of self-assembly on friction.

First, under engine conditions, the additive molecules can undergo a mixture of thermal and chemical degradation, e.g., hydrolysis. To assess the impact of such effects, the structural and tribological properties of GMO and its hydrolysis products were surveyed extensively [61]. The hydrolysis products included oleic acid and glycerol, and the solution of GMO and/or its hydrolysis products was confined between mica surfaces at $P = 10^5 \text{ Pa}$ and $T = 298 \text{ K}$. Keeping the additive content fixed at 10 wt% in *n*-heptane, it was observed that hydrolysis leads to an increase in μ , and that after complete hydrolysis of GMO, the friction coefficient had increased by 50%. This is correlated with rather subtle structural changes. GMO itself adsorbs on to mica surfaces from heptane in the form of surface (hemi-)micelles, while the hydrolysis products adsorb more weakly. Hence, hydrolysis leads to a decrease of the amount of additive on the surfaces, and a concomitant increase in friction.

The second effect is the interaction between lubricant additives. Lubricants are extremely complex fluids, and to date, there has not been a systematic survey of the cooperative and/or competing interactions between different additives. In recent work, the interaction between OFMs and dispersants (used to keep soot in solution) has been studied in MD simulations, and some significant effects on

Figure 5: (a)–(c) Snapshots from MD simulations of 10 wt% GMO in squalane confined between α -Fe₂O₃ (100) surfaces at $T = 353$ K and (a) $P = 10^5$ Pa, (b) $P = 10^8$ Pa, and (c) $P = 10^9$ Pa. The solvent is shown in a transparent representation, the oxygen atoms of GMO are shown in red (to highlight association of the polar groups), and the oleate tails are shown as black sticks. Two periodic replicas are shown in each case. The surfaces are identical in all simulations, but thermal fluctuations and the periodic boundary conditions mean that atoms may appear on one side or the other of the primary simulation cell. (d) Friction coefficient μ as a function of shear rate $\dot{\gamma}$ in confined liquid layers of 10 wt% GMO in squalane at $P = 10^8$ Pa [66].

290 friction have been uncovered. The results of this work (by two of the authors,
GT and PJC) are currently being prepared for publication [66].

6. Conclusions

Molecular simulations of additive adsorption, self-assembly, and friction in
oils can be used to demonstrate some very complex behaviour which may have a
295 direct effect on the performance of lubricants. In the classical picture, additive
molecules are surfactant-like species which form monolayers on the surfaces of
moving parts of an engine. This gives a reduction in the ordering of the oil at
the solid-oil interface, which is correlated with a reduction in friction. An ex-
ample of such classical lubrication is by carboxylic acids adsorbed on iron-oxide
300 surfaces [19]; indeed, this was first considered in the 1920s [2, 3, 4]. Recent
work shows that some surfactant-like additives self-assemble in bulk solution,
leading to the formation of structures such as reverse micelles. An example is
glycerol monooleate, a very widely used organic friction modifier, dissolved in
simple hydrocarbon solvents [30]. In addition, functionalised polymers adopt
305 very different conformations depending on how the functional groups are dis-
tributed along the polymer backbone [62]. These types of structures can persist
under confinement between moving surfaces (such as in engines) and compete
with monolayer adsorption. The balance of self-assembly and adsorption has
been shown to have an impact on the friction coefficient; this has been illus-
310 trated in the case of glycerol monooleate in various solvents, confined between
inorganic surfaces [31, 61]. Therefore, to establish structure-property relation-
ships in lubricants, it is essential to understand first how molecular structure
dictates the fundamental processes of adsorption and self-assembly. Lubricants
are extremely complex fluids, and having discovered how several different types
315 of additives behave in isolation, it is now important to learn how interactions
between different additives can lead to either competitive or cooperative ef-
fects. There is a lot of work left to do, both experimentally and in molecular
simulations.

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