



Nonequilibrium molecular dynamics simulations of stearic acid adsorbed on iron surfaces with nanoscale roughness

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ABSTRACT

Nonequilibrium molecular dynamics (NEMD) simulations have been used to examine the structure and friction of stearic acid films adsorbed on iron surfaces with nanoscale roughness. The effect of pressure, stearic acid coverage, and level of surface roughness were investigated. The direct contact of asperities was prevented under all of the conditions simulated due to strong adsorption, which prevented squeeze-out. An increased coverage generally resulted in lower lateral (friction) forces due to reductions in both the friction coefficient and Derjaguin offset. Rougher surfaces led to more liquidlike, disordered films; however, the friction coefficient and Derjaguin offset were only slightly increased. This suggests that stearic acid films are almost as effective on contact surfaces with nanoscale roughness as those which are atomically-smooth.

1. Introduction

The requirement to reduce the energy consumption and thus CO₂ emissions from engineering systems has resulted in a general lowering of lubricant viscosity in order to minimise hydrodynamic friction losses. However, this means that an increasing number of engineering components operate under boundary lubrication conditions, where solid asperities come into direct contact, leading to high friction and wear. As a result, lubricant additives which can reduce friction and wear under boundary conditions, such as organic friction modifiers (OFMs), are of increasing importance [1].

OFMs are amphiphilic molecules that contain both a polar head group and a nonpolar hydrocarbon tail group. The most widely studied OFM molecule in both experiments [2–6] and MD simulations [7–15] is stearic acid; a carboxylic acid with a saturated, linear C₁₈ alkyl chain. The acid head group adsorbs to metal or ceramic surfaces and strong, cumulative van der Waals forces between proximal nonpolar tails leads to the formation of incompressible monolayers that prevent contact between solid surfaces and reduce adhesion and friction [1,8].

In order to fully understand the performance of OFM additives, it is necessary to obtain a detailed picture of: (i) the nanoscale structure of their films and (ii) their tribological behavior [7,8]. Detailed structural information on OFM films can be obtained from experimental techniques such as sum frequency spectroscopy (SFS) [16], polarized neutron

reflectometry (PNR) [2], the surface force apparatus (SFA) [3], and in situ atomic force microscopy (AFM) [4]. The tribological behavior of OFM films can also be investigated using SFA [3] and AFM [4] as well as dedicated boundary friction experiments [5,6] which employ low sliding velocities (mm s^{−1}) and high pressures (GPa) in order to maintain boundary lubrication conditions [8].

Classical nonequilibrium molecular dynamics (NEMD) simulations can be used to simultaneously probe the nanoscale structure and friction of OFM films, making it a valuable complement to experiments [8]. The use of accurate all-atom force fields enables the structure and friction of large molecular systems to be reliably analysed over time [9].

The effect of surface roughness on the performance of OFMs is not fully understood [1]. Most previous NEMD simulations of OFM films on metal surfaces have utilised atomically-smooth slabs, with only atomic corrugation [7–12], although the influence of artificial asperities placed on top of atomically smooth slabs have also been considered [13–15]. The presence of nanoscale roughness has been shown to significantly influence the adhesion of solid surfaces through both MD simulations and AFM experiments [17]. The effect of 3D nanoscale fractal roughness on the friction between sliding surfaces has also been investigated for both dry sliding [18–20] and in the presence of lubricant molecules [21–23] in large-scale NEMD simulations. These previous simulations suggested that the friction coefficient depends on how effectively the lubricant is able to prevent the direct

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contact of asperities on opposing surfaces [22]. Nonpolar lubricant molecules can be easily squeezed-out from between asperities [24,25], but strongly-adsorbed OFMs are expected to be more difficult to remove, making them more effective in reducing asperity contact and thus friction in the boundary lubrication regime [8]. Other NEMD simulations of alkanes between amorphous and crystalline surfaces showed that the layering of lubricant films was strongly suppressed on rougher amorphous surfaces, resulting in a more liquidlike film [26]. This may have significant implications regarding the ability of OFM films to separate opposing solid surfaces with nanoscale roughness.

The kinetic friction coefficient in nanotribological systems can be obtained using the extended Amontons-Coulomb law: $F_L = \mu F_N + F_0$, where F_L and F_N are, respectively, the average total lateral and normal forces acting on the outermost layer of atoms in each of the slabs and F_0 is the Derjaguin offset, the friction force at vanishing load, which is generally attributed to adhesive forces [7,15,27]. Recent SFA experiments of palmitic acid OFMs in PAO base oil highlighted F_0 as a significant contribution to F_L under relatively low applied pressures (< 10 MPa) [27]. Previous NEMD simulations showed that the Derjaguin offset increased with increasing surface roughness, decreased with increasing stearic acid coverage, and became negligible when sufficient lubricant was present to separate the stearic acid films [15]. In our previous NEMD simulations, we demonstrated that the friction coefficient is reduced at high coverage of stearic acid, due to the formation of solidlike monolayers which allow very little interdigitation and yield slip planes between well-defined molecular layers [8]. In this study, we will probe the effect of; (i) higher pressures (0.5–2.0 GPa), in order to test the limits of operability of OFMs, and (ii) surfaces with different levels of 3D root mean square (RMS) roughness (0.2, 0.5, 0.8 nm), in order to assess the effect of nanoscale roughness on the structure and tribological behavior of OFM films. The roughness added in this study is expected to be similar to that found on experimental surfaces, since it is added using a random midpoint displacement (RMD) algorithm, which generates surfaces with a quantifiable RMS roughness [18]. Conversely, in previous confined NEMD simulations of stearic acid, the roughness was varied by changing the size of artificial roughness features [13–15].

The ‘smooth’ steel surfaces used in tribological experiments generally have a RMS roughness of approximately 10 nm [28,29], though other surfaces, such as gold, can be produced with a RMS roughness well below 1 nm [30]. Therefore, all of the RMS roughness values used in this study represent an extremely smooth experimental surface; however, accurate representation of larger RMS roughness values would require prohibitively large simulation areas [26]. Moreover, since the roughness features considered here are on the atomic scale, they have the most potential to weaken OFM films by disrupting intermolecular forces between neighbouring molecules. The current simulations will highlight the effect of changes in the nanoscale structure within the film due to changes in surface roughness on both the friction coefficient and the Derjaguin offset. The results obtained with stearic acid will also be directly compared to results for *n*-hexadecane under similar conditions [22], in order to highlight the reasons for the differences in their friction reduction performance in the boundary lubrication regime [5,6].

2. Methodology

2.1. Simulation setup

A representative example of the systems simulated in this study is shown in Fig. 1a. It consists of two stearic acid monolayers adsorbed on α -iron slabs with 3D nanoscale RMS roughness (Fig. 1b). The α -iron slabs are chosen as a model for steel, which is of significant academic and industrial interest. Though α -iron oxide would be a more accurate representation of a steel surface [8], no classical MD force-field is currently available which can accurately model its deformation under

the high pressures applied in these simulations. Stearic acid was chosen as a model OFM, an important class of boundary lubricant additive, which has been used in numerous previous experiments [2–6] and MD simulations [7–15]. Our previous NEMD study showed that whilst there were significant variations in the structure and friction of stearic acid films and those formed by other types of OFM (amides and glycerides), all gave the same general trends [8]. Unlike in our previous study [8], no lubricant molecules were added between the stearic acid films. Preliminary squeeze-out simulations showed that only two molecular layers of *n*-hexadecane remained between stearic acid films at 0.5 GPa [8], and since higher pressures (0.5–2.0 GPa) were applied in the current simulations, very few *n*-hexadecane molecules were expected to remain between the asperities. A more complete understanding of lubricant squeeze-out in the presence of OFM films would certainly be an interesting target of future MD simulations and AFM experiments, but is beyond the scope of this current study. All structures were constructed using the Materials and Processes Simulations (MAPS) platform from Scienomics SARL.

Most surfaces have roughness on several length scales, including the nanoscale, that can be described by a self-affine fractal scaling law [18,32]. Here, the Hurst exponent and the root mean square (RMS) roughness can be used to quantify the amount of roughness [19]. Using the random midpoint displacement (RMD) algorithm, rough surfaces can be generated which are periodic across their boundaries [19]. The RMD algorithm, with a Hurst exponent of 0.8, was used to independently generate the same RMS nanoscale roughness (0.2, 0.5 or 0.8 nm) in the top and bottom slabs [18,22]. In order to avoid generating only a few large asperities, the RMD algorithm did not start from the centre of only one square (entire slab), but rather four smaller, equally sized squares [19]. The slabs themselves had approximate x , y , z dimensions of 11, 11, 5 nm. Periodic boundary conditions were applied in the x and y directions. The dimensions of the solid surfaces confining the stearic acid films are much larger in the current simulations than those used in many previous NEMD studies [7–9,13–15], in order to provide a more faithful representation of the statistical distribution of the heterogeneous surface morphology [26]. On experimental surfaces, the typical height of a roughness feature is expected to be approximately 2–3 orders of magnitude smaller than its lateral dimensions [33]. To replicate this in NEMD simulations would require a prohibitively large system size and hence the ‘steepness’ of the roughness features in these and previous NEMD simulations [18,33] is expected to be somewhat exaggerated. Nonetheless, the use of an RMD algorithm provides a more realistic representation of nanoscale surface roughness than harmonic [34] or other artificially introduced [15] roughness features.

Stearic acid molecules were oriented perpendicular to, and initially 3 Å from, the interior surfaces of the two slabs (Fig. 1a). The surface coverage, Γ , can be defined as the average number of stearic acid molecules present in a given surface area (nm^{-2}). Three coverages of stearic acid were considered; a high surface coverage ($\Gamma=4.56 \text{ nm}^{-2}$) close to the maximum theoretical value [35]; a medium coverage ($\Gamma=3.04 \text{ nm}^{-2}$) approximately 2/3 of the maximum coverage; and a low coverage ($\Gamma=1.52 \text{ nm}^{-2}$) around 1/3 of the maximum coverage (Fig. 1b). Note that the Γ values assume an atomically smooth surface. The high, medium and low coverages correspond to 600, 400, and 200 stearic acid molecules adsorbed on each of the 131.6 nm^2 slabs respectively. The highest coverage simulated has also been observed experimentally [35]. Simulations with no stearic acid molecules between the slabs were also conducted for comparison.

Classical MD simulations were performed using LAMMPS [36]. The MD equations of motion were integrated using the velocity-Verlet algorithm with an integration time-step of 1.0 fs. Fast-moving bonds involving hydrogen atoms were constrained with the SHAKE algorithm [37]. The stearic acid molecules were represented by the L-OPLS-AA force-field [38]. This is an updated form of the OPLS-AA force-field [39] which was explicitly parameterised for long-chain

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