Slip of Alkanes Confined between Surfactant Monolayers Adsorbed on Solid Surfaces

James P. Ewen,*†§ Sridhar Kumar Kannam,‡§ B. D. Todd,¶ and D. Dini†‡

INTRODUCTION

The dynamics of flow in nanofluidic devices¹ and nanoelectromechanical systems (NEMS)² can be accurately described only through a detailed understanding of the flow at fluid–solid interfaces.¹ This context, recent experimental and molecular simulation studies have shown that the common assumption in continuum hydrodynamics that fluid adjacent to a sliding surface moves at the same velocity as the surface (no-slip boundary condition) often breaks down at the nanoscale.³ A large proportion of such studies have investigated the slip of alkanes on surfactant monolayers adsorbed on smooth solid surfaces. Many of these studies report a slip length, defined as an extrapolated distance relative to the fluid–solid interface where the tangential velocity component vanishes.⁵ However, there is significant variation in both the magnitude and the shear rate dependence of the slip lengths from these experiments.⁵ For example, total internal reflection fluorescence recovery after photobleaching (TIR-FRAP) experiments suggested that slip rates independent (measured between 10² and 10⁵ s⁻¹) slip lengths of 10 to 30 nm, with longer n-alkanes having higher viscosities giving more slip.⁶ In addition to surfaces coated with surfactant SAMs, slip of alkanes has also been observed on surfactant films formed from solution. For example, TIR-FRAP experiments also showed that the addition of a surfactant [stearic acid (SA)] to hexadecane confined between smooth sapphire surfaces led to an increase in the slip length from 150 to 350 nm.⁷ Moreover, adding hexadecylamine to n-alkanes confined between smooth mica surfaces in SFA experiments switched the boundary conditions from no-slip to partial slip.⁷ In these SFA experiments, the maximum slip length again increased with the increasing n-alkane chain length from octane to tetradecane (1–15 nm).⁷

The large variation between slip length measurements from different experiments on similar systems suggests that different mechanisms may be acting to promote slip.⁵,⁶ Experiments which suggested smaller (<50 nm) slip lengths for alkanes on adsorbed surfactant monolayers³,⁶ are more consistent with the slip mechanism devised by Tolstoi and reviewed by Blake.⁸ This mechanism suggests that slip is due to enhanced liquid mobility at the surface and is essentially an extension of Eyring’s activated flow model for bulk liquid viscosity.⁵ Conversely, the much larger slip lengths measured in some experiments⁴,⁵ have subsequently

ABSTRACT: The slip and friction behavior of n-hexadecane, confined between organic friction modifier surfactant films adsorbed on hematite surfaces, has been studied using nonequilibrium molecular dynamics simulations. The influence of the surfactant type and coverage, as well as the applied shear rate and pressure, has been investigated. A measurable slip length is only observed for surfactant films with a high surface coverage, which provide smooth interfaces between well-defined surfactant and hexadecane layers. Slip commences above a critical shear rate, beyond which the slip length first increases with increasing shear rate and then asymptotes toward a constant value. The maximum slip length increases significantly with increasing pressure. Systems and conditions which show a larger slip length typically give a lower friction coefficient. Generally, the friction coefficient increases linearly with logarithmic shear rate; however, it shows a much stronger shear rate dependency at low pressure than at high pressure. Relating slip and friction, slip only occurs above a critical shear stress, after which the slip length increases linearly with increasing shear stress and then asymptotes. This behavior is well-described using previously proposed slip models. This study provides a more detailed understanding of the slip of alkanes on surfactant monolayers. It also suggests that high coverage surfactant films can significantly reduce friction by promoting slip, even when the surfaces are well-separated by a lubricant.
been explained through the formation of gas/vapor films or nanobubbles at the interface, as initially proposed by de Gennes.

In addition to experiments, nonequilibrium molecular dynamics (NEMD) simulations have been used extensively to study slip of liquids confined between solid surfaces. For high-slip systems, such as water flowing on graphene surfaces or through carbon nanotubes, accurate determination of the slip length with NEMD has been shown to be less accurate than equilibrium molecular dynamics methods. However, for the partial-slip systems of interest in this study, NEMD simulations have been used extensively to further understand slip phenomena as well as to estimate slip lengths for a range of confined alkane systems. Most NEMD studies have investigated the slip behavior in highly confined (<10 molecular layers) alkane films between atomically smooth solid surfaces. The slip lengths from these NEMD simulations depend on the system and conditions but are typically <10 nm. In these studies, the slip length generally increased with alkane viscosity, slab stiffness, sliding velocity, and pressure.

NEMD simulations of highly confined systems have also shown that the slip length decreases with increasing film thickness and is drastically reduced when the confining surfaces contain atomic-scale roughness. SFA and TIR-FRAP experiments have also shown significant reductions in the slip length on rougher surfaces. The slip length of water confined between atomically smooth surfaces coated by alkylsilane SAMs and adsorbed methanol films has also been measured with NEMD simulations. Several NEMD simulation studies have probed the structure, flow, and friction behavior of alkanes confined between surfactant monolayers; however, prior to this current study, slip lengths in such systems had not been successfully quantified.

NEMD simulations have also been central in developing more accurate models to describe liquid slip between solid surfaces. From these NEMD results, Thompson and Troian developed an equation for slip where, above a critical shear rate, the slip length is a power law function of the shear rate. Conversely, Lichter et al. suggested the variable-density Frenkel–Kontorova (vdFK) model, which predicts a plateau of the slip length at a high shear rate (rather than divergence). The model developed by Spikes and Granick to describe data from SFA experiments predicts the same behavior, but here the slip length asymptotes at high shear stress rather than high strain rate. Wang and Zhao extended Eyring’s molecular kinetic theory (MKT) to describe the slip behavior. By assigning appropriate values of the tuneable parameters, the extended MKT model is able to describe the important features from the slip models due to Thompson and Troian, Lichter et al. (vdFK), and Spikes and Granick.

In addition to accelerating flow in nanofluidic devices and NEMS, it has been proposed that slip could be exploited to reduce friction in macroscopic tribological systems. Specifically, slip has been used to rationalize results from macroscopic tribology experiments which showed that the addition of an organic friction modifier (OFM) to n-hexadecane could significantly reduce friction in the hydrodynamic lubrication regime when the surfaces are well-separated. OFMs are amphiphilic surfactant molecules that contain nonpolar aliphatic tailgroups attached to polar headgroups. They are based solely on C, H, O, and N atoms and are not environmentally harmful and do not poison exhaust after-treatment devices. The most widely studied OFM headgroups are carboxylic acids; however, amines, amides, and glyc erides are more industrially relevant. Commercial OFMs generally contain unbranched aliphatic tailgroups containing 12–20 carbon atoms because of their effective friction reduction, high base oil solubility, and high availability from natural fats and oils. OFMs adsorb to metal, ceramic, or carbon-based surfaces through their polar headgroups, and strong, cumulative van der Waals forces between proximal nonpolar tailgroups lead to the formation of incompressible monolayers. These monolayers are known to significantly reduce friction and wear in the boundary lubrication regime (where the load is primarily supported by surface asperities) by preventing direct contact between solid surfaces. However, it is less clear if OFMs also reduce friction in the hydrodynamic lubrication regime (where the load is supported by the lubricant). When OFM monolayers form on surfaces inside a tribological contact, the planes of methyl groups at the end of the vertically adsorbed OFM molecules create nonwetting, oleophobic surfaces over which lubricants could slip.

In this study, large-scale NEMD simulations will be used to investigate the friction and the slip behavior of hexadecane, confined between OFM films, under hydrodynamic lubrication conditions. Several different OFM types [SA, stearamide (SAM), and glycerol mono-stearate (GMS)] and coverages (1.44–4.32 molecules nm⁻²) will be explored to understand their influence on the friction and the slip behavior. The dependence of the slip length and the friction coefficient on the applied shear rate (10⁴ to 10⁶ s⁻¹) and pressure (0.1–1.0 GPa) will also be investigated. This study provides unique insights into the slip of alkanes on surfactant monolayers, as well as the relationship between slip and friction. These results also provide support for previously proposed mechanisms and models for slip in such systems. A deeper understanding of the slip phenomenon is expected to be valuable not only for improving the molecular design of lubricant additives but also for understanding and controlling flow and friction in nanofluidic devices and NEMS.

### METHODOLOGY

**System Setup.** A representative example of the systems simulated in this study is shown in Figure 1a. It consists of a lubricant (n-hexadecane) layer confined between two OFM monolayers which are adsorbed on atomically smooth hematite slabs. The hexadecane layer is sufficiently thick (>15 molecular diameters) such that no molecular structuring was evident in the middle of the film, and thus any confinement-induced viscosity increase was expected to be negligible. All systems were constructed using the Materials and Processes Simulations (MAPS) platform from Scienomics SARL. Classical MD simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) code.

Figure 1b shows the three different OFM types considered in these simulations; SA, SAM, and GMS. SA was selected to allow comparisons to previous experiments and NEMD simulations, whereas SAM and GMS are more commercially relevant. The hexadecane lubricant was chosen because of its well-defined properties and common use in both experimental and modeling tribology studies.

In all of the MD simulations, (100) slabs of α-iron(III) oxide (hematite) with dimensions (xyc) of approximately 55 × 55 × 12 Å were used as the substrates. Periodic boundary conditions were applied in the x and y directions. The surface was cleaved such that the Fe/O ratio remained at 2:3 to ensure that surfaces with no overall charge were produced.

Three different OFM surface coverages were considered. The coverage, Γ, is defined as the number of OFM molecules in a
Figure 1. Simulation details: setup for compression and sliding simulations (a). Example shown for SA at 4.32 nm$^{-2}$ after compression and before sliding. Fe atoms are shown in pink, O in red, terminal C in yellow, and the other all C in cyan. Headgroup H is shown in white, while H atoms in the alkyl groups are omitted for clarity. Periodic boundary conditions (orange dotted line) are applied in the $x$ and $y$ directions. Snapshot rendered using Visual Molecular Dynamics (VMD).34 Chemical structures of OFMs simulated in this study (b): SA, SAm, and GMS.

given surface area (nm$^{-2}$). The limiting headgroup area for carboxylic acids, amides, and glycerides (assuming monodentate binding) is around 0.22 nm$^2$, which corresponds to a maximum theoretical coverage of 4.55 nm$^{-2}$ for the OFMs.47 In these simulations, a high surface coverage ($\Gamma = 4.32$ nm$^{-2}$) is simulated by adsorbing 132 OFM molecules on each $\approx 30$ nm$^2$ slab to form a close-packed monolayer. Two other surface coverages are considered: a medium coverage ($\Gamma = 2.88$ nm$^{-2}$), approximately 2/3 of the maximum coverage; and a low coverage ($\Gamma = 1.44$ nm$^{-2}$), around 1/3 of the maximum coverage. In situ AFM experiments48 and depletion isotherms49 have shown that OFMs with saturated tailgroups (e.g., SA, SAm, and GMS) can form high coverage monolayers on solid surfaces. Multilayer OFM films have also been observed in recent in situ AFM experiments,50 although their role in lubrication remains unclear and they are not considered in this current study.

The OFM molecules were oriented perpendicular to, and initially 3 Å above, the interior surfaces of the two hematite slabs (Figure 1a). This produced OFM films similar to those formed by Langmuir–Blodgett experiments.47,51 Between 450 (high coverage) and 650 (low coverage) hexadecane molecules were then randomly distributed in the region between the OFM films. This resulted in a similar total number of atoms (approximately 50 000 including the surface atoms) and film thickness for all of the coverages studied.32

Parameters from the long hydrocarbon-optimized potentials for liquid simulations all-atom force field (L-OPLS-AA)52 were used to represent the carbon and hydrogen atoms in the alkyl chains (both OFMs and hexadecane), and standard OPLS-AA53,54 parameters were used for the headgroup atoms (see ref 33 for full details). Accurate density and viscosity prediction of bulk hexadecane using L-OPLS-AA under ambient and high pressure conditions has been confirmed in a previous publication.55 Lennard–Jones interactions were cut off at 12 Å, and “unlike” interactions were evaluated using the geometric mean mixing rules, as prescribed in the OPLS force field.53

Electrostatic interactions were evaluated using a slab implementation of the particle–particle, particle–mesh (PPPM) algorithm56 with a relative force accuracy of 10$^{-5}$.57

Surface–hexadecane and surface–OFM interactions were represented by the Lennard–Jones and Coulomb potentials; the hematite surface parameters selected were developed by Berro et al.57 for alkane adsorption. The hematite slab atoms were “frozen” in the corundum crystal structure58 to facilitate more accurate slip length analysis. Previous NEMD simulations have shown that the use of rigid slabs can lead to an unphysical velocity-slip behavior when they are in direct contact with a nonwetting fluid;59 however, here, the flexible OFM films form the interface with the lubricant and are sufficient to prevent such a behavior (see Results and Discussion).

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.58 The Nosé–Hoover thermostat,59,60 with a time relaxation constant of 0.1 ps, was used to maintain the target temperature, $T = 300$ K. The pressure ($P = 0.1–1.0$ GPa) was controlled by applying a constant normal force to the outermost layer of atoms in the upper slab, keeping the $z$ coordinates of the outermost layer of atoms in the lower slab fixed (Figure 1a).34,61

Simulation Procedure. First, the system was energy-minimized before a density similar to that of liquid hexadecane (0.75 g cm$^{-3}$) was achieved in the fluid between the slabs by moving the top slab down at 10 m s$^{-1}$. The system was then pressurized ($P = 0.1–1.0$ GPa), thermostatted in directions perpendicular to the compression ($x$ and $y$), and allowed to equilibrate at 300 K. Initially, the slab separation varied in a damped harmonic manner, so sliding was not applied until a constant average slab separation was obtained and the average hydrostatic pressure within the hexadecane film was close to its target value (within 1%).32 These compression simulations were generally around 2 ns in duration.

After compressive oscillation became negligible, a velocity, $v_x$, was added in the $x$ direction to the outermost layer of atoms in the top slab (Figure 1a), and sliding simulations were conducted for between 2 and 20 ns (depending on $v_x$). Lower sliding velocities required longer simulations for the block-averaged $x$-velocity profile and the friction coefficient to reach a steady state. The values of $v_x$ applied were between 1 and 200 m s$^{-1}$. Accurate determination of the friction coefficient and particularly the slip length becomes challenging at even lower sliding velocities, while shear heating becomes more difficult to control above the selected range.34 A combination of high sliding velocity (or shear rate) and pressure are particularly relevant for components which primarily operate in the elastohydrodynamic lubrication (EHL) regime.62

A consequence of the rigid slabs is that the thermostat cannot be applied directly to the slab atoms, as is common in confined NEMD simulations.55 Applying the thermostat directly to fluid molecules confined between rigid surfaces has been shown artificially influence their behavior under sliding conditions59 and also lead to the erroneous slip behavior.63 Therefore, during the sliding simulations, any heat generated was dissipated using a thermostat acting only on the OFM layers (Figure 1a), applied perpendicular to the sliding direction ($y$ and $z$). Using this approach, there was a negligible increase in the lubricant film temperature under shear, even at the highest sliding velocity considered. Moreover, the variation in the slip with sliding velocity is consistent with NEMD simulations of alkanes.
confined between thermostatted, flexible metal slabs (see Results and Discussion).18

RESULTS AND DISCUSSION

Slip Length Analysis. The slip length analysis will be presented first, followed by the shear rate and pressure dependence of slip and friction, and finally the interdependence of slip and friction. Figure 2a shows a representative NEMD system snapshot (SAM, $\Gamma = 4.32 \text{ nm}^{-2}$). Note that, consistent with previous NEMD simulations,33 the tilted OFM monolayers move at the same velocity as the slabs to which they are adsorbed. This is the case for all of the simulations, and thus the OFM velocity profiles are omitted for clarity. Comparing the red (assumed no-slip) and blue (measured) hexadecane velocity profiles shows that the confined lubricant layer is only partially sheared,21 and slip occurs at both of the OFM–hexadecane interfaces, not at the hematite–OFM interfaces (see also Figures 3–6).38,39

Figure 2b shows the definition of the slip length (purple double-headed arrows) and slip velocity (orange double-headed arrows) in OFM-lubricated systems.4,11

Figure 3. Effect of OFM surface coverage on the mass density profiles for the OFMs (green) and hexadecane (orange) and the measured velocity profile for hexadecane (blue). Representative example shown for SA, $\Gamma = 1.44$ (a), 2.88 (b), and 4.32 nm$^{-2}$ (c); $P = 0.1 \text{ GPa}$; $v_s = 100 \text{ m s}^{-1}$. The solid red line shows a linear velocity profile when a no-slip boundary condition at the OFM–hexadecane interface is assumed. The purple double-headed arrow between red and blue vertical dotted lines shows the calculated slip length, which is only detectable in (c).

Figures 3–6 show mass density profiles in the z-direction for the hexadecane (orange) and OFM (green) molecules. The measured hexadecane x-velocity profile in the z-direction (blue) and the assumed no-slip velocity profile (red) for a fully sheared hexadecane layer are also shown. Note that these figures are rotated 90° relative to the schematics in Figure 2. The sharp, intense OFM mass density peaks on the far left- and right-hand sides of Figures 3–6 indicate the adsorption of the headgroups on the slabs, while the less intense peaks which extend further from the surface are due to the tailgroups.33 Slip occurs when...
there is a net nonzero velocity difference between the hexadecane layer and the OFM layers at their interface.3 The interface where slip occurs (red vertical dotted lines) can be clearly identified by the intersection of the hexadecane and OFM mass density profiles. The center of the mass density and velocity profiles has been shifted to zero for clarity. This does not affect the measured slip length because it is an average between the top and bottom slabs.

Figure 3 shows the effect of OFM surface coverage on the OFM and hexadecane mass density profiles as well as the hexadecane velocity profile. Comparing Figure 3a–c, the OFM films become substantially thicker and more strongly layered with increasing coverage. Both sum frequency generation spectroscopy64 and radial distribution functions from NEMD simulations33 have also shown that the OFMs form solid-like films at high coverage. There is much less overlap of the OFM and hexadecane mass density profiles at high coverage (Figure 3c) than at medium (Figure 3b) and low coverage (Figure 3a), indicating reduced interdigitation.33 Consequently, under all of the conditions studied, the velocity profiles only show a measurable slip length at high coverage (4.32 nm$^{-2}$). In Figure 3a,b, the assumed no-slip velocity profile (red) overlaps with the measured velocity profile (blue). Conversely, in Figure 3c, there is clear separation between the measured profile and the no-slip profile, allowing the slip length (0.9 nm) to be calculated. This observation agrees with experimental results which have shown much larger slip lengths for high coverage OFM films compared to low coverage films,25 as well as those which have shown a transition from no-slip to partial slip after high coverage films were allowed to form on the surface.4,7

Figure 4 shows the effect of sliding velocity (or shear rate) on the mass density and velocity profiles. As with previous NEMD simulations,32,33 the mass density profiles are insensitive to sliding velocity in the range tested. The velocity profiles show an increase in the slip length with increasing sliding velocity; from 0.3 nm at 10 m s$^{-1}$ (Figure 4a) to 0.6 nm at 20 m s$^{-1}$ (Figure 4b), to 0.8 nm at 50 m s$^{-1}$ (Figure 4c), and to 0.9 nm at 100 m s$^{-1}$ (Figure 3c). This observation is consistent with several previous experiments57 and NEMD simulations which also showed a general increase in the slip length with increasing sliding velocity.17−21

Figure 5 shows the effect of the OFM type on the mass density and velocity profiles at low pressure (0.1 GPa). The OFM mass density profiles for SA (Figure 5a) and SAm (Figure 5b) are very similar but the GMS profile (Figure 5c) shows that its films are
slightly thicker owing to the larger headgroup size. There is much less overlap of the hexadecane and OFM mass density profiles for SAM (Figure 5b) and GMS (Figure 5c) compared to SA (Figure 5a), indicating reduced interdigitation. At 0.1 GPa and 100 m s⁻¹, this leads to larger slip lengths for high coverage SAM (1.1 nm) and GMS (1.3 nm) films compared to SA (0.9 nm).

Figure 6 shows the effect of the OFM type on the mass density and velocity profiles at high pressure (1.0 GPa). Similar to at low pressure, SAM (Figure 6b) and GMS (Figure 6c) films are less interdigitated than SA (Figure 6a) films, leading to larger slip lengths. Comparing Figures 5 and 6 shows the effect of pressure on the structure and flow behavior. For all of the OFMs, the mass density profiles show that there is a reduction in film thickness ≈10% moving from low pressure (Figure 5) to high pressure (Figure 6). The mass density profiles also indicate stronger layering both in the OFM and particularly the hexadecane films at high pressure relative to low pressure. The increased “first layer density” observed here for the hexadecane layer at higher pressure has been correlated with larger slip lengths in previous NEMD simulations. Comparing Figures 5a and 6a suggests that for SA, interdigitation between the hexadecane and OFM layers is reduced at higher pressure, owing to the denser OFM films. For all of the OFMs at 100 m s⁻¹, the slip length increases significantly, moving from low to high pressure: 0.9 nm (Figure 5a) to 2.6 nm (Figure 6a) for SA, 1.1 nm (Figure 5b) to 4.3 nm (Figure 6b) for SAM, and 1.3 nm (Figure 5c) to 4.8 nm (Figure 6c) for GMS. The increase in the slip length with the increasing pressure is consistent with previous NEMD simulations and macroscopic tribology experiments which showed the same trend.65

Shear Rate and Pressure Dependence of Slip and Friction. Figure 7a shows the change in the slip length with log(shear rate) for high coverage (Γ = 4.32 nm⁻²) SA, SAM, and GMS films at low (0.1 GPa) and high (1.0 GPa) pressure. Note that here, the applied shear rate is calculated using the no-slip velocity profile and the hexadecane layer thickness rather than the overall film thickness (see Figure 2b). No slip occurs below a critical shear rate, above which the slip length increases linearly with log(shear rate) and then asymptotes toward a constant value. The critical shear rate decreases from ≈10⁹ s⁻¹ at low pressure to ≈10⁸ s⁻¹ at high pressure. The critical shear rates from these simulations are relatively high with respect to those observed in previous experiments for similar systems as well as the shear rates experienced in real components.66 The slip length asymptotes to approximately 1 nm at low pressure and between 2 and 5 nm at high pressure, depending on the OFM type. SAM
and GMS give consistently larger slip lengths than SA, particularly at high pressure, because of reduced OFM–hexadecane interdigitation (see Figure 5). The magnitudes of these slip lengths are lower than those measured for alkanes on adsorbed surfactant monolayers in AFM and SFA experiments (10–30 nm), performed under milder pressure and shear rate conditions. NEMD simulations of water slip on alkyl monolayers also underpredicted the slip length by a similar degree compared to the experiment. The exact reason for this discrepancy remains unclear, but it could be because the current simulations use atomically smooth surfaces and are representative of the slip mechanism proposed by Tolstoi and reviewed by Blake. Alternative slip mechanisms, such as the formation of multilayer OFM films or nanobubbles, could be the route of the larger slip lengths and lower critical shear rates observed in some SFA and TIR-FRAP experiments of similar systems. The asymptotic behavior of the slip length at high shear rates is consistent with results from previous NEMD simulations and AFM experiments which have studied alkane slip. Such a behavior can be rationalized through a transition from "defect slip" to "global slip" and captured using both the vdFK and extended MKT slip models. An increase in the slip length with increasing pressure has also been noted in both previous NEMD simulations and tribology experiments. This observation suggests that as the pressure is increased, the viscous friction between individual hexadecane molecules increases more than friction at the OFM–hexadecane interface. Both AFM and SFA experiments have shown that longer chain alkanes with a larger viscosity give larger slip lengths on surfactant monolayers. In future NEMD studies, it would be interesting to investigate the slip of larger alkanes with viscosities closer to real lubricants on surfactant monolayers.

The friction behavior of the OFM films and its relation to slip was also investigated. The kinetic friction coefficient, $\mu$, was obtained using the extended Amontons–Coulomb law under the high load approximation: $F_L/F_R = F_0/F_R + \mu \approx \mu$. Here, $F_L$ and $F_R$ are defined as the block-averaged lateral force (shear stress) and the normal force acting on each hematite slab in response to the fluid during sliding, respectively, and $F_0$ is the load-independent Derjaguin offset, representing adhesive surface forces. Previous NEMD simulations of the friction between OFM films separated by a lubricant layer have confirmed the validity of this approximation. In agreement with experimental results, the friction coefficient is greater at low (1.44 nm$^{-2}$) and medium (2.88 nm$^{-2}$) coverage, where no slip was observed (Figure 3a,b), compared at high coverage (4.32 nm$^{-2}$), where a slip length could be measured (Figure 3c). The differences in friction between the high coverage case and the low and medium coverage cases are broadly similar to those observed in previous NEMD simulations of OFM films.

Figure 7b shows the change in the friction coefficient with $\log$ (shear rate) for high coverage (1.44 nm$^{-2}$) SA, SAm, and GMS films at low (0.1 GPa) and high (1.0 GPa) pressure. The friction coefficient generally increases linearly with $\log$(shear rate), which is consistent with the stress-augmented thermal activation theory and macroscopic tribology experiments. The friction coefficient shows a much stronger shear rate dependence at low pressure than at high pressure. At low shear rates (<10$^5$ s$^{-1}$), the friction coefficient is larger at high pressure than at low pressure, whereas at higher shear rates, the reverse is true. The slip length is always greater at high pressure, suggesting that friction may be more effectively reduced in the global slip regime, which only occurs at higher shear rates. A decrease in both the magnitude of the friction coefficient and the slope of its increase with sliding velocity at higher pressure has also been observed in tribology experiments of SA dissolved in hexadecane under hydrodynamic lubrication conditions. NEMD simulations of pure lubricant molecules under EHL conditions, where slip occurs within the film itself rather than at the solid–fluid interface, also showed a similar friction behavior. The slip length (Figure 7a) and the friction coefficient (Figure 7b) both generally increase with the increasing shear rate; however, at a given shear rate, systems with a larger slip length generally give a lower friction coefficient. This supports the postulate that OFM films can promote slip and thus reduce friction in the hydrodynamic regime. At high pressure, the friction coefficient drops slightly upon the transition from defect slip to global slip. These results also suggest that friction reduction by OFMs in the hydrodynamic regime will be greatest when the slip length is maximized through a combination of the high pressure and high shear rate, as are typical in the EHL regime.

For all of the conditions studied, SA gives a significantly higher friction coefficient than SAm and GMS. This observation is in
agreement with previous NEMD simulations and friction experiments under boundary lubrication conditions. This behavior can be most clearly explained by comparing the mass density profile in Figure 5a with those in Figure 5b,c; this shows that compared to SA films, SAm and GMS films are more solid-like and less interdigitated with the hexadecane layer. The reduced interdigitation leads to significantly larger slip lengths for SAm and GMS compared to SA (Figure 7a) and ultimately lower friction (Figure 7b). This finding is expected to be useful in designing new OFMs to control friction and flow in a range of applications.

Interdependence of Slip and Friction. It is difficult to establish quantitative relationships between slip and friction from these NEMD simulations because shear thinning of the hexadecane film will also reduce friction, particularly under the higher pressures and shear rates studied. However, it was possible to study the change in the slip length and slip velocity with shear stress and compare the trends with previously proposed models for slip. Figure 8a shows the relationship between the shear stress and the slip length for high coverage (4.32 nm$^2$) OFM films at low pressure (0.1 GPa). Slip occurs only above a critical shear stress, after which the slip length increases linearly with shear stress and then asymptotes, which is in agreement with the slip model proposed by Spikes and Granick. The critical shear stress increases with increasing hexadecane–OFM interdigitation from GMS, to SAm, to SA (Figure 5) and is <0.01 GPa for all of the OFMs at low pressure.

The slip length values gathered from Figures 3–6 can also be used to calculate slip velocities (orange arrows in Figure 2). Figure 8b shows the effect of shear stress on the slip velocity for high coverage (4.32 nm$^2$) OFM films at low pressure (0.1 GPa). The slip velocity–shear stress behavior is well-described using Eyring’s MKT, extended to include the critical shear stress and energy dissipation at the interface by Wang and Zhao. In this model (Eq 1), the slip velocity is given by

$$v_s = v_0 \sinh \left( \frac{\tau}{\tau_0} \right)$$

where $\tau$ is the shear stress, $\tau_0$ is a characteristic shear stress, $f_d$ is a dissipation factor, and $v_0$ is a characteristic velocity. In this study, the product of $f_d$ and $v_0$ was used in the fitting for simplicity. To fit the dotted lines in Figure 8b, both $\tau_0$ and $f_d$ increase with increasing interdigitation, from GMS to SAm and to SA (Table 1). This suggests that the potential energy barriers for slip to occur are larger when there is more interdigitation, which is similar to the effect of stronger solid–fluid interactions seen in previous NEMD studies. Intuitively, the critical shear stress values obtained for these partial-slip systems (3.0–7.2 MPa) are much larger than observed in NEMD simulations of high-slip (water inside carbon nanotubes) systems (0.003–0.2 MPa).

An important remaining question following these NEMD simulations is the resilience of slip with respect to surface roughness. The presence of nanoscale roughness has been shown to significantly reduce the slip length of alkanes confined by solid surfaces in NEMD simulations and experiments. However, recent NEMD simulations showed that high coverage of OFM films can give smooth, low friction interfaces even on surfaces with realistic nanoscale roughness. Thus, it is expected that unlike for NEMD simulations of alkanes confined between bare surfaces with nanoscale roughness, such surfaces coated with high coverage OFM films should still show slip. Although this is beyond the scope of this current study, it is certainly an interesting area to explore and it will be pursued in future NEMD investigations.

**Table 1. Extended MKT (Eq 1) Fitting Parameters Used in Figure 8b and Asymptotic Values of the Slip Length and Estimate of the Critical Shear Stress from Figure 8a for All OFMs ($P = 0.1$ GPa)**

|          | SA      | SAm    | GMS    |
|----------|---------|--------|--------|
| $\tau_0$ (GPa) | 0.0065  | 0.0050 | 0.0045 |
| $v_0$ (m s$^{-1}$) | 0.33    | 0.18   | 0.17   |
| $L_s$ (nm)     | 0.8     | 1.1    | 1.3    |
| $\tau_c$ (GPa) | 0.0072  | 0.0051 | 0.0030 |

**SUMMARY AND CONCLUSIONS**

In this study, the slip and friction behavior of $n$-hexadecane, confined between OFM surfactant films adsorbed on hematite surfaces, has been studied using NEMD simulations. The influence of the OFM type (SA, SAm, and GMS) and coverage (1.44–4.32 nm$^2$) on the OFM type (SA, SAm, and GMS) and coverage (1.44–4.32 nm$^2$), as well as the applied shear rate (10$^8$ to 10$^{10}$ s$^{-1}$) and pressure (0.1–1.0 GPa), have been investigated. The slip length is found to be highly sensitive to the OFM type and coverage as well as the applied shear rate and pressure. A measurable slip length is only observed for OFM films with a high surface coverage, which give a smooth interface between well-defined OFM and hexadecane layers. At low and medium coverage, the hexadecane and OFM layers are significantly interdigitated, which prevents slip, resulting in higher friction. At high coverage, slip only occurs above a critical shear rate, which depends on the applied pressure as well as the OFM type. Above the critical shear rate, the slip length increases with increasing shear rate and subsequently asymptotes toward a constant value. The maximum slip length increases significantly with increasing pressure from ≈1 nm at 0.1 GPa to 2–5 nm at 1.0 GPa. As has been noted for other systems, there seems to be a lower propensity for slip in these NEMD simulations, which show relatively high critical shear rates and low slip lengths, compared to previous experiments. This suggests that different slip mechanisms could be acting in these experiments.

For a given nonequilibrium state point, systems which show a larger slip length typically give a lower friction coefficient. Generally, the friction coefficient increases linearly with the logarithmic shear rate, in accordance with the stress-augmented thermal activation theory. However, the friction coefficient shows a much stronger shear rate dependence at low pressure (0.1 GPa), where only modest slip lengths are measured, than at high pressure (1.0 GPa), where the slip lengths are much larger. At low shear rates, the friction coefficient is higher at high pressure than at low pressure, while at high shear rates, the reverse is true. GMS and SAm films are less interdigitated than SA films, leading to significantly larger slip lengths and lower friction coefficients. This finding is expected to be useful in designing new surfactants to control hydrodynamic friction and flow in a range of applications.

The friction and slip behavior are interrelated and, in agreement with the slip model due to Spikes and Granick, slip occurs only above a critical shear stress, after which the slip length increases linearly with shear stress and then asymptotes toward a constant value. At low pressure, the slip velocity–shear stress behavior is well-described using the sinh relationship in Eyring’s
MKT model for slip, extended to include a critical shear stress and energy dissipation at the interface by Wang and Zhao. This study has provided a more detailed understanding of how alkane slip occurs on surfactant monolayers adsorbed on solid surfaces. Indeed, to our knowledge, it is the first to successfully measure the slip length in such systems using NEMD. These simulations have also provided compelling evidence that OFMs can significantly reduce friction even when the surfaces are well-separated, as in the hydrodynamic lubrication regime. The simulations also suggest that friction reduction by OFMs will be greatest when the slip length is maximized through a combination of high pressure and high shear rate, as is typical in the EHL regime. Future NEMD studies will probe the sensitivity of hydrodynamic friction and slip to lubricant viscosity and surface roughness.

**AUTHOR INFORMATION**

**Corresponding Author**
E-mail: j.ewen@imperial.ac.uk.

**ORCID**

James P. Ewen: 0000-0001-5110-6970
B. D. Todd: 0000-0003-4683-5719
D. Dini: 0000-0002-5518-499X

**Author Contributions**

J.P.E. and S.K.K. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

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