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Coarse-Grained Molecular Dynamics Simulations of Organic Friction Modifier Adsorption on Rough Surfaces under Shear

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Abstract: Reducing friction energy losses is crucial in mechanical systems, often achieved through lubrication strategies employing friction modifiers. These additives adsorb onto surfaces, forming boundary film to prevent solid–solid contacts. However, atomistic simulation techniques used to study these additives often ignore surface roughness due to high computational cost. This study addresses this gap by employing Coarse-Grained Molecular Dynamics (CG MD) to investigate the impact of surface roughness on the adsorption of Organic Friction Modifiers (OFMs) under shear. Traditional self-diffusion methods prove inadequate for determining the damping coefficients in CG models because of strong OFM adsorption effects. Therefore, shear-induced motion is introduced for the coefficient determination. The simulation reveals that a symmetrical model (identical opposing surfaces) shows OFM slip, desorption, and re-adsorption trends on rough surfaces, while an asymmetrical model (smooth cylinder on a flat surface) demonstrates increased adsorption on rough flat surfaces (up to 60.9%) compared to smooth flat surfaces under similar shearing conditions. However, rough flat surfaces with a smaller wavelength (6 nm) exhibit faster OFM desorption along the asperity region, up to four times more than a 24 nm wavelength surface. This research emphasizes the importance of considering surface roughness in simulating OFM behavior for lubrication applications.

Keywords: coarse-grained; molecular dynamics; surface roughness; friction modifiers



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1. Introduction

Enhancing lubricity for mating surfaces is imperative in mechanical systems to minimize their energy losses due to friction. This is often achieved by incorporating small quantities of friction modifier additives into low-viscosity base oils [1–5]. In contrast to commonly used friction modifiers that contain sulfur and phosphorus, such as Molybdenum Dithiocarbamate (MoDTC) and Molybdenum Dithiophosphate (MoDTP), Organic Friction Modifiers (OFMs) are composed solely of carbon, hydrogen, oxygen, and nitrogen, thereby garnering significant attention and usage in pursuing greener lubrication [2,6,7]. However, OFMs are generally not as effective as molybdenum compounds in reducing friction [8,9]. Therefore, it is crucial to further improve the performance of OFMs.

Typical OFM molecules comprise at least one polar head group and one alkyl chain tail. Previous studies have suggested that OFMs form adsorbed films on sliding surfaces, preventing direct solid–solid contacts, thereby reducing friction in the boundary and mixed lubrication regime [6,10–12]. The chemistry of OFMs and solid surfaces determines their interaction strength. Additionally, the morphology of solid surfaces, including surface roughness and textures, determines the pressure distribution in the contact region. Consequently, these factors affect the structural and mechanical properties of OFM adsorption films under shear. A thorough understanding of these correlations is essential for improving the friction reduction performance of OFMs.

Several advanced experimental technologies have been employed to investigate the surface adsorption of OFMs. Atomic Force Microscopy (AFM) has been utilized to measure the morphology and frictional properties of adsorbed films [13–17]. Quartz Crystal Microbalance (QCM) has been adopted to assess not only adsorption mass but also adsorption kinetics [18–21]. Additionally, Neutron Reflectometry (NR) has been used to analyze the structure of adsorption films in more detail, including the number of layers and the thickness and density of each layer [22–24]. These experimental approaches significantly contribute to understanding the effect of OFM chemistry on surface adsorption, primarily under static conditions. Regarding the polar head groups, which govern the surface adsorption strength, studies have indicated that carboxyl and amine groups are more effective than alcohol, ester, and nitrile groups [2,6,20,25]. Additionally, increasing the number of polar groups can enhance adsorption strength through multi-site adsorption or chelate effect [20,26–29]. Studies have also shown that straight tails, such as saturated or trans-unsaturated alkyl chains, form more densely packed adsorption films than kink tails, such as cis-unsaturated alkyl chains, resulting in better friction-reducing performance [15,30]. Nevertheless, measuring adsorbed OFM films on rough surfaces becomes challenging due to their typical thickness of approximately 1 to 2 nm [14,15]. Therefore, there remains a scarcity of research on the correlation between surface roughness and the adsorption efficacy of OFMs. Furthermore, the limitations of experimental technologies become apparent in the lack of thorough analyses concerning the distribution and mechanisms of adsorption and desorption on rough surfaces, especially in the presence of shearing [31].

To address this gap, Molecular Dynamics (MD) simulations are often employed to fundamentally elucidate the adsorption of molecules like friction modifiers at the atomic level. Shi et al. [32] investigated the impact of molecular polarity and temperature on the physisorption behavior of OFMs. Ewen et al. [33] focused on the slip and friction behavior of alkanes on monolayer OFM films adsorbed on solid surfaces during shear motion. Chen et al. [34] recently analyzed the adsorption behavior of *N*-(2,2,6,6-tetramethyl-1-oxyl-4-piperidinyl)-dodecaneamide (TEMPO-based) OFM on iron oxide surfaces, revealing the mechanism behind its experimentally proven superior lubrication performance. Concerning surface roughness, Eder et al. [35] studied different molecular surface coverages and rough substrates, focusing on the Derjaguin offset. Ewen et al. [36] demonstrated that OFMs can strongly adsorb onto surfaces with random nanoscale roughness (0.2–0.8 nm RMS) to prevent direct contact with solids under high-pressure conditions. Their study highlighted the correlation between nanoscale roughness and stearic acid coverage, indicating lower friction forces in systems with higher coverage.

While the above studies contributed valuable insights, it is crucial to note that the most widely used atomistic simulation techniques have size limitations, where the surface roughness dimensions were either minimized or the system was completely immersed in a lubricating solution [37–39]. One significant concern with this approach is the potential oversight of the space for liquid molecule dispersion out of confinement during shearing. This assumption may impact the number of molecules available for adsorption within the confinement.

To address the limitation and simulate larger systems that better mimic realistic contact conditions, we propose using Coarse-Grained (CG) models to simulate the adsorption behavior of OFMs on rough surfaces. CG models allow for the simulation of larger systems with significant surface roughness. However, there remains a challenge in developing CG models that can accurately reproduce the static and dynamic characteristics of target systems [40,41]. Expanding on our previous research [42], we introduce an enhanced approach to replicate the dynamic characteristics of CG models against All-atom (AA) models. This improved methodology is applied to larger-scale rough surface structures, enabling the study of the motion and distribution of OFMs during shearing processes in a more representative manner.

2. Simulation Details

2.1. Simulation Method

In this study, MD simulations were performed using CG models and Dissipative Particle Dynamics (DPD) [43–45]. The equation governing the motion of CG beads is expressed as follows:

$$M_i \ddot{\mathbf{r}}_i = \mathbf{F}_i^C + \mathbf{F}_i^D + \mathbf{F}_i^R, \quad (1)$$

Here, M_i and $\mathbf{r}_i$ represent the mass and position of CG bead i , and $\mathbf{F}_i^C$, $\mathbf{F}_i^D$, and $\mathbf{F}_i^R$ denote the conservative, damping, and random forces exerted on CG bead i , respectively. $\mathbf{F}_i^C$ is derived from the negative derivative of interactive potentials between CG beads (CG potentials), and $\mathbf{F}_i^D$ and $\mathbf{F}_i^R$ are calculated as follows:

$$\mathbf{F}_i^D = \sum_j \mathbf{f}_{ij}^D = \sum_j -\zeta^\parallel w_D^\parallel(r_{ij}) (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij} - \zeta^\perp w_D^\perp(r_{ij}) [\mathbf{v}_{ij} - (\mathbf{e}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{e}_{ij}], \quad (2)$$

$$\mathbf{F}_i^R = \sum_j \mathbf{f}_{ij}^R = \sum_j \sigma^\parallel w_R^\parallel(r_{ij}) (\mathbf{e}_{ij} \cdot \boldsymbol{\theta}_{ij}) \mathbf{e}_{ij} + \sigma^\perp w_R^\perp(r_{ij}) [\boldsymbol{\theta}_{ij} - (\mathbf{e}_{ij} \cdot \boldsymbol{\theta}_{ij}) \mathbf{e}_{ij}], \quad (3)$$

Here, $\mathbf{e}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$ denotes the unit vector from bead j to i , $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ represent the relative velocity of bead i to j , and $\boldsymbol{\theta}_{ij}$ is a time-varying three-dimensional vector with normally distributed random numbers as its elements. The superscripts $\parallel$ and $\perp$ indicate directions parallel and perpendicular to $\mathbf{e}_{ij}$, respectively. The parameters ζ (referred to as damping coefficient) and σ and weight functions w_D and w_R serve to adjust the strength of damping and random forces. To achieve the canonical ensemble, the following relationships must hold for both the parallel and perpendicular components:

$$\sigma^2 = 2k_B T \zeta, \quad (4)$$

$$[w_R(r_{ij})]^2 = w_D(r_{ij}) = \left[\max(0, 1 - r_{ij}/r_c^{\text{DPD}}) \right]^2, \quad (5)$$

where k_B is the Boltzmann constant, T is the temperature, and r_c^{DPD} is the cutoff distance for the damping and random forces. For simplicity, we used $\zeta^\parallel = \zeta^\perp$ and $w_D^\parallel(r_{ij}) = w_D^\perp(r_{ij})$ in this study.

The CG potentials and damping coefficient must be determined a priori. The former affects the static and dynamic properties of simulation systems, whereas the latter solely affects the dynamic properties of simulation systems. Therefore, this study initially derived the CG potentials by matching static properties obtained from AA simulations and then determined the damping coefficient by aligning with dynamic properties from AA simulations.

All AA and CG MD simulations were conducted using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [46], specifically with an in-house extended DPD package for the CG simulations [45]. The simulation results were visualized using the Open Visualization Tool (OVITO) [47].

2.2. Materials and Coarse-Grained Models

Dodecane ($\text{C}_{12}\text{H}_{26}$), stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$), and hematite plates with (100) surface orientation were used as base oil, OFM additive, and solid surfaces, respectively. As illustrated in Figure 1, dodecane and stearic acid molecules were coarse-grained by mapping three consecutive carbon atoms and their bonding atoms into a single bead, with the interaction center defined as the center of mass of the constituent atoms. Thus, each dodecane and stearic acid were modeled as four and six beads, respectively, connected by springs. The bead containing the carboxyl group was polar, while the others were nonpolar. For simplicity, the constituent beads of dodecane and stearic acid are collectively referred to as “liquid beads” hereafter. The hematite plates were coarse-grained by arranging solid

beads in a simple tetragonal lattice with lattice constants $a = b = 5.714 \text{ \AA}$ and $c = 5.814 \text{ \AA}$ (see Figure 1).

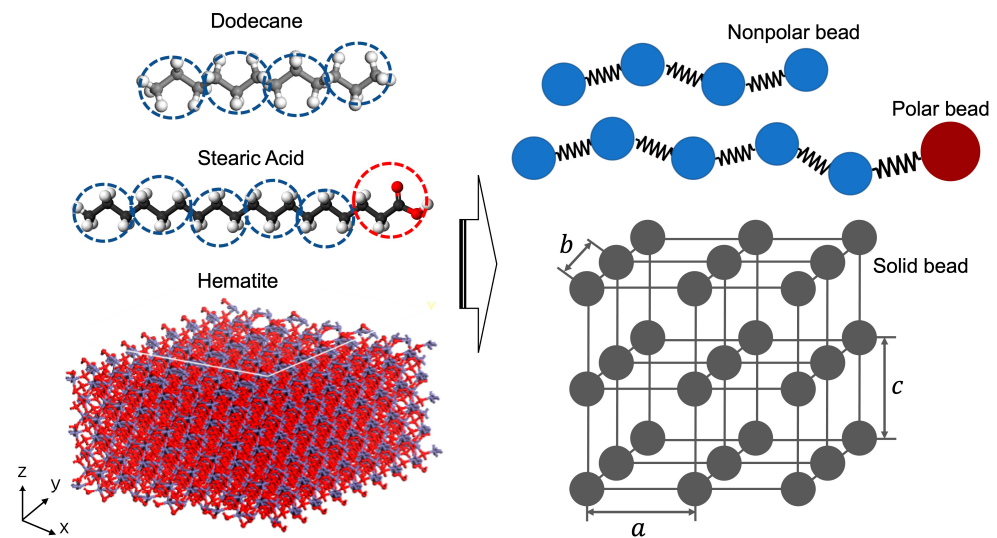


Figure 1. Schematic of coarse-grained models (right) mapped from all-atom models (left). a , b , and c are the lattice constants in the x , y , and z directions, respectively.

As depicted in Figure 2, CG potentials included bond-length potentials (U_{bl-np} and U_{bl-p}), bond-angle potentials (U_{ba-np} and U_{ba-p}), nonbonded liquid–liquid interaction potentials (U_{ll-np} and U_{ll-p}), and nonbonded liquid–solid interaction potentials (U_{ls-np} and U_{ls-p}). The subscripts “np” and “p” indicate involvement without and with polar beads, respectively, with U_{ll-np} being the only exception, which was also applied to polar and nonpolar liquid bead pairs. Notably, U_{ll-p} and U_{ll-np} were applied to liquid–bead pairs not involved in the bond–length and bond–angle interactions. These potentials were derived through the iterative Boltzmann inversion method, aligning with reference distribution functions characterizing static structural properties obtained from AA simulations, the same as in our previous studies [42,48]. Specifically, our previous work [42] extensively covered the derivation and validation of U_{ll-np} , U_{bl-np} , and U_{ba-np} for dodecane, demonstrating their high accuracy and transferability across a wide pressure range of up to 1 GPa. The remaining CG potentials, U_{bl-p} , U_{ba-p} , U_{ll-p} , U_{ls-p} , and U_{ls-np} , alongside their validation, are detailed in Appendix A.

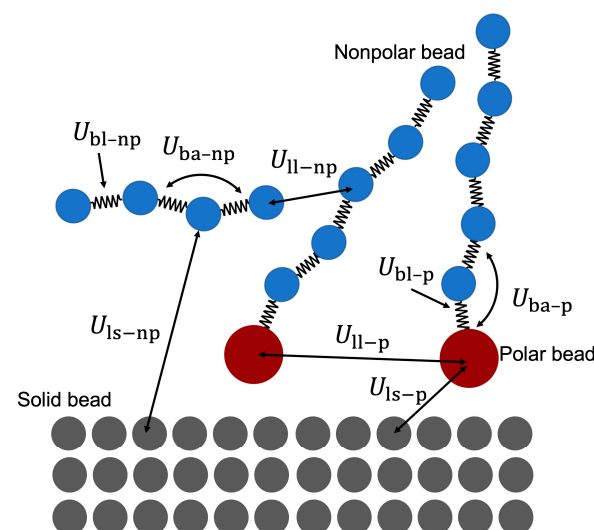


Figure 2. Schematic of all potentials between CG beads.

2.3. Determination of Damping Coefficients

The damping coefficients included ζ_{ll-p} , ζ_{ll-np} , ζ_{ls-p} , and ζ_{ls-np} for bead pairs of polar liquid, nonpolar liquid, polar liquid–solid, and nonpolar liquid–solid. Note that ζ_{ll-np} was also used for bead pairs of polar and nonpolar liquids. Conventionally, damping coefficients are adjusted by matching the self-diffusion coefficient of thermal motion obtained from AA simulations. However, due to the strong interactions of the polar end groups, stearic acid molecules form dimers in the bulk and adsorb on solid surfaces [49,50]. Therefore, thermally induced motion rarely occurs between the polar end groups and between them and solid surfaces, making it challenging to adjust ζ_{ll-p} and ζ_{ls-p} by the conventional method, as evident from Equation (2). In this study, we addressed this challenge by employing shear-induced motion rather than thermal motion [51].

In brief, ζ_{ll-np} was initially determined by matching the shear viscosities from non-equilibrium AA and CG MD simulations of bulk dodecane systems under shear. Subsequently, ζ_{ll-p} was determined similarly using bulk stearic acid systems and the previously determined ζ_{ll-np} . For adjustment of ζ_{ls-np} and ζ_{ls-p} , we matched the Coefficients of Friction (CoF) from non-equilibrium AA and CG MD simulations, using a single layer of dodecane and stearic acid, respectively, lying flat between two hematite (100) surfaces, and applying a normal pressure and moving the upper solid surface horizontally. Appendix B provides details of the simulation setups and calculation of viscosities and CoF.

Figures 3 and 4 show the variation of bulk shear viscosities and CoF with the liquid–liquid and liquid–solid damping coefficients in the CG simulations, respectively. The values obtained from the parent AA simulations are also plotted in the figures with horizontal lines for comparison. These shear-related properties increase monotonically with the damping coefficients, showcasing their effectiveness in fine-tuning the damping coefficients. Table 1 summarizes the final values of ζ_{ll-np} , ζ_{ll-p} , ζ_{ls-np} , and ζ_{ls-p} , along with the corresponding shear-related properties from the CG and AA simulations. The good agreement validates the high accuracy of our CG models, even for reproducing dynamic properties.

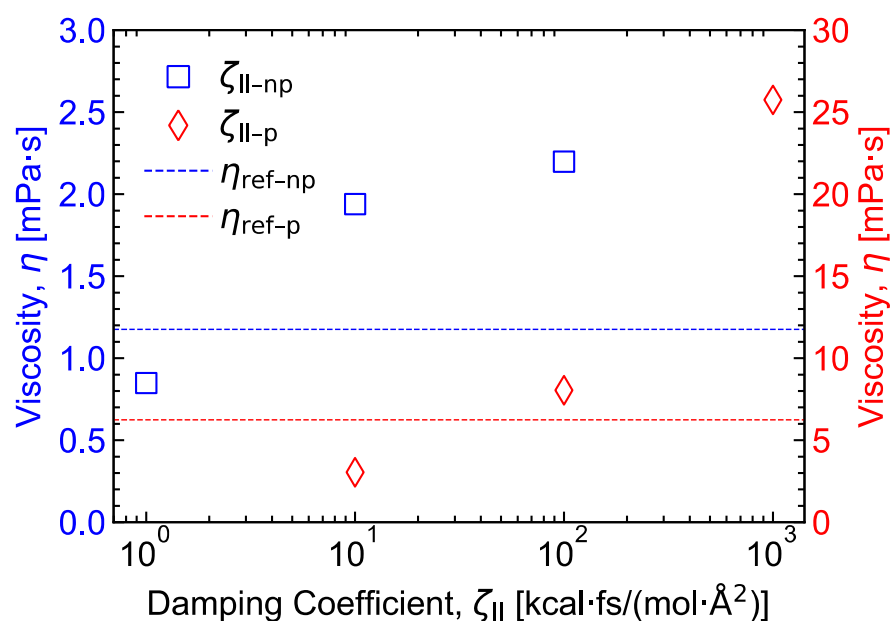


Figure 3. Variation of viscosity with the damping coefficients between liquid beads. Markers and horizontal lines indicate the results from CG and AA simulations, respectively.

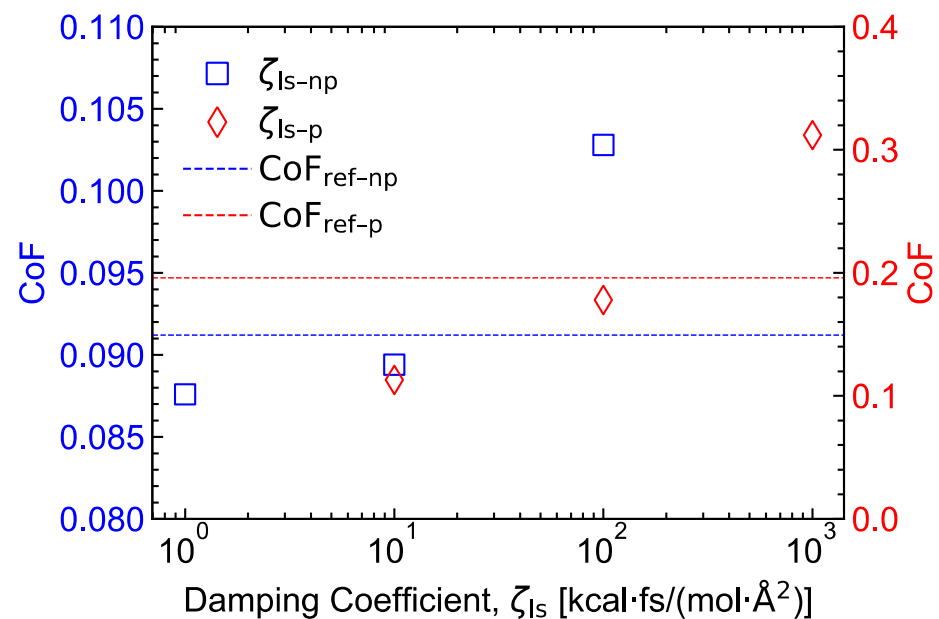


Figure 4. Variation of CoF with the damping coefficients between liquid and solid beads. Markers and horizontal lines indicate the results from CG and AA simulations, respectively.

Table 1. Determined values of damping coefficients and comparison of viscosity and CoF between coarse-grained and all-atom simulations.

ζ [(kcal·fs/(mol·Å ²))]	Coarse-Grained	All-Atom
Viscosity, η [mPa·s]		
$\zeta_{ll-np} = 4.1$	1.34	1.18
$\zeta_{ll-p} = 36$	5.98	6.24
CoF		
$\zeta_{ls-np} = 18$	0.0906	0.0912
$\zeta_{ls-p} = 132$	0.211	0.196

2.4. Models and Conditions of CG Shear Simulations

This study used two types of models, symmetric and asymmetric, for the CG shear simulations, as shown in Figures 5 and 6. The symmetric model had identical smooth or rough solid surfaces on the top and bottom, while the asymmetric model had a smooth cylindrical solid surface at the top and a smooth or rough flat surface at the bottom. In the symmetric model, the entire region between the solid surfaces was pressurized, whereas, in the asymmetric model, the pressure was only present in the region below the flat apex (24 nm in length) of the upper cylindrical surface, allowing liquid films to disperse from the pressurized region to surrounding spaces.

Both models had dimensions of 48 and 4 nm in the x and y directions, respectively, with periodic boundary conditions applied. A one-dimensional sinusoidal function $z = A \sin(2\pi x/\lambda)$ was used to describe the roughness of the upper and lower solid surfaces in the symmetric model and the lower solid surface in the asymmetric model. To capture the essence of surface roughness effect at reasonable computational costs, the amplitude A was fixed at 1.7 nm, and the wavelength λ was varied to 24, 48 nm, and infinity in the symmetric model, and 6, 12, 24, 48 nm, and infinity in the asymmetric model. It is to note that $\lambda = \infty$ means smooth surfaces. The radius of curvature of the cylindrical upper surface was 40 nm.

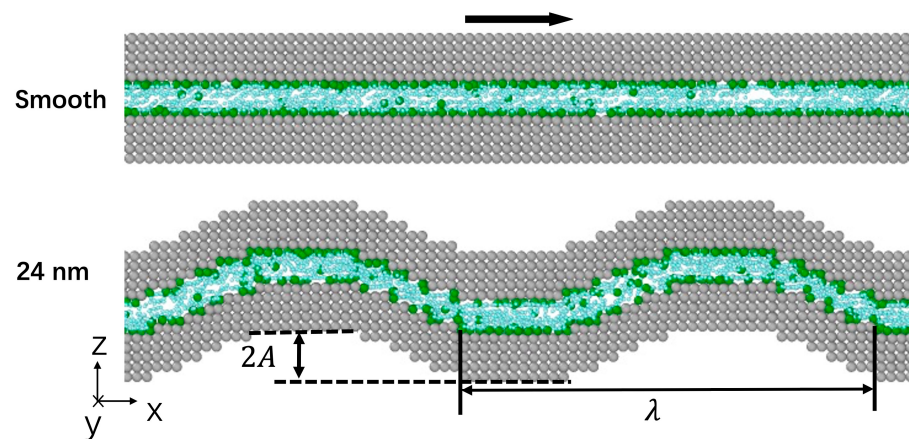


Figure 5. Front view of symmetric models. The gray, light blue, and green represent the solid, nonpolar liquid, and polar liquid beads, respectively. The top arrow indicates the shear direction of the upper solid.

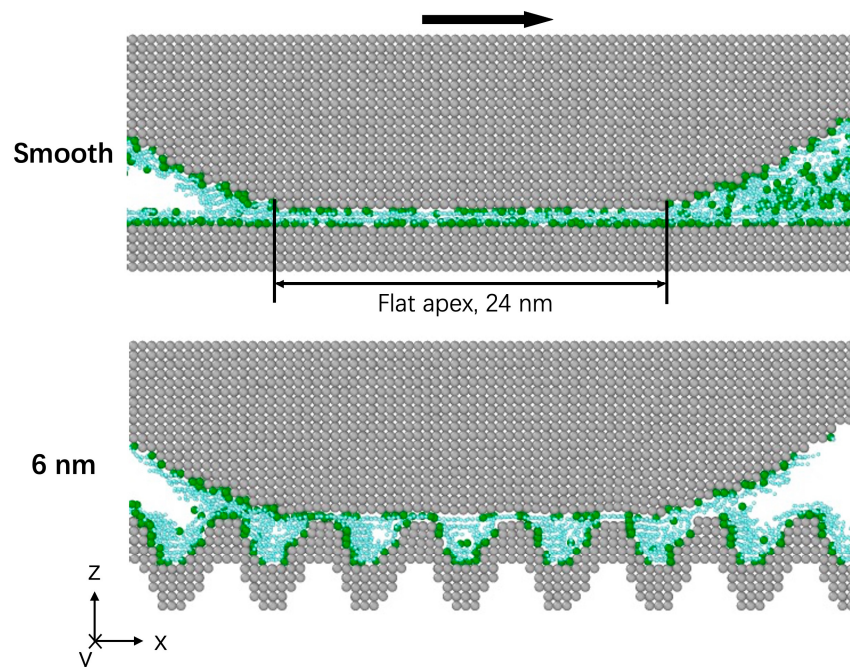


Figure 6. Front view of asymmetric models. The gray, light blue, and green represent the solid, nonpolar liquid, and polar liquid beads, respectively. The top arrow indicates the shear direction of the upper solid.

A monolayer physically adsorbed film was formed by placing the polar liquid beads of 168 stearic acid molecules on each solid surface, with the molecular chains perpendicular to the surface. This corresponded to an areal density of 0.875 molecules per nm^2 . Then, a mixed solution of 300 dodecane and 300 stearic acid molecules was inserted into the central region between the two solid surfaces. The liquid films were then compressed by applying a constant pressure of 0.5 GPa on the upper solid surface for 0.5 ns. The shear simulation was performed by moving the upper solid surface at 10.0 m/s in the x direction while keeping the lower solid surface stationary. The system temperature was maintained at 353.15 K, and the simulation timestep was set to 5.0 fs. Movie S1 in the Supplementary Materials demonstrates the shear motion in the asymmetric model with a wavelength of 6 nm.

3. Results and Discussion

3.1. Symmetric Models

3.1.1. Adsorption Behavior

In the symmetrical model, Figure 7a depicts the time-dependent changes in OFM adsorption during the shearing of identical opposing surfaces. The adsorption criterion is that the distance between the OFM polar beads and their nearest solid beads is less than 0.7 nm, corresponding to the equilibrium distance of interaction between the polar liquid bead and the solid bead (U_{ls-p}). The adsorption fraction is calculated using $n(t)/N$, where $n(t)$ represents the number of adsorbed OFMs at time t , and $N = 636$ is the total number of OFMs. It is noted that the number of adsorbed OFM molecules presented is only along the bottom surface. Figure 7a reveals that the adsorption of OFM reaches a steady state after 20 ns; however, contrasting the stable saturation on the smooth surfaces, fluctuations in OFM adsorption are observed on the rough surfaces. The mean adsorption fraction is calculated from the final 30 ns of the simulations, as shown in Figure 7b. The adsorption fraction decreases slightly with increasing roughness wavelength, by 3.2% (24 nm) and 6.2% (48 nm) compared with the smooth surfaces. The error bars indicate that the variations in adsorption fraction on the rough surfaces are approximately twice as large as those on the smooth surfaces, emphasizing higher fluctuations on rough surfaces. These findings suggest that, in comparison to the stable adsorption of OFMs on smooth surfaces, as also confirmed in previous simulation studies [7,32], the adsorption of OFMs on rough surfaces is less stable.

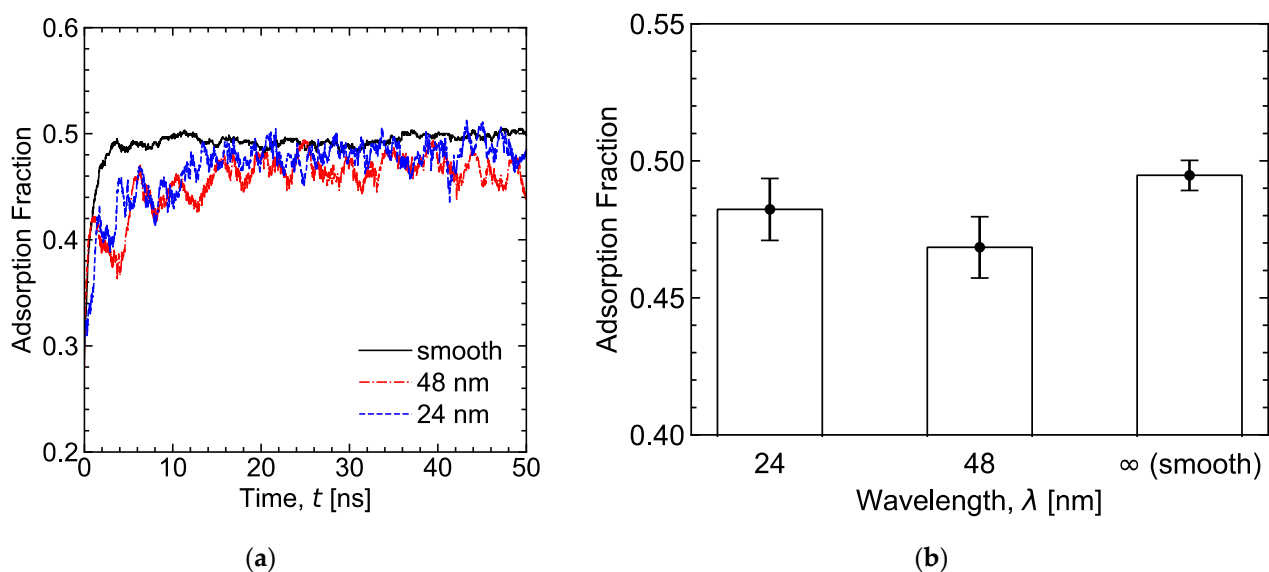


Figure 7. (a) Adsorption trend throughout the simulation duration in the symmetric model. (b) Mean and standard deviation (indicated by error bars) of adsorption fraction during the last 30 ns of the simulations for surfaces with different wavelengths.

3.1.2. Interpretation of Fluctuating OFM Adsorption Behavior

Figure 8a examines the fluctuating adsorption behavior of the OFM molecules on the rough surfaces in the symmetric model. Although the fluctuation period for the surfaces with a 48 nm wavelength is half that for the surfaces with a 24 nm wavelength, the reasons for the fluctuations are the same, as explained below. Therefore, the subsequent discussion will focus on the 24 nm wavelength. As observed at 18.8, 19.4, and 19.9 ns, there are three significant states of the fluctuations: local maximum adsorbed OFM molecules, transitioning state, and local minimum adsorbed OFM molecules. Snapshots of these states are provided in Figure 8b–d.

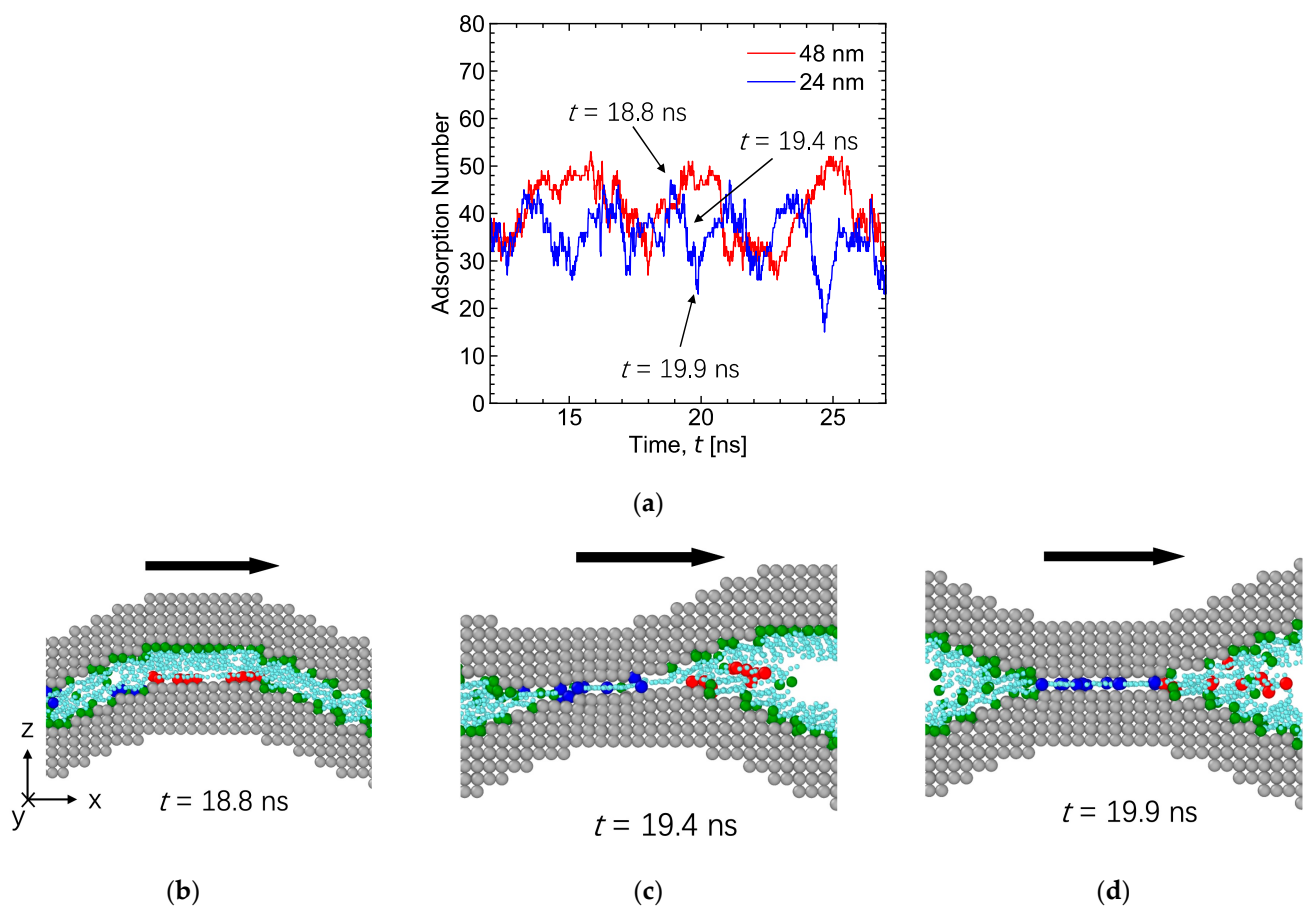


Figure 8. (a) Fluctuations in OFM adsorption on rough surfaces in the symmetric model. (b–d) Snapshots showing three characteristic states for adsorption of OFM molecules on the surfaces with 24 nm wavelength. Dodecane molecules are omitted for clarity. The gray, light blue, and green represent the solid, nonpolar liquid, and polar liquid beads, respectively. The red and blue indicate polar liquid beads that initially adsorbed and re-adsorbed onto the convex region of the lower surface, respectively. The arrows at the top of the snapshots indicate the shear direction of the upper solids.

To comprehend the movement of OFMs during shearing, attention is focused on a cluster of polar beads (depicted in red) already adhered to the convex areas of the lower corrugated rough surface in Figure 8b. Under sufficiently high pressure during shearing, this cluster of OFMs (in red) slips from the convex region as opposing peaks align, as in Figure 8c. As the shearing progresses, these OFM molecules slide away from the convex region, detaching and migrating to the concave region. Concurrently, another cluster of OFMs (depicted in blue) is sheared onto the vacant sites along the convex region. In Figure 8d, these OFM molecules (in blue) re-adsorb onto the convex region of the opposing surface. Meanwhile, the disengaged molecules (in red) are either carried away until they coincide with another convex region or re-adsorb along the transitional slope region of the surface feature. This slip, desorption, and re-adsorption cycle persists throughout the simulation, contributing to the fluctuating adsorption trend illustrated in Figure 7a. The cyclic behavior is attributed to the identical opposing rough surfaces (i.e., roughness amplitude and wavelength), potentially resulting in a less stable layer of adsorbed OFM.

3.2. Asymmetric Models

3.2.1. Adsorption Behavior

In the asymmetrical model, Figure 9a illustrates the variation in OFM adsorption over a 300 ns simulation as a smooth cylinder slides across a smooth, flat surface or a flat surface, with sinusoidal roughness wavelengths ranging from 6 to 48 nm. On the smooth

surface, the plot indicates an initial increase followed by a gradual decrease in adsorbed OFM, finally leveling off into a steady state. This initial rise is attributed to the wedge effect induced by the cylindrical indenter, drawing in additional molecules, including those not initially adsorbed. Some of these molecules may adhere to available sites, increasing adsorption coverage within the confinement. However, sufficiently high pressure and shear forces could also lead to the slip and subsequent removal of adsorbed OFMs within the confined space. This cyclic process continues until a steady state is reached, typically around 200 ns in the simulation.

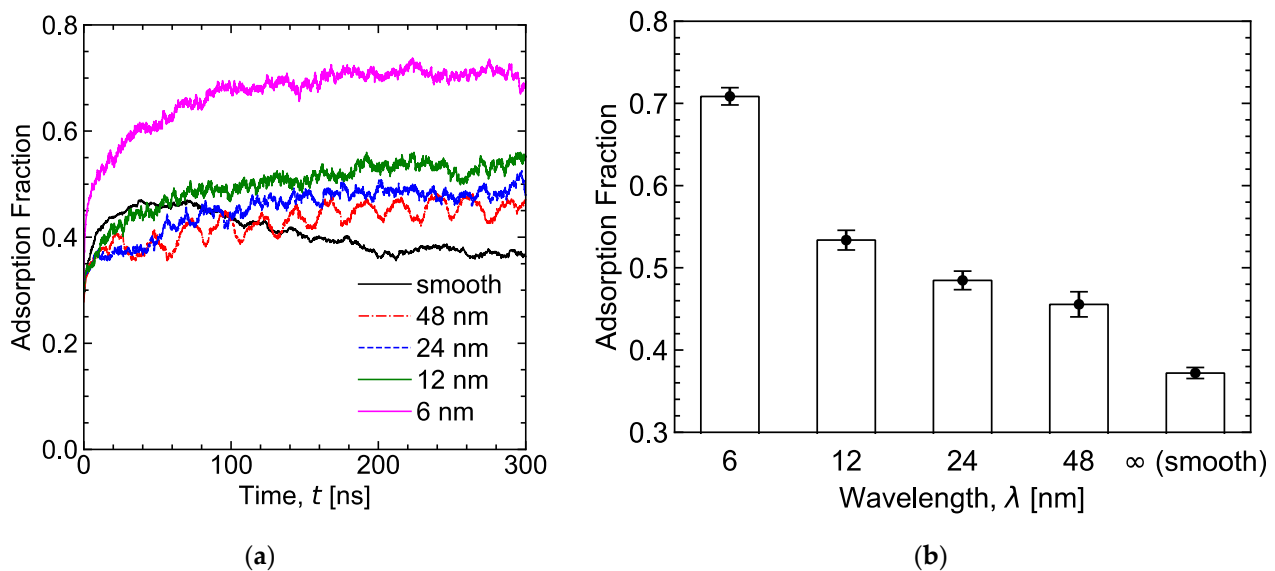


Figure 9. (a) Adsorption trend throughout the simulation duration in the asymmetric model. (b) Mean and standard deviation (indicated by error bars) of adsorption fraction during the last 100 ns of the simulations for surfaces with different wavelengths.

Similarly, simulations involving flat bottom surfaces with varying roughness reach a steady state at around 200 ns, displaying a consistent increase before saturation. The total number of adsorbed OFM molecules increases with smaller roughness wavelength values. Comparing this behavior with sliding on the smooth flat surface, the contact experiences an increase in mean OFM adsorption sites ranging between 9.9% (48 nm) and 60.9% (6 nm), as depicted in Figure 9b. The impact of surface roughness in the asymmetric model is clearly more pronounced than in the symmetric model shown in Figure 7b. Notably, the curvature of the indenter closely resembles the surface asperity curvature with a 48 nm wavelength, leading to a similar fluctuation as observed in Figure 7a. This behavior reflects the cyclic slip, desorption, and re-adsorption pattern of OFM molecules observed previously. The fluctuations diminish when the curvature of the indenter deviates from the surface asperity curvature.

The study further investigates specific locations on the rough surface where OFM molecules adhere, including the concave, convex, and transitional slope regions within the confinement, as shown in Figure 10. For all the rough surfaces, the adsorption fraction is the highest on the slope region. This is because that the total area of slope regions is the largest, providing more adsorption sites than the convex and concave regions. Moreover, due to the corner effect, more solid beads are in close contact with the polar beads adsorbed on the slope regions compared to the other regions, thereby resulting in stronger adsorption in the slope regions.

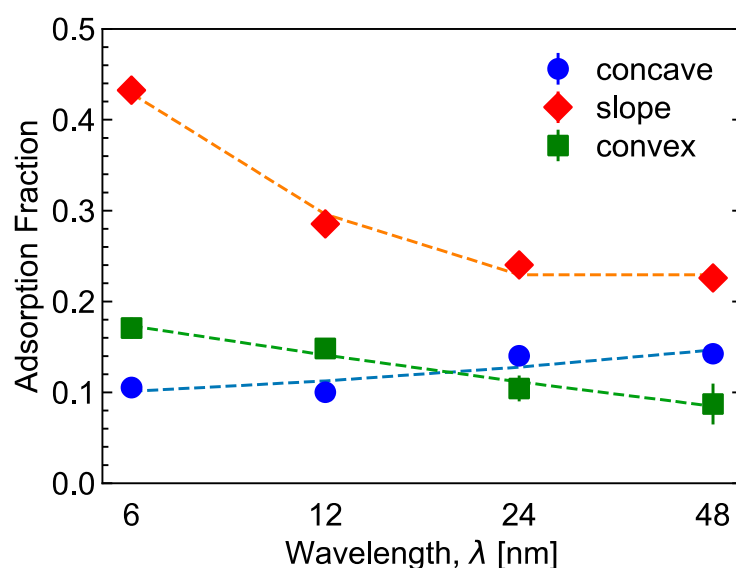


Figure 10. Average adsorption fraction over the last 100 ns in different regions of rough surfaces with varying wavelengths.

With decreasing wavelength, i.e., increasing surface roughness, the adsorption fraction increases on the slope and convex regions but decreases on the concave regions. Particularly, the change induced by surface roughness is more pronounced in the slope regions than in the convex and concave regions, which dictates the trend of increasing adsorption fraction with decreasing wavelength as observed in Figure 9b. The reasons are discussed below, based on the motions of OFMs as shown in Movie S2 in the Supplementary Materials. Due to the shear motion of the upper surface in the horizontal direction, OFMs possess horizontal rather than vertical velocity. As seen in Movie S2, OFM molecules not adsorbed onto the convex regions tend to traverse horizontally in the shallower cavity regions instead of diffusing vertically into the deeper cavity regions. If there are unoccupied slopes in the shallower regions, OFMs are likely to adsorb onto these slopes; otherwise, they move to the next convex region. As the wavelength decreases, although the total area of the slopes remains nearly constant, the area of slopes in the shallower region increases. This provides more favorable adsorption sites, resulting in a higher number of adsorbed OFMs on the slope regions. Additionally, with decreasing wavelength, the distance and travelling time of OFMs between neighboring convexes decrease. The shortened time make it more difficult for OFMs to diffuse to the deeper cavity regions, thereby leading to a decreased adsorption in the concave regions. Moreover, compared to OFMs in larger cavities of surfaces with longer wavelengths, OFMs in smaller cavities of surfaces with shorter wavelengths are more likely to entrain into the contacting interface, consequently resulting in an increased adsorption fraction in the convex regions.

3.2.2. Interpretation of OFM Desorption in Shearing

Focusing on the convex region, where boundary friction is expected to occur, the desorption time (t_d) for OFMs on a convex region is calculated as $t_d = t_{\text{end}} - t_0$, where t_{end} is the time at which the last initially adsorbed OFM leaves the original convex region, and t_0 is the time at which shearing commenced. Figure 11 presents the desorption time, indicating the duration needed for OFM, initially pre-adsorbed in convex regions, to completely desorb from their original locations. The plot illustrates a noticeable increase in the desorption time with larger roughness wavelength values. The variations in desorption time can be attributed to the increased number of surface peaks or asperities, with a smaller wavelength value correlating to an expedited OFM desorption process.

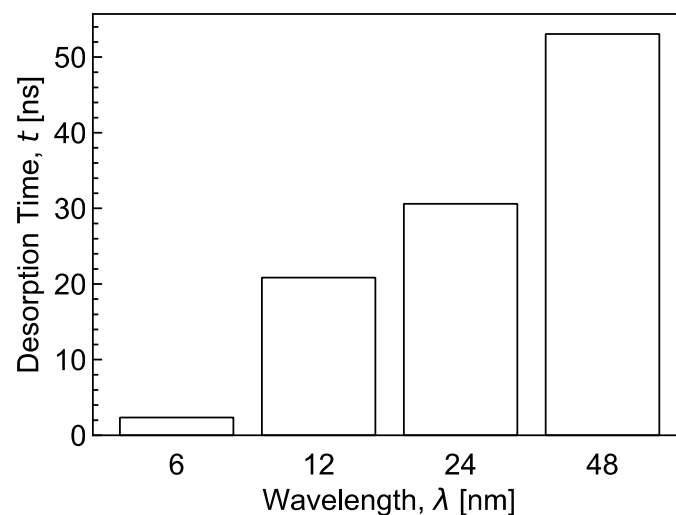


Figure 11. Time for OFM desorption from convex regions on rough surfaces with varying wavelengths.

To further interpret OFM desorption time, the current study employs the Greenwood and Williamson (GW) rough surface contact model [52]. The model assumes only one rough surface, similar to the asymmetric model simulated in the present study. Following this model, predictions for asperity contact area and contact load for the asymmetrical model, between the flat apex of the upper cylindrical surface and the rough flat surface, are made based on the following equations [52]:

$$\text{Total asperity contact area (m}^2\text{)} : A_a = \pi(\xi\beta\sigma)F_1(h/\sigma)A, \quad (6)$$

$$\text{Total asperity contact load (N)} : P_a = \frac{4}{3}(\xi\beta^{1/2}\sigma^{3/2})F_{3/2}(h/\sigma)EA, \quad (7)$$

where E , A , and h refers to the reduced modulus of elasticity, apparent contact area, and gap between the upper and lower surfaces, in the units of Pa, m², and m, respectively. Equations (6) and (7) highlight that the primary roughness geometrical factors influencing asperity area and load are $(\xi\beta\sigma)$, and $(\xi\beta^{1/2}\sigma^{3/2})$, respectively.

Utilizing the model, the rough surfaces generated with different wavelength values are translated into GW parameters, as detailed in Table 2. Since the amplitude remains constant, the variations in the adopted configurations of rough surfaces result in the same RMS roughness of 1.204 nm. The distinction lies in the mean asperity peak radius (β) and density (ξ). Following the GW parameters, a surface with a smaller wavelength value yields higher asperity density and smaller-sized asperities (based on curvature radius).

Table 2. Surface properties based on Greenwood and Williamson's rough surface contact model.

Wavelength [nm]	RMS Roughness, σ [nm]	Mean Asperity Peak Radius, β [nm] [53]	Mean Asperity Peak Density, ξ [nm ⁻²] [53]	Mean Asperity Slope (rad) [54]	$(\xi\beta\sigma)$ ($\times 10^{-2}$)	$(\xi\beta^{1/2}\sigma^{3/2})$ ($\times 10^{-3}$)
6	1.204	0.5431	27.7778	1.1304	1.8170	27.0585
12		2.1477	6.9444	0.5654	1.7964	13.4524
24		8.5834	1.7361	0.2827	1.7948	6.7232

Table 2 reveals a consistent total asperity contact area across the various generated rough surfaces, while the load supported by surface asperities exhibits a significant difference. Surfaces with a 6 nm wavelength value are expected to carry an asperity load up to three times larger than those with a 24 nm wavelength value. The faster desorption rate

observed for smaller wavelength values in Figure 11 is likely attributed to the increased load on surface asperities or the convex region, resulting in quicker desorption of OFM molecules. The faster desorption could also encourage more OFM molecules to migrate to the transitional slope region during shear, further increasing the adsorbed molecules in this region, as shown in Figure 10.

Additionally, Table 2 highlights the association between smaller wavelength values and higher mean asperity slopes. Sliding on such slopes often aligns with Euler's interlocking mechanism, where shear is proportionate to the tangent of the asperity slope. In scenarios involving potential solid wear particles (of similar length scale as the surface roughness) in the concave region, the surplus of adsorbed OFM molecules along the transitional slope between the concave and convex regions, particularly with smaller wavelength values, offers a more convenient pathway for these particles to slide out of the concave region with greater ease. Consequently, an enhanced number of adsorbed OFMs in this region is a mitigating factor, reducing the potential for erosive wear.

4. Conclusions

In this study, CG MD was employed to model OFM adsorption under shear in two distinct configurations: (1) symmetric model (identical opposing surfaces) and (2) asymmetric model (smooth cylinder on flat surface). The construction of the CG model faced challenges due to the strong effect of OFM adsorption and dimer cluster, making the traditional self-diffusion methods unsuitable for determining the damping coefficients of DPD. To address this challenge, shear-induced motion was employed, allowing the CG model to accurately match the viscosity of the AA model in liquid–liquid situations and the CoF of the AA model in liquid–solid situations. This approach yielded a more appropriate determination of the damping coefficients, improving the relevance of the CG model in simulating OFM behavior under shear conditions.

The symmetric model, considering identical opposing surfaces in shear, reveals that, despite a higher number of adsorbed OFMs by up to 6.2%, a distinct cyclic slip, desorption, and re-adsorption process occurs when opposing surfaces share similar roughness wavelength and amplitude during shear. This cyclic behavior, absent in the atomically smooth flat-on-flat configuration, emphasizes the complex nature of OFM adsorption behavior under shear conditions in the presence of surface roughness.

Simulations with a more realistic contact scenario with the asymmetric model involving a smooth cylinder sliding on a rough flat surface also show an overall increase in adsorbed OFMs, reaching a substantial 60.9%. This increase is observed primarily in a rough flat surface with a 6 nm wavelength compared to sliding on a smooth flat surface. However, it is important to note that this configuration's surplus of adsorbed molecules mainly accumulates along the transitional slope between convex and concave regions. This rough flat surface also exhibits faster OFM desorption along the convex or asperity region, attributed to the larger load carried by the asperity along the convex regions, reaching up to four times compared to a rough surface with a 24 nm wavelength.

In summary, this study observed the varying OFM adsorption and desorption behavior under diverse shear conditions, particularly concerning surface roughness. Unlike observations on atomically smooth surfaces, the cyclic patterns of OFM desorption and re-adsorption between rough surfaces, alongside enhanced adsorption in realistic contact scenarios, underscore the pivotal role of surface roughness in dictating the dynamic behavior of OFM adsorption under shear.

The study highlights the potential ramifications of overlooking surface roughness when simulating or designing OFM molecular structures. Such oversights may compromise the reliability of friction-reducing performance. Striking a balance between simulation details and complexity while accurately modeling rough surfaces is essential. This ensures a comprehensive understanding of OFM interactions under varying shear conditions, facilitating reliable predictions and informed design choices for OFMs in lubrication applications.

Supplementary Materials: The following supplementary information can be downloaded at: <https://www.mdpi.com/article/10.3390/lubricants12020030/s1>, Movie S1: Shear motion in the asymmetric model with a wavelength of 6 nm. Movie S2: Representative motions of OFMs observed in the asymmetric model with a wavelength of 12 nm. The other OFM and dodecane molecules are omitted for clarity.

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Appendix A. Coarse-Grained Potentials and Validation

Appendix A.1. Liquid–Liquid Potentials

The figures below present the bonded potentials for bond-length (U_{bl-p}) and bond-angle (U_{ba-p}), as well as the nonbonded potential (U_{ll-p}) for polar beads, alongside their corresponding distribution functions. In all the distribution functions, the coarse-grained (CG) results reasonably closely match the all-atom (AA) results, validating the accuracy of the corresponding CG potentials.

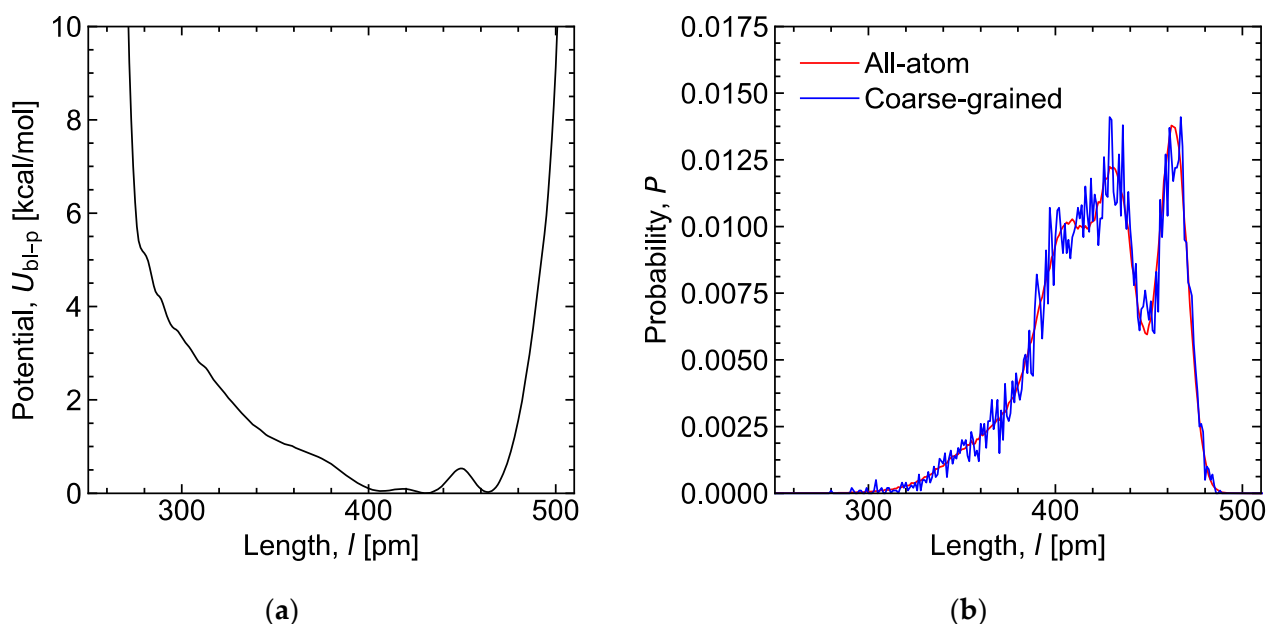


Figure A1. (a) Coarse-grained bond-length potential involving polar bead, U_{bl-p} . (b) Bond length distribution functions derived from simulations of an isolated stearic acid using all-atom and our coarse-grained models.

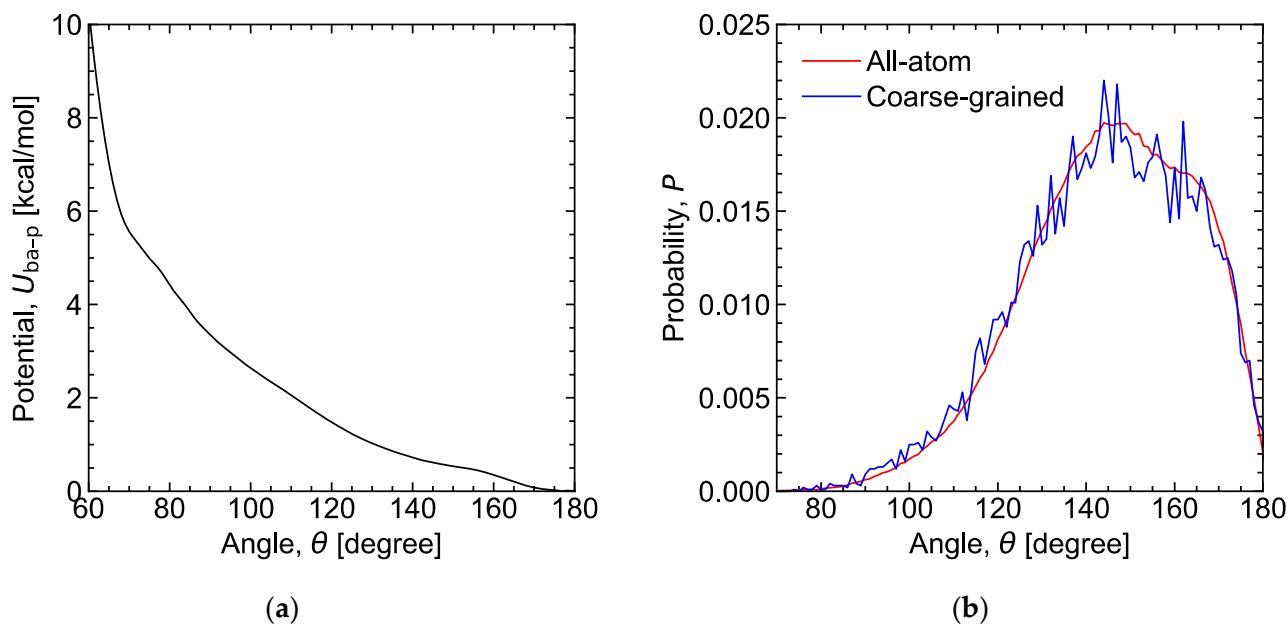


Figure A2. (a) Coarse-grained bond-angle potential involving polar bead, U_{ba-p} . (b) Bond angle distribution functions derived from simulations of an isolated stearic acid using all-atom and our coarse-grained models.

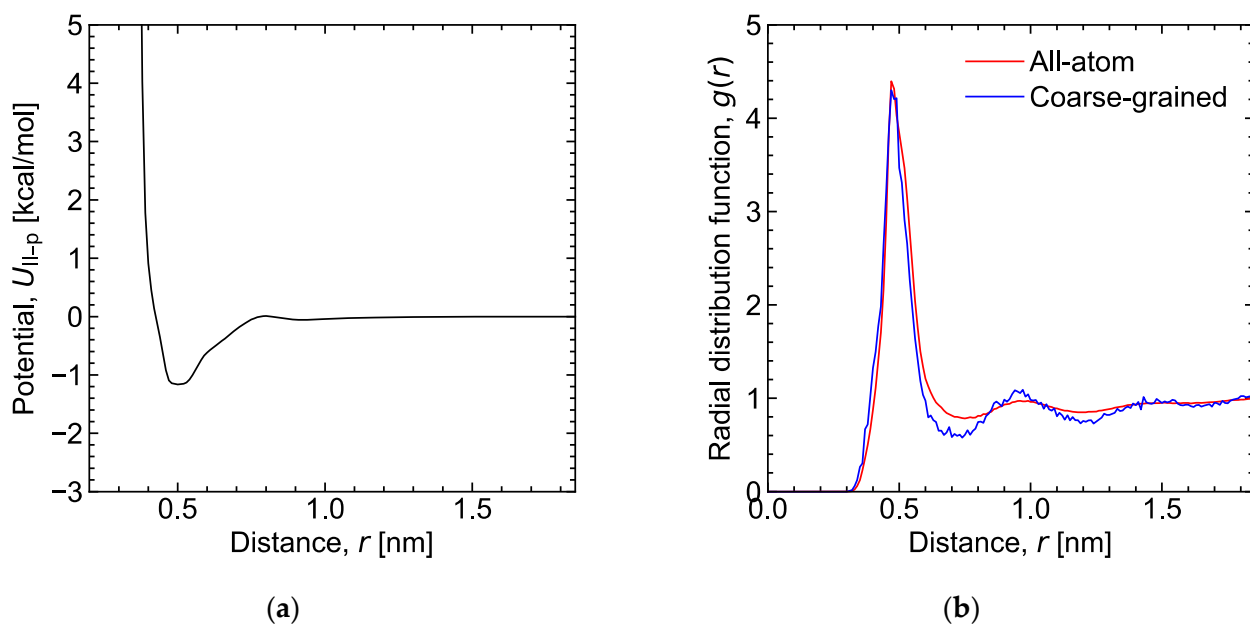


Figure A3. (a) Coarse-grained nonbonded polar liquid-liquid potential, U_{II-p} . (b) Radial distribution functions of polar beads derived from simulation of bulk stearic acid systems using all-atom and our coarse-grained models.

Appendix A.2. Liquid-Solid Potentials

The figures below present the nonpolar and polar liquid-solid potentials, U_{ls-np} and U_{ls-p} , alongside the number density distributions (NDDs) of nonpolar and polar liquid beads versus their distance from the solid surface. In Figure A4b, the CG result strongly aligns with the AA one. Similarly, Figure A5b demonstrates a close match between the first peak in the CG and AA results. These validate the effectiveness of the CG liquid-solid potentials in reproducing the structures of dodecane and adsorbed stearic acid films on hematite surfaces.

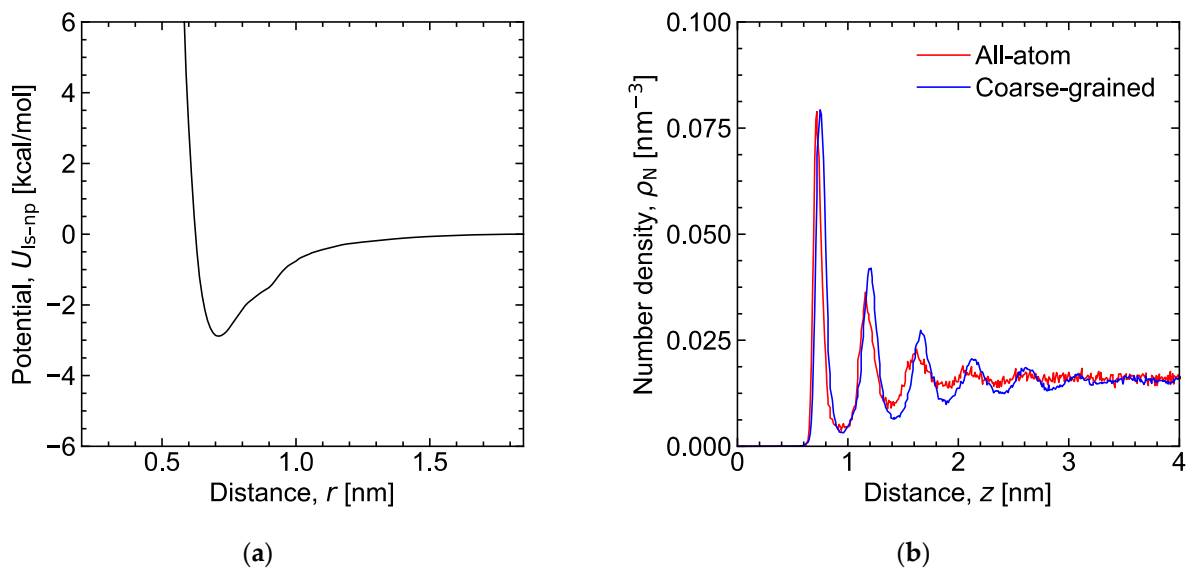


Figure A4. (a) Coarse-grained nonbonded nonpolar liquid–solid potential, U_{ls-np} . (b) Number density distribution functions of nonpolar liquid beads derived from simulation of a dodecane film on a hematite plate using all-atom and our coarse-grained models.

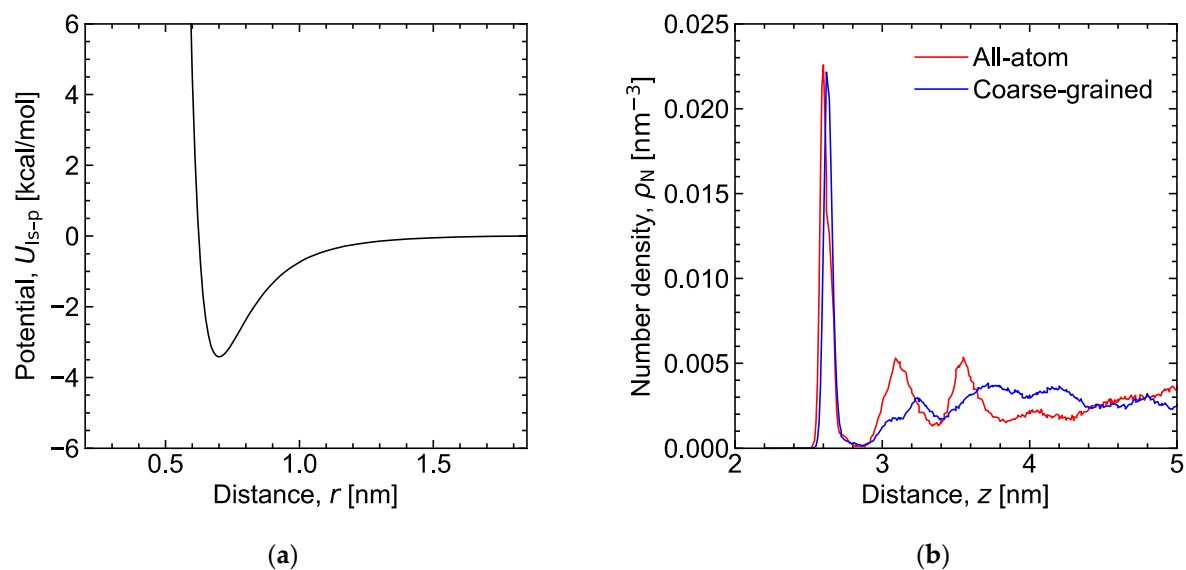


Figure A5. (a) Coarse-grained nonbonded polar liquid–solid potential, U_{ls-p} . (b) Number density distribution functions of polar liquid beads derived from simulation of a stearic acid film on a hematite plate using all-atom and our coarse-grained models.

Appendix B. Simulation Setup for Fine-Tuning Damping Coefficients

Appendix B.1. Liquid–Liquid Damping Coefficients

As described in the main text, the liquid–liquid damping coefficients ζ_{ll-np} and ζ_{ll-p} were determined by matching the shear viscosities from non-equilibrium AA and CG simulations of bulk dodecane and stearic acid systems under shear, respectively. All simulations maintained a temperature of 353.15 K. The bulk dodecane system comprised 405 molecules in a box of 6.25 nm $\times$ 6.25 nm $\times$ 4.17 nm in the x , y , and z directions, yielding a density of 0.69 g/cm³ at 0.1 MPa, which was the same as in our previous study [42]. The bulk stearic acid system contained 283 molecules in a box of 6.26 nm $\times$ 6.26 nm $\times$ 4.17 nm in the x , y , and z directions, producing a density of 0.83 g/cm³, which approximates the

experimental value under identical temperature and pressure conditions [55]. Periodic boundary conditions were applied to all the three directions.

To derive bulk viscosities, a constant engineering strain rate was applied to deform the simulation boxes and the motion of the systems was calculated using the SLLOD algorithm [51]. As depicted in Figure A6, shear was applied to the x - z plane in the x direction at a velocity of 1 m/s, generating a velocity gradient in the y direction. Viscosities were calculated using the equation $\eta = -P_{xy}/s$, where P_{xy} is the pressure tensor and s ($= v_x/l_y$) is the shear rate with v_x being the shear velocity and l_y being the box length in the y direction. Each shear simulation spanned 3.1 ns. The individual viscosity values shown in Figure 3 and Table 1 in the main text are the average over the last 1 ns of three independent simulations.

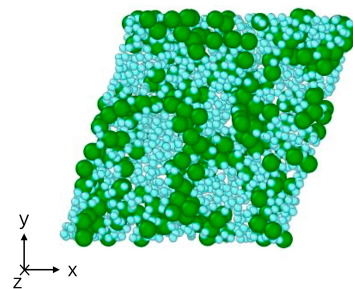


Figure A6. Snapshot from coarse-grained shear simulation of bulk stearic acid. The green and light blue represent the polar and nonpolar beads, respectively.

Appendix B.2. Liquid–Solid Damping Coefficients

As described in the main text, the liquid-solid damping coefficients ζ_{ls-np} and ζ_{ls-p} were determined by matching the coefficients of friction (CoF) from non-equilibrium AA and CG simulations, which involved the shearing of a monolayer layer of dodecane and stearic acid, respectively, between two hematite substrates. As depicted in Figure A7, the solid substrates measured 4.03 nm and 4.12 nm in the x and y directions, respectively, with periodic boundary conditions applied. The confined liquid film comprised 50 dodecane or 30 stearic acid molecules.

A normal pressure of 0.5 GPa and a shear velocity of 10 m/s in the x direction were applied to the top layer of the upper substrate, while the bottom layer of the lower substrate remained fixed. CoFs were computed by dividing the shear stress in the x direction of the x - y plane by the normal pressure. Each shear simulation spanned 5 ns. The individual CoF values shown in Figure 4 and Table 1 in the main text are the average over the last 2 ns of three independent simulations.

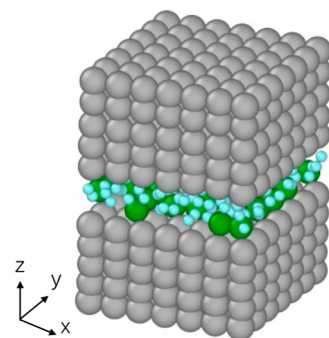


Figure A7. Snapshot from coarse-grained shear simulation of confined monolayer stearic acid film between solid substrates. The green, light blue, and gray represent the polar and nonpolar liquid beads and solid beads, respectively.

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