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Thin film lubrication of hexadecane confined by iron and iron oxide surfaces: A crucial role of surface structure

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Abstract

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Keywords

film, lubrication, hexadecane, confined, iron, oxide, surfaces, crucial, thin, role, structure, surface

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Thin film lubrication of hexadecane confined by iron and iron oxide surfaces: A crucial role of surface structure

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A comparative analysis of thin film lubrication of hexadecane between different iron and its oxide surfaces has been carried out using classical molecular dynamic simulation. An *ab initio* force-field, COMPASS, was applied for *n*-hexadecane using explicit atom model. An effective potential derived from density functional theory calculation was utilized for the interfacial interaction between hexadecane and the tribo-surfaces. A quantitative surface parameterization was introduced to investigate the influence of surface properties on the structure, rheological properties, and tribological performance of the lubricant. The results show that although the wall-fluid attraction of hexadecane on pure iron surfaces is significantly stronger than its oxides, there is a considerable reduction of shear stress of confined *n*-hexadecane film between Fe(100) and Fe(110) surfaces compared with FeO(110), FeO(111), Fe₂O₃(001), and Fe₂O₃(012). It was found that, in thin film lubrication of hexadecane between smooth iron and iron oxide surfaces, the surface corrugation plays a role more important than the wall-fluid adhesion strength. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4933203>]

I. INTRODUCTION

Hydrocarbon based lubricants play an important role in the metal forming of steel materials,^{1–3} where iron oxides are formed on the surface of the products. Over the last two decades, there have been extensive studies of thin film lubrication of alkane between metal tribo-pairs using molecular dynamics (MD) method.^{4–7} Attempts have been made to assess the role of Fe₂O₃(001) surfaces in thin film lubrication;^{8–10} however, a thorough understanding of tribological and structural properties of hexadecane on different iron and iron oxides surfaces as well as their surface orientations is still missing. Additionally, previous investigations employed a simple model, in which each methyl or methylene group was described using a united-atom (UA) model and tribo-surfaces were modeled by harmonic spring without the consideration of electrostatic contribution. The literature reveals that using a UA model for alkane yields an interfacial molecular structure different from explicit atom (EA) models.¹¹ Moreover, a reliable interaction potential between alkanes and the tribo-surface is still lacking due to the limited experimental data and a systematic parameterization. Our recent study has overcome these limitations by deriving an interfacial force-field from quantum mechanics/molecular mechanics methods (QM/MM potential) characterized for alkane on iron and iron oxide surfaces.¹² A MD simulation was therefore carried out to compare the tribological and structural properties of hexadecane between these tribo-pairs.

Under confined conditions, the thin alkane film's behavior differs from its bulk state due to the solid-like phenomenon.^{13,14} A glass transition characterized by an enormous increase

in shear viscosity, the epitaxial ordering of surface-adjacent molecules, the density oscillation across the film thickness, and the interfacial velocity slip; all of which have been observed for linear alkanes.¹⁵ This phenomenon results in low friction, which is necessary for the performance of tribological systems.^{16,17} The solid-like phenomenon becomes more significant when the thin film undergoes severe conditions, for example, when the film thickness goes below a few nanometers,^{6,18} due to high applied loads,¹⁹ and sliding velocity (shear rate).^{16,17} The lubricant's molecular structure also has an important role, given that the alkanes with longer molecular chain length have been shown to give improved wear resistance than shorter molecules.¹⁹ Further, the branched alkanes remain more liquid-like in confinement as compared to linear ones and yield an increase in shear stresses.²⁰ With regards to the influence of the tribo-pair, the surface morphology^{14,15} and the wall-fluid adhesion strength^{9,20} have been shown to play the vital roles. High surface corrugation results in a reduction of in-plane ordering of lubricant, interfacial slip, and consequently increases the friction of tribological systems.^{14,21,22}

In practice, there are several iron oxide compounds which correspond to different oxidation state of iron.²³ Our previous results revealed that *n*-alkanes prefer to adsorb on pure iron surface rather than iron oxides.¹² When considering the roles of both of surface corrugation and wall-fluid interaction strength, the question whether the lower wall-fluid interaction strength of iron oxide surfaces can yield a better tribological performance is still a controversial issue. Further, another question emerges: How do the iron, iron oxides, as well as their different surface orientations affect the behavior of the thin film? The aim of this study is to understand the fundamental mechanism of rheological and tribological behaviors of alkane between these surfaces. A systematic theoretical analysis of thin film lubrication of *n*-hexadecane confined between different iron

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FIG. 1. Snapshot of a representative model system of hexadecane confined between $\text{Fe}_2\text{O}_3(001)$ surfaces. Iron, oxygen, carbon, and hydrogen are presented as purple, red, grey, and white colors, respectively. This color convention is applied throughout.

and iron oxide surfaces was therefore carried out to investigate this issue. A surface parameterization, proposed by Savio *et al.*,⁸ was taken into account to analyze the role of surface corrugation.

II. METHODOLOGIES

A. Molecular model

Behaviour of non-equilibrium molecular dynamics model of confined pressurised and sheared liquid depends on a set of parameters such as film thickness, applied normal load, shear rate, and solid-liquid atom interaction parameters.^{24,25} As this work aimed to study structural alteration and tribological performance of lubricant confined between different

surfaces, only cases with similar loading pressure and film thickness were considered. A MD simulation was performed to compare the tribological performance of hydrocarbon lubricant between iron and iron oxide surfaces when the film thickness was confined to an order of magnitude of a few nanometers. A snapshot of a representative model system is shown schematically in Fig. 1. It was constructed by a 3 nm-thick alkane lubricant sandwiched between geometrically smooth iron and iron oxide surfaces. As shown in Table I, different surface structures as well as surface orientations were utilized in this study. The initial domain sizes for these surfaces were chosen in such a way that a surface area of $35 \times 35 \text{ \AA}^2$ was kept for all surface models, and the periodic boundary condition was applied in shear and transversal directions. Each surface was 10 $\text{\AA}$ thick and was created by cleaving from its regular crystalline structure through Miller indexing. As the domain size was a little different for each type of surface model, the number of lubricant molecules was therefore chosen such that the initial thickness in the z-direction was almost identical for all types of surface models.

In practical industrial processes such as metal forming, ball-bearing, and others,¹⁻³ the hydrocarbon based lubricant is subjected to high applied pressures and shear load by metal surfaces. A uniform normal load, as given in Table I, was therefore applied on atoms of the top layer during compression and shearing states. Because the interaction between iron atoms of iron oxide surfaces described by Columbic repulsive force (Table II) was weak, the uniform load was applied only on the top oxygen layer. This uniform load corresponded to an applied pressure of 500 MPa. The simulation procedure was divided into three simulation stages: In the first stage, the model was relaxed for 0.5 ns to neglect unrealistic atomic contacts, followed by a dynamic stage for the next 0.5 ns with applied load on the top region while the bottom region was fixed. The temperature of the system was controlled at 300 K by applying Nose-Hoover thermostat during with a damping parameter of 100 fs on thermostated layer of surfaces (Fig. 1). After that the surface was moved in x direction (it is a default for all cases except for Fe(111) surface model which moved in both x and y (denoted as (010) direction)) with a constant sliding velocity of 10 m/s, while the applied load and thermostat were

TABLE I. Surface structures, lattice constants, Miller indices, domain sizes, number of hexadecane molecules, scanning distances, and applied load for different employed iron and iron oxide surfaces.

Surfaces	Structures	Miller indices	Lateral lattice constants		Domain sizes		No. $\text{C}_{16}\text{H}_{34}$	Sampling steps		Applied load ($10^{-3} \text{ eV/\AA}$)
			a ($\text{\AA}$)	b ($\text{\AA}$)	X ($\text{\AA}$)	Y ($\text{\AA}$)		Δx ($\text{\AA}$)	Δy ($\text{\AA}$)	
Fe	BCC	(100)	2.867	2.867	34.40	34.40	82	0.205	0.205	25.641
		(110)	4.054	2.867	36.48	34.4	87	0.217	0.205	18.131
		(111)	4.965	4.054	34.75	36.48	88	0.207	0.217	31.404
		(111)(010)	4.054	4.965	36.48	34.75	88	0.217	0.207	31.404
FeO	Cubic	(100)	4.332	4.332	34.66	34.66	83	0.206	0.206	14.641
		(110)	3.063	4.332	36.76	34.66	87	0.219	0.206	41.412
		(111)	7.503	3.063	37.52	36.76	96	0.223	0.219	71.727
Fe_2O_3	Rhombohedral	(001)	8.721	5.035	34.88	35.25	85	0.208	0.210	22.839
		(012)	5.035	5.419	32.51	40.28	91	0.194	0.240	42.575

TABLE II. Potential parameters of Buckingham potential for FeO and Fe₂O₃.^{27,28} *B*, ρ , and *C* correspond to iron cation-oxygen and oxygen-oxygen interaction; the cation-cation interaction is described only by Columbic repulsive force.

Atoms	<i>Z</i> (e)	<i>B</i> (eV)	ρ (Å)	<i>C</i> (Å ⁶ eV)
O	-0.945	9 022.821	0.265	85.092
Fe ²⁺	0.945	13 032.949	0.190	0.000
Fe ³⁺	1.4175	8 020.285	0.190	0.000

kept constant. The rheological and tribological properties of lubricant and lubricated systems were averaged during the last 10 ns of shearing state. 1 fs was chosen as the simulation time step with the total simulation time of 40 ns (40 000 000 time steps).

B. Force-field

An EA model was employed for all MD simulations in which all carbon and hydrogen atoms in the alkane molecules were represented explicitly. The COMPASS force-field was used for lubricant,²⁶ while the Buckingham potential, as presented in Table II, was applied for the oxide surfaces.^{27,28} This potential had reproduced the thermodynamic and structural properties of FeO and Fe₂O₃ in natural silicate melt at both low and high pressure.^{27,28} The employed atomic charges for iron oxides, as presented in Table II, are a little higher than those obtained from our previous study using density functional theory (DFT) calculation.¹² However, this charge discrepancy does not affect significantly the current model systems due to the minor contribution of electrostatic energy in the interaction between hexadecane film and iron oxide surfaces.¹² Although Lennard-Jones (LJ) potential is applicable for metallic surfaces, it is not accurate at reproducing the surface properties compared to the embedded atom model (EAM) potential.²⁹ Therefore, a many-body force-field using Finnis-Sinclair EAM (EAM/FS) potential³⁰ was applied for pure iron. All initial configurations were constructed in the commercial Material Studio software, then transferred to LAMMPS code³¹ to perform the MD simulations.

The nonbond interactions between the surface and lubricant, as well as between the lubricant molecules were modelled by LJ 9-6 potential along with the long-range Columbic interaction with a cutoff distance of 12.5 Å, as prescribed in the COMPASS force-field. The valence terms such as stretching, bending, torsion, and inversion were also included to model the lubricant molecules in this work. However, due to the complexity expressions along with a large number of parameters, for clarity all parameters of the COMPASS force-field can be found from Ref. 26. The 9-6 parameters derived from quantum methods, which had been developed from our previous study,¹² were employed to describe the interfacial interaction between the lubricant and the surfaces.

C. Shear viscosity

A non-equilibrium molecular dynamic simulation has been conducted to evaluate the zero-shear viscosity of hexadecane at ambient condition. The shear of the fluid was performed using Forcite package in Material Studio 7.0.

A triple periodic box shaped domain of $45 \times 45 \times 45$ Å³ (Fig. 2(a)) containing 182 randomly distributed hexadecane molecules was used for this calculation. Initially, the geometry was optimized followed by a dynamic calculation for 1.0 ns using NPT ensemble at 298 K and 10⁵ Pa (1 bar) to obtain the bulk properties of hexadecane at ambient condition. The Berendsen barostat ensemble was utilized with decay constant of 0.1 ps, and the COMPASS force-field was applied for hexadecane. Ewald and atom-based summation methods were applied, respectively, for the electrostatic and van der Waals interactions with cutoff distance of 12.5 Å.

A boundary driven condition, so-called Lee and Edwards boundary conditions,³² was applied to the model in which the image cells moved continuously over the central one at a defined strain rate $\gamma \equiv \partial u_x / \partial y$ of the flow. The periodic boundary condition ensured that the particles leaving the central cell were replaced by their periodic image. The shear of the fluid took place by deforming the boundary in such a way using the sliding-brick or deforming cube presentation. The cells were distorted with the flow, and particles also deformed with the cell. This simulation was carried out under constant

FIG. 2. Simulation domain size ($45 \times 45 \times 45$ Å³) of hexadecane with a central cell and their image cells for (a) initial stage and (b) sheared stage.

pressure, and the thermostat was applied to remove sheared induced heat. The simulation time for this shear calculation was varied from 5.0 to 10 ns for different shear rate. A steady shear rate ($\dot{\gamma}$) from 10^9 to 10^{12} s^{-1} , which corresponds to the upper and lower shear rate bounds in MD simulation,^{16,33} is applied in this calculation. The shear viscosity was defined as the ratio of the shear stress to the applied shear rate $\eta = \tau/\dot{\gamma}$.

D. Surface characterization

It was revealed in the literature that the tribo-surface properties have a substantial influence on the lubricity of fluid in nanotribology.^{14,15} Many simple surface characterization approaches had been employed such as surface energy^{9,34} or surface commensurability.³⁵

The oxidation of iron not only yields the difference in surface properties, including crystalline structure, of tribo-surface, but also results in different molecular behavior and adhesion strength of the thin alkane film.¹² To analyze the role of these influences in thin film lubrication of alkane between iron and its oxides surfaces, a comprehensive surface parameterization proposed by Savio *et al.*⁸ was employed to consider the interaction energy and commensurability between surface and lubricant molecules by the concept of surface corrugation. Although this method was implemented at zero temperature, it could quantitatively predict the surface properties under standard conditions.⁸

As shown in Fig. 3, a representative scanning technique on $\text{Fe}_2\text{O}_3(012)$ surface using a uniform layer of scanning atoms with the sampling steps of $\sim 0.2 \text{ \AA}$ was used. The scanning distances (Δx , Δy) in lateral directions for each surface are shown in detail in Table I. To simplify the scanning model, only the carbon site of the alkane without explicit hydrogen atoms was used. A new interfacial potential obtained from a parameterization of interfacial interaction between butane using UA model and iron as well as iron oxides surfaces was applied for scanning atoms. The adsorption energies and configurations obtained from previous DFT calculation¹² were utilized as the training set for this parameterization. As the contribution of electrostatic component in the interaction between alkane and the surfaces was insignificant,^{12,36} it was not taken into current surface parameterization. The fitting procedure was similar to that described in a previous study.¹²

The coordinates of scanning atoms were fixed in lateral directions, whilst they were set free in a direction normal to the surface during the optimization process. This is to allow the scanning atoms to stay at equilibrium distances that corresponded to the lowest surface potential. The surface potential energy landscape, surface commensurability, and resisting force were investigated to determine these influences on the structural and tribological properties of confined lubricant.

FIG. 3. A representative scanning technique is presented on $\text{Fe}_2\text{O}_3(012)$ surface. For clarity, the atoms on the top layer of the surface are highlighted with the darker colors than those underneath.

The surface commensurability was determined based on the commensurability height expressed in following equation:⁸

$$h_{comm} = \sqrt{\frac{1}{N} \sum_{i=1}^N (h_{eq}(x, y) - \bar{h}_{ep})^2}, \quad (1)$$

where $h_{eq}(x, y)$ presents equilibrium distance at atom i^{th} and $\bar{h}_{ep}$ is the averaged equilibrium distance over N atoms of scanning layer.

It has been shown from the literature that the surface potential energy plays a vital role in thin film lubrication.⁹ To quantify the potential energy of a surface, a physical component ($\bar{V}_{scan}$) was evaluated by averaging the interaction energies between the scanning atoms and the surface over all scanning atoms. The surface energy corrugation was then determined by the root-mean-square of the sum of deviations between local interaction energy $V_{scan}(x, y)$ at atom i^{th} and the mean value $\bar{V}_{scan}$ in the following expression:⁸

$$V_{corr} = \sqrt{\frac{1}{N} \sum_{i=1}^N (V_{scan}(x, y) - \bar{V}_{scan})^2}. \quad (2)$$

For different scan lines on a surface, the distinct force traces are obtained in spite of having the same potential energy landscape.³⁷ However, the sliding atom favors to stay at the minimum energy level, and as a result, the minimum force path deviates from a straight scanning direction to form a zigzag pattern.^{8,37} The resisting force was therefore defined as the minimum gradient of corrugation potential in the sliding direction,

$$F(x) = \min_{\Delta y} \left((V_{scan}(x, y) - V_{scan}(x + \Delta x, y + \Delta y)) / \sqrt{\Delta x^2 + \Delta y^2} \right). \quad (3)$$

FIG. 4. Density profile of hexadecane film across film thickness for (a) Fe, (b) FeO, and (c) Fe₂O₃ surfaces at applied pressure of 500 MPa, and temperature of 300 K.

To quantify the maximum resistance of atom movement, Savio *et al.* assumed that the corrugation force (F_{corr}) was the maximum value of resisting force ($F(x)$).⁸ However, in some circumstances discussed in Section III C, this value could be negative or zero. In this work, the corrugation force was defined as the amplitude of resisting force and given in following expression:

$$F_{corr} = |F(x)_{max} - F(x)_{min}|. \quad (4)$$

The surface parameter was then determined as a function of surface commensurability and corrugation force by the

following equation:⁸

$$\zeta_{surf} = F_{corr} \cdot h_{comm}. \quad (5)$$

III. RESULTS

A. Lubrication of hexadecane between iron and iron oxide surfaces

Under confinement and sliding motion of the surfaces, the momentum was transferred into the fluid resulting in layering structure and solid-like behavior of molecules adjacent to the surfaces.^{38,39} This layering density profile oscillated with the highest degree of layering at the wall-fluid interface, then gradually reduced toward the bulk material in the middle of the film gap. There are seven distinct layers across the film thickness for all surface models due to the similar initial film thickness (Fig. 4). However, there is a difference in in-plane ordering of each surface which is characterized by the degree of layering at the interface. In fact, as reported in Table III, the largest peak of 3.33 g/cm³ in the density profile is found on the Fe(110) surface, whilst it is only 0.93 g/cm³ for FeO(111). This statistical component decreases in the following order Fe(110) > FeO(100), Fe(100) > FeO(110) > Fe₂O₃(012) > Fe(111) > Fe(111)(010) > Fe₂O₃(001) > FeO(111). This order is consistent with our previous finding for the adsorption of butane on Fe(110), FeO(110), and Fe₂O₃(001).¹² Generally, there is a less ordering of hexadecane between Fe₂O₃ surfaces when compared with pure iron and FeO, except FeO(111).

It is noted that although there is a remarkable difference in the degree of layering, the summation of density in this layer differs insignificantly. Particularly, as presented in Table III, this component varies in a range from 11.23 g/cm³ to 13.76 g/cm³. It is due to the insensitivity of surface coverage of hexadecane with surface potential.¹² The results also show that the obtained film thickness is dependent on surface model, although it was initially similar. As a result, the average lubricant density is also different, but this difference is quite small and within 0.1 g/cm³.

The high in-plane ordering of hexadecane on Fe(110), FeO(100), Fe(100), FeO(110), Fe₂O₃(012), and Fe(111) surfaces yields a solid-like behavior in the thin film lubricant. As shown in Fig. 5, this solid-like phenomenon is characterized by a substantial slip of lubricant at both walls. An interesting observation is that there appears to be a plug-slip

TABLE III. Rheological and tribological properties of different iron and iron oxide surface models.

Surfaces	ρ_{max} (g/cm ³)	$\sum_{1^{st} layer} \rho$ (g/cm ³)	ρ_{ave} (g/cm ³)	τ_{xz} (MPa)	$\Delta\tau_{xz}$ (MPa)	μ	t (Å)	$\partial u / \partial z$ (ns ⁻¹)	η_{eff} (mPa s)
Fe(100)	2.59	11.65	0.937	6.18	±4.88	0.012	27.35	0.06	108.04
Fe(110)	3.33	11.51	0.948	2.56	±3.06	0.005	27.06	0.02	129.29
Fe(111)	1.73	11.69	0.939	15.36	±7.03	0.031	27.36	0.22	68.97
Fe(111)(010)	1.62	13.76	0.918	35.95	±9.39	0.062	27.98	6.14	5.04
FeO(100)	2.59	11.33	0.940	8.44	±6.35	0.017	27.20	0.43	19.82
FeO(110)	2.54	11.35	0.940	8.19	±6.17	0.016	26.89	0.12	70.60
FeO(111)	0.93	11.60	0.841	65.81	±9.75	0.144	30.63	7.62	9.42
Fe ₂ O ₃ (001)	1.55	11.23	0.909	56.44	±9.70	0.114	28.12	5.95	9.48
Fe ₂ O ₃ (012)	1.85	12.73	0.903	19.00	±6.53	0.040	28.46	0.99	19.24

FIG. 5. Velocity profiles of hexadecane film across film thickness and their appropriate fitting lines for different iron and iron oxide surfaces sliding in (100) direction (except Fe(111)(010) surface model system) at applied pressure of 500 MPa, and temperature of 300 K.

phase, whereby the whole film acts as a rigid solid-like block for Fe(110), FeO(100), Fe(100), FeO(110), Fe(111), and Fe₂O₃(012) surfaces. For the films at the same thickness confined by FeO(111), Fe₂O₃(001), and Fe(111) surfaces, an inhomogeneous velocity profile shows almost stick boundaries as well as linear internal deformation. Remarkably, for the same system model of Fe(111), the velocity profiles are different for different sliding directions, in particular, an inhomogeneous velocity profile, with internal deformation, is seen for the case of sliding in the (010) direction, whereas full slip is observed at the interface for the (100) direction (Fig. 5). This effect could stem from a number of sources; however, in this work, we only focus on the influence of surface corrugation and interaction strength of the studied surfaces.

A linear function was used to fit the velocity profile of these surface models based on obtained statistical data of lubricant velocity. Then, the effective shear rate $\partial u / \partial z$, which was the slope of the linear function, was determined for each surface model. The obtained results, as presented in Table III, show that the shear rate for Fe(110) surface is nearly zero, whilst it is significant for Fe₂O₃(001) (5.95 ns^{-1}), Fe(111)(010) (6.14 ns^{-1}), and FeO(111) (7.62 ns^{-1}).

In tribology, the shear stress and friction coefficient (μ) are crucial physical components to assess the tribological performance a model system. It is noted that the shear stresses increase in an order contrasting with that observed for degree of layering. Particularly, the highest shear stress of 65.81 MPa is found for FeO(111) and the lowest value of 2.56 MPa for Fe(110). Notably, the shear stress of 56.44 MPa for Fe₂O₃(001) is higher than the value of 45.5 MPa obtained from the work by Savio *et al.*⁸ using a UA model. Furthermore, by varying the Lennard-Jones energy parameter (0.5–15 times) of the iron atoms of Fe₂O₃(001) surface, Berro *et al.*⁹ reported a friction coefficient of 0.073–0.09, lower than that obtained from this work (Table III). This discrepancy could be due to the employed model for alkane, in which the explicit steric effects¹¹ of hydrogen atoms are taken into account in the current EA model, and to the difference in the interfacial interaction parameters.

To assess the solid-like behavior of hexadecane on the considered surfaces, the shear viscosity, which is defined as the ratio of shear stress and effective shear rate, is shown in Table III. It is noted that the viscosity of lubricant confined between Fe(110), FeO(100), FeO(110), Fe(111), and Fe(100) surfaces, in a decreasing order, is higher than Fe₂O₃(001), FeO(111), and Fe(111)(010).

The molecular alignment of hexadecane molecules of aforementioned surface models was also considered. The snapshots of molecular configuration of the first layer of thin hexadecane film confined between different iron and its oxide surface are shown in Fig. 6. It is noted that there is a parallel alignment of hexadecane molecules on the surfaces. This observation is consistent with the experimental observation of adsorption of alkanes on Au(111) surfaces,⁴⁰ and other theoretical investigations.^{36,41} However, there is a random alignment of hexadecane molecules with Fe(100), Fe(110), Fe₂O₃(001), and FeO(111) surfaces whilst the preferred aligning directions are seen with Fe(111), Fe(111)(010), FeO(100), FeO(110), and Fe₂O₃(012). Remarkably, a favored molecular alignment in the (100) direction of Fe(111) surface is found for the case of sliding in this direction (Fig. 6(c)) and (010) (Fig. 6(d)). Thus, it can be concluded that the local alignment of molecules at the Fe(111) surface is insensitive with the sliding direction.

B. Shear viscosity

The calculated density of hexadecane using COMPASS force-field at ambient condition is 0.77 g/cm^3 , which is consistent with experimental measurement.⁴⁴ The obtained results, as presented in Fig. 7, show that the viscosity decreases with the increase of shear rate. However, the predicted zero-viscosity and the thinning regime from the current work are different from those obtained by Berro *et al.*,³³ who employed the AMBER96 force-field for hexadecane. Particularly, the zero-viscosity in this work is 3.082 cP, which is close to the experimental measurement of 3.0248 cP,^{42,43} but it is higher than 2.43 cP and 2.08 cP that obtained from their work using the hybrid diffusion method and 2D thermostat method, respectively. Thus, it can be noted that the COMPASS force-field can describe properly the density and viscosity of hexadecane. The onset of thinning regime for COMPASS force-field is $2 \times 10^9 \text{ s}^{-1}$, whilst it is $4 \times 10^9 \text{ s}^{-1}$ for AMBER96.

C. Surface characterization

Table IV shows a comparison of the adsorption energies and the carbon site's minimum equilibrium distances from the surfaces between the current MD calculation using UA model and the reference data obtained from previous DFT calculation.¹² The errors within 5% are found for Fe(110) and Fe₂O₃(001) surfaces, whilst some higher deviations are reported for FeO(110). The minimum cost ($f(\varepsilon_i, \sigma_i)$)¹² of the potential parameterization over chosen molecular configurations of butane adsorbed on Fe(110), FeO(110), and Fe₂O₃(001) surfaces are 1.2%, 8.6%, and 2.7%, respectively.

The fitting results are shown in Table V. The adhesive strengths (ε_{ij}) of atomic interactions between the surface's atoms with the carbon site (CH_x) are higher than those

FIG. 6. Snapshots of molecular configuration of hexadecane at the first layer of thin film confined between different iron and iron oxide surfaces sliding in (100) direction (except Fe(111)(010) surface model system) at applied pressure of 500 MPa and temperature of 300 K.

obtained from previous interfacial potential parameterization for carbon.¹² This new interfacial potential was then utilized for the surface parameterization.

Fig. 8 shows that there is a correlation between the atomic structure and the scanned potential energy landscape of the surface. In this study, the surface potential energy is defined

as the interaction energy between the scanning atom and surface. For pure iron, the lowest surface energy is found on the top of interfacial iron atoms (on-top sites) while the highest surface energies are found on hollow sites (Figs. 8(a)–8(c)). This observation is consistent with our previous DFT calculation which shows that *n*-butane molecule is more stable at

FIG. 7. Variation of viscosity of hexadecane determined from MD simulation at ambient condition. The dashed line, dotted line, and dashed-dotted lines, respectively, correspond to Carreau fits of COMPASS-NEMD, AMBER-2D thermostat, and AMBER-hybrid diffusion methods. The asterisks indicate the results obtained by Berro *et al.*³³ and the arrow presents the experimental Newtonian viscosity.

location between iron rows of Fe(110) surface rather than at on-top sites.¹² Furthermore, from *ab initio* calculations, Lo and Ziegler found that most two-carbon species preferred to adsorb at the hollow site on Fe(100).⁴⁵ A similar propensity is found for iron oxides; however, the higher surface energy is observed at iron atom rather than oxygen. It could be due to the stronger interaction strength between scanning atom (characterized by a carbon site) and iron as shown in Table V.

As reported in Table VI, pure iron surfaces have larger surface energies ($-\bar{V}_{scan}$) than iron oxides. This tendency is consistent with our previous observation in which the largest interaction energy between alkane and surface is found on Fe(110).¹² The Fe₂O₃(001) surface shows the highest energy corrugation of 0.169 kcal/mol while it is only 0.017 kcal/mol for Fe(110). This energy corrugation strongly depends on the surface structure. For instance, for nearly the same surface energies such as Fe(111) ($-\bar{V}_{scan} = 1.345$ kcal/mol) and Fe(100) ($-\bar{V}_{scan} = 1.379$ kcal/mol), the Fe(111) surface ($-\bar{V}_{corr} = 0.134$ kcal/mol) is more corrugated than Fe(100)

TABLE V. LJ 9-6 interfacial potential parameters for the interactions between C₄H₁₀ and Fe(110), FeO(110), and Fe₂O₃(0001).

Surface	Pairwise	ϵ_{ij} (eV)	σ_{ij} (Å)
Fe	Fe-C(H _x)	0.009	4.35
	Fe-O(H _x)	0.010	3.78
FeO	O-C(H _x)	0.004	4.53
	O-O(H _x)	0.004	4.53
Fe ₂ O ₃	Fe-C(H _x)	0.016	3.75
	O-C(H _x)	0.003	4.43

($-\bar{V}_{corr} = 0.044$ kcal/mol). A similar observation was found with FeO, in which the (111) surface is significantly more corrugated than (100) and (110). The surface corrugation increases in the following order, Fe(110) < FeO(100) < Fe(100) < FeO(110) < Fe(111) < Fe(111)(010) < FeO(111) < Fe₂O₃(012) < Fe₂O₃(001).

The surface energy affects the lubricant's properties, i.e., the in-plane ordering, density profile, and the shear stress of confined shear model.⁹ However, even surfaces with the same interaction strength and energy corrugation of Fe(111), the shear stresses can be different, for the case of sliding in different directions (Table III). The role of resisting force can be used to explain this issue. As shown in Figs. 9-11, there is a correlation between the resisting force and surface potential energy landscape. In fact, the periodicity of resisting forces is consistent with potential energy landscape and atomic structure of the surfaces in sliding direction. For Fe(111) surface, for example, the resisting force differs in different sliding directions although it has the same potential energy landscape, in particular, a corrugation force of 0.112 kcal/mol Å is found for the case of sliding in (100) direction while there is 0.466 kcal/mol Å for (010) direction. This corrugation force discrepancy could be explained by the difference of atomic spacing in these directions. Particularly, for an approximate sliding distance, there are 14 periodicities of resisting force, which is also appropriate with 14 atomic spaces, in (100) direction (Fig. 9(c)), while this is only nine periodicities in (010) (Fig. 9(d)).

TABLE IV. Adsorption energies ($-E_{ad}$) and structural parameters (ΔZ_{CHx}) of C₄H₁₀ on Fe(110), FeO(110), and Fe₂O₃(0001) surfaces obtained from previous DFT calculation and the current MD calculation.

Surfaces	Figures ^a	$-E_{ad}$			ΔZ_{CHx}		
		DFT ^a (eV)	UA (eV)	Error (%)	DFT ^a (Å)	UA (Å)	Error (%)
Fe(110)	2a	0.498	0.504	1.24	3.92	3.86	-1.58
	2b	0.499	0.504	1.06	3.85	3.84	-0.24
	2c	0.441	0.440	-0.34	3.77	3.70	-1.82
	2d	0.442	0.440	-0.46	3.75	3.69	-1.49
FeO(110)	2e	0.375	0.410	9.37	3.33	3.43	3.06
	2f	0.415	0.428	3.13	3.79	3.32	-12.31
	2g	0.349	0.353	1.32	3.21	3.41	6.07
	2h	0.382	0.395	3.37	3.55	3.19	-10.02
Fe ₂ O ₃ (0001)	2i	0.372	0.390	4.72	3.46	3.40	-1.65
	2j	0.372	0.366	-1.64	3.54	3.51	-0.73
	2k	0.351	0.358	2.25	3.21	3.16	-1.42
	2l	0.338	0.325	-3.75	3.26	3.21	-1.51

^aData obtained from previous DFT calculation by Ta *et al.*¹²

FIG. 8. Atomic surface structures and their relevant scanned potential energy landscapes for different iron and iron oxide surfaces. The contour level of potential energy for each surface can be referred to Figs. 9-11.

For iron oxides, the correlation between resisting force and surface energy is shown in Figs. 9-11. The corrugation force obtained on $\text{Fe}_2\text{O}_3(012)$, $\text{FeO}(100)$, and $\text{FeO}(110)$ surfaces is small (<0.2 kcal/mol $\text{\AA}$) but it is remarkably larger for $\text{Fe}_2\text{O}_3(001)$ (0.418 kcal/mol $\text{\AA}$) and $\text{FeO}(111)$ (0.657 kcal/mol $\text{\AA}$). It is noted that there are two frequencies of resisting force for $\text{FeO}(111)$ surface (Fig. 10(c)). This could be due to the influence of the surface potential; in particular, both iron and oxygen are presented on the top atomic layer of $\text{FeO}(111)$ surface; however, the minimum surface energy is seen at the iron rows (Fig. 8(f)), which correspond to the largest resisting force (Fig. 10(c)). The second peak of resisting force occurs at the position of the second iron layer, underneath and between the iron and oxygen of the first atomic layer. Clearly, the difference in interaction strength and equilibrium distance between the scanning atom and the iron oxide surface's atoms has resulted in a complex potential energy landscape and resisting force. As presented in Table VI, the corrugation force increases in following order $\text{Fe}_2\text{O}_3(012) < \text{Fe}(110)$

$< \text{FeO}(100) < \text{Fe}(111) < \text{Fe}(100) < \text{FeO}(110) < \text{Fe}_2\text{O}_3(001) < \text{Fe}(111)(010) < \text{FeO}(111)$.

It is also noted that there is a correlation between the surface commensurability (h_{comm}) and the interfacial atomic spacing (λ) (Table VI). This correlation is confirmed through the fact that when the denser packed crystal surface, which corresponds to lower atomic spacing, is observed the smoother surface is obtained. This observation is consistent with the work by Savio *et al.*⁸ and Cui *et al.*³⁴

The corrugation force, which was defined as the maximum resisting force by Savio *et al.*,⁸ and its relevant surface parameter are also taken into account in this study. However, it should be noted that there are either negative corrugation force for the cases of $\text{Fe}(110)$ and $\text{Fe}_2\text{O}_3(012)$ surfaces or zero for $\text{FeO}(100)$. These values consequently result in unphysical meaning of surface energy parameter. A modified corrugation force, as expressed in Equation (4), was used in this study and the obtained results for this component as well as the surface energy parameter are shown in Table VI.

TABLE VI. Surface energies, corrugation forces, commensurability heights, and surface parameters for different iron and iron oxide surfaces.

Surfaces	$-\bar{V}_{\text{scan}}$ (kcal/mol)	V_{corr} (kcal/mol)	F_{corr}^a (kcal/mol/ $\text{\AA}$)	F_{corr} (kcal/mol/ $\text{\AA}$)	h_{comm} ($\text{\AA}$)	ζ^a (10^{-3} kcal/mol)	ζ (10^{-3} kcal/mol)	λ ($\text{\AA}$)
Fe(100)	1.379	0.044	0.043	0.132	0.063	2.71	8.32	2.87
Fe(110)	1.547	0.017	-0.006	0.064	0.020	-0.12	1.28	2.03
Fe(111)	1.345	0.134	0.033	0.112	0.166	5.48	18.59	2.48
Fe(111)(010)	1.345	0.134	0.207	0.466	0.166	34.36	77.36	4.05
FeO(100)	1.104	0.030	0.000	0.069	0.042	0.00	2.90	2.17
FeO(110)	0.980	0.082	0.069	0.172	0.118	8.14	20.30	3.06
FeO(111)	0.917	0.160	0.189	0.657	0.235	44.42	154.40	7.50
$\text{Fe}_2\text{O}_3(001)$	1.223	0.169	0.107	0.418	0.251	26.86	104.92	4.36
$\text{Fe}_2\text{O}_3(012)$	1.191	0.160	-0.039	0.052	0.201	-7.84	10.45	2.71

^aParameters evaluated based on expressions proposed by Savio *et al.*⁸

FIG. 9. Resisting forces and surface energy landscapes for different iron surfaces: (a) Fe(100); (b) Fe(110); (c) Fe(111); and (d) Fe(111)(010).

Notably, for Fe(100) and Fe₂O₃(001) surfaces, the surface energy parameters are an order of magnitude lower than those obtained from the work of Savio *et al.*⁸ They reported the values of 0.259 and 2.574 kcal/mol for Fe(100) and Fe₂O₃(001), respectively. This discrepancy is due to the chosen scanning potential in which, shown in Table V, the energy interaction parameter ϵ_{ij} of wall atoms in contact with the fluids are significantly smaller than those used by Savio *et al.*⁸ Among considered iron and iron oxide surfaces, the FeO(111) surface shows the highest surface energy parameter, due to its largest corrugation force and surface commensurability. For Fe(111) surface, despite the same surface commensurability of 0.166 Å, the surface parameter for the case of sliding in (010) direction is higher than that in (100) direction due to its significant larger corrugation force.

IV. DISCUSSION

The adhesion strength between hexadecane and iron surfaces is stronger than its oxides in an decreasing order of

Fe > FeO > Fe₂O₃.¹² However, the obtained results show a more solid-like behavior and considerably lower shear stresses for Fe(100), Fe(110), and Fe(111) surfaces than FeO(111) and Fe₂O₃(001). The reason for this observation could be due to that the weak interaction strength between alkane and iron, which is reported as a physisorption,^{45,46} is not large enough to have a crucial influence on the tribological performance of hexadecane film in iron oxides.

For the same number of seven layers, the degree of ordering, as shown in Fig. 4, are lower than that obtained by Cui *et al.*¹⁸ There are many reasons for this discrepancy: The weak interaction strength could be a possible reason. In fact, the wall–fluid interaction strength, as given in Table V, is smaller than that used in their work ($\epsilon_{wf} = 1.747$ kJ/mol (0.018 eV)).¹⁸ Moreover, the thickness of the simulated film of 3 nm is thicker than ~2 nm used in their work. The increase of the film thickness leads to a decrease of order.¹⁸ Importantly, the employed EA model for lubricant could result in less order than UA model because the branched molecules result in the weaker layering and larger slip near the wall.²⁰

FIG. 10. Resisting forces and surface energy landscapes for different FeO surfaces: (a) FeO(100); (b) FeO(110); and (c) FeO(111).

An interesting observation is that the in-plane ordering of lubricant depends on the crystal orientation of the surfaces but it is insensitive with the sliding orientation. In fact, Table III shows that the peak of the density profile for the first lubricant layer is different for distinct surface orientations, but it is similar for Fe(111) and Fe(111)(010). This observation shows a good agreement with the work by Soong *et al.*⁴⁷ who investigated a Couette flow in a nanochannel of different face-centered cubic crystal lattices. However, the results also reveal that there is a dependence of effective shear rate and shear viscosity on both surface orientation and sliding direction. These observations point out that the surface structure has a significant influence on structural and rheological properties of lubricant. A quantitative correlation between the surface properties and the degree of layering is illustrated in Fig. 12; this shows a decrease of the peak of density profile with an increase of surface corrugation energy, corrugation force, and surface commensurability. This finding is consistent with the work by Jabbarzadeh *et al.* who found that the in-plane order of

dodecane confined between amorphous surfaces was reduced significantly compared to crystalline surfaces.¹⁵

There is an inverse relationship between the surface corrugation parameter, which is described as a function of corrugation force and surface commensurability, and the degree of layering of confined lubricant (Fig. 12(d)). In fact, as shown in Tables III and VI, the highest degree of layering and lowest shear stress are found for Fe(110) surface which possesses the lowest surface corrugation parameter. In contrast, the FeO(111) surface with highest surface corrugation parameter shows the lowest in-plane ordering and a remarkably high shear stress. One can notice that there are two main trends: the density peak increases significantly when the surface interaction parameter tends to zero; however, the density peak becomes plateau at bulk lubricant density when ζ_{surf} approaches an infinite value.

The statistical correlation between the surface properties and tribological performance is presented in Fig. 13. The shear stress, as well as the friction coefficient (for a similar applied pressure), increases nonlinearly with the corrugation energy.

FIG. 11. Resisting forces and surface energy landscapes for different Fe_2O_3 surfaces: (a) $\text{Fe}_2\text{O}_3(0001)$ and (b) $\text{Fe}_2\text{O}_3(012)$.

However, there is a difference in shear stress for some surfaces having the similar corrugation energy. For instance, the $\text{FeO}(111)$ and $\text{Fe}_2\text{O}_3(012)$ surfaces have same corrugation energy of 0.16 kcal/mol, but shear stress is higher for $\text{FeO}(111)$ surface than $\text{Fe}_2\text{O}_3(012)$. Similarly, for the same corrugation

energy of 0.134 kcal/mol, the shear stress in (010) direction of $\text{Fe}(111)$ surface is higher than (100). The role of sliding direction, which was characterized by corrugation force, and surface commensurability were taken into account to explain the relationship between surface's properties and shear stress

FIG. 12. Correlation of degree of layering characterized by the peak of density profile of the first lubricant layer adjacent to the surface with (a) corrugation potential, (b) corrugation force, (c) surface commensurability, and (d) surface parameter. Data points are results obtained from MD simulation, and the dashed-dotted line is fitted curve.

FIG. 13. Dependence of shear stress of molecular system on (a) corrugation potential, (b) corrugation force, (c) surface commensurability, and (d) surface parameter. Data points are results obtained from MD simulation, the dashed-dotted line is fitted curve.

of molecular system. Figs. 13(b) and 13(c) show an increase of shear stress with corrugation force and surface commensurability; however, this increasing tendency is still uncertain. A comprehensive surface energy parameter ζ_{surf} , as a function of corrugation force and surface commensurability, predicts properly the tendency of increasing shear stress (Fig. 13(d)).

By varying the crystalline lattice spacing, Savio *et al.*⁸ reported two major regions for shear stress, the linear and plateau regions, and the onset of plateau region for hexadecane was at a surface corrugation parameter of 0.66 kcal/mol which corresponds to a maximum shear stress of ~ 44 MPa. Our results reveal that when the shear stress increases up to 65.81 MPa, this plateau region still does not occur. This discrepancy could be due to the difference in lubricant model and the interfacial interaction potential, in particular, an explicit atom model of lubricant with a QM/MM potential was employed in our work while a united atom model was applied in their model. However, there is an agreement between their work and the current result is that the shear stress increases with the surface corrugation parameter. The hyperbolic tangent function was adequately employed to present the correlation between shear stress and the surface interaction parameter (Fig. 13(d)).

The mechanism of high shear stress on molecular-scale rough surfaces such as $\text{Fe}_2\text{O}_3(001)$, $\text{Fe}(111)(010)$, and $\text{FeO}(111)$ could be in the behavior of the liquid layer adjacent

to the wall. This first layer is completely fixed into the surfaces. As a result, the stick boundary is moved into the thin film and lies between the first and second layers.¹⁵ A relatively stronger momentum and energy exchange between the wall and fluid via this boundary, and consequently it yields an internal deformation of lubricant.³⁹ The shear stress as well as the momentum resistance of the lubricant therefore increases for these surface models.

Another influence of surface on structural properties of lubricant is the local orientation of molecules. The snapshots of molecular configuration of the first layer of thin hexadecane film confined between different surfaces, as illustrated in Fig. 6, reveal that the lubricant molecules do not align in a preferred direction for isotropic surfaces such as $\text{Fe}(100)$ and $\text{Fe}_2\text{O}_3(001)$. It could be due to the potential of the isotropic surfaces that create the similar energy potential landscape in both lateral directions. In contrast, the favored molecular alignments are seen on anisotropic surfaces such as $\text{Fe}(111)$, $\text{Fe}(111)(010)$, $\text{FeO}(100)$, $\text{FeO}(110)$, and $\text{Fe}_2\text{O}_3(012)$. The relative wall-fluid incommensurability is a possible explanation for the distinct molecular orientation on these surfaces.⁸ The atomic spacing on the top layer of $\text{Fe}(110)$ surface in sliding direction, as reported in Table VII, is comparable with the size of CH_x groups of hexadecane molecule (~ 2 Å);²⁶ hence, it is not able to fit between interfacial atomic rows.

TABLE VII. Comparison of Newtonian viscosity for different employed potentials of hexadecane.

Lubricant	Model	η_0 (mPa s)	η_0 (expt.) (mPa s)
<i>n</i> -hexadecane	COMPASS-NEMD	3.082	
	AMBER-2D thermostat	2.08 ^a	3.0248 ^b
	AMBER-hybrid diffusion method	2.43 ^a	

^aResults obtained by Berro *et al.*³³^bResult obtained from experiment.^{42,43}

However, for Fe(111), Fe(111)(010), FeO(100), FeO(110), and Fe₂O₃(012) surfaces, this atomic spacing is larger allowing the hexadecane molecules to align between atomic rows, where the energy is minimal (Fig. 8). However, this explanation is not reasonable for Fe(100), Fe₂O₃(001), and FeO(111) surfaces, where their respective relevant atomic spacings are 2.87 Å, 4.36 Å, and 7.50 Å; larger than the size of CH_x groups. The isotropy of surface⁴⁷ can be considered as an explanation for the uncertainty in local molecular alignments at Fe(100) and Fe₂O₃(001) surfaces. For FeO(111), this scenario is may be more complicated. The atomic space of 7.50 Å for this surface is much larger than the size of CH_x groups, and so the hexadecane molecules therefore could be able to adopt a non-linear conformation in order to fill up the large available space between atomic rows.

Table III reveals that the shear rate of Fe₂O₃(001), Fe(111)(010), and FeO(111) surfaces is beyond the shear thinning of bulk hexadecane, while it is lower for other surfaces. The onset of shear thinning under confined condition depends on the structural properties of surface and thin film thickness.¹⁵ For rough surfaces, e.g., Fe₂O₃(001), Fe(111)(010), and FeO(111), the onset of shear thinning could be much higher than smooth crystalline surfaces, e.g., Fe(100), Fe(110), Fe(111), FeO(100), FeO(110), and Fe₂O₃(012). Additionally, the obtained effective viscosity for Fe(111)(010) (5.04 mPa s) is close to the bulk viscosity of hexadecane (~3 mPa s). This effective viscosity is enhanced by two orders of magnitude for other cases in which the surfaces are smoother. A similar observation had been found by Jabbarzadeh *et al.*¹⁵ who reported a viscosity of dodecane film (6 layers) confined between crystalline walls was enhanced 20 times compared to the amorphous walls.

V. CONCLUSION

The current study has carried out a MD simulation to investigate the thin film lubrication of hexadecane, which is widely used as a model lubricant in simulation and experimental studies, between different iron and its binary oxide surfaces. The realistic model systems have been constructed using EA model for lubricant with a reliable force-field-COMPASS, and a QM/MM potential obtained from our previous study to describe the wall-fluid interaction. Different surface structures as well as their crystal orientations were utilized to analyze the influences of iron oxides on rheological and tribological properties of the confined lubricant. A comprehensive surface parameterization method suggested by Savio *et al.*⁸ has been

implemented to address the role of surface corrugation. The findings can be summarized as follows:

- (i) Despite a stronger adhesion strength of hexadecane on metal iron surfaces than its oxides, there is a higher degree of layering and lower shear stress of FeO(100), FeO(110), and Fe₂O₃(001) surfaces compared to Fe(111). The role of wall-fluid interaction strength in tribological performance of hexadecane between smooth iron and its oxide surfaces is found to be less significant than the surface corrugation. The highest shear stress has been found for FeO(111) surface while the lowest one is for Fe(110). A plug-slip phase of lubricant has been found for all but Fe₂O₃(001) and FeO(111) surfaces which have highest shear stress.
- (ii) The in-plane ordering of lubricant depends on the crystal orientation of the surfaces, but it is insensitive to the sliding orientation. In contrast, there is a dependence of effective shear rate and shear viscosity on both surface orientation and sliding direction.
- (iii) The surface properties have a significant influence on structural, rheological, and tribological of lubricant. The shear stress increases with surface corrugation parameter whilst there is an inverse decrease of molecular in-plane ordering with this parameter.
- (iv) The commensurability and isotropy of the surface affect the local orientation of lubricant molecules. There is a favored molecular alignment of hexadecane molecules on Fe(111), FeO(100), FeO(110), and Fe₂O₃(012) surfaces while there is an uncertainty in local alignments at other surfaces.

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