The crucial role of chemical detail for slip boundary conditions: Molecular dynamics simulations of linear oligomers between sliding aluminum surfaces

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Abstract.

We study the slip boundary conditions of short, linear paraffins and olefins confined between two sliding aluminum surfaces with molecular dynamics. Our simulations are based on a recently developed force field for the interaction between organic molecules and bulk aluminum. The lubricant molecules investigated all consist of six monomers but differ in the existence or location of merely one double bond. It turns out that this small change in the chemistry of the lubricant molecules can alter slip lengths quite dramatically, and is not strongly correlated with surface energies and bulk viscosity of the lubricant. For example, α and β -hexene have similar large negative slip length of $\Lambda \approx -8$ Å, even though α -hexene adheres twice as strongly to the surface as β -hexene. Eliminating the double bond in β -hexene reduces the surface energy by another factor of two, but increases Λ from -8 Å to 120 Å. These results and those of additional simulations based on unrealistic, albeit occasionally used model potentials, make us conclude that surface energies and/or molecular geometries alone are not reliable indicators for slip boundary conditions. Instead, it is necessary to consider the full chemical detail. As a more encouraging result, we find that the bulk viscosity appears to describe the dissipation within the sheared fluid close to the wall quite well, despite significant ordering near the boundaries. Moreover, all our systems show a relatively weak dependence of the slip length on the normal pressure.

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1. Introduction

During the past decade, computational tribology has made tremendous progress toward making quantitative predictions for the dissipation in specific systems. Examples are the sliding between two surfaces bearing self-assembled monolayers, [1, 2] hydrogenpassivated amorphous or diamond-like carbon [3, 4, 5, 6], and embedded nanotubes [7]. These simulations were driven by new surface treatments and other technological innovations. However, sliding "generic" metal surfaces that are separated by short organic molecules have not yet received the same attention from the "realistic" atomistic simulation community as the just-mentioned, more high-tech applications. The apparently simple metal-organic molecule systems are significant whenever sliding metal surfaces are not quickly saturated with oxygen, as it happens, for example, during cutting, polishing, and machining. These processes are far more common than typical high-tech applications and their importance is evidenced by the yearly worldwide consumption of about 2.5 million tons of metalworking fluids [8].

There have been many molecular dynamics simulations of boundary conditions of simple lubricants near crystalline surfaces that were based on generic bead spring models [9, 10, 11, 12, 13, 14, 15], which are commonly believed to capture all relevant ingredients to a qualitative understanding of boundary conditions. However, it is doubtful if simple models are sufficiently refined to estimate the order of magnitude of the parameters used in constitutive equations describing flow boundary conditions. For example, it is easy to grossly over or underestimate effects when addressing questions such as: how well slip length correlates with adhesion [16]; if friction depends significantly on normal pressure [17]; how much the viscosity of a fluid is affected by the ordering near confining walls [18]; how quickly the slip length increases when temperature is reduced [14] or the shear rate increased [10]. In the context of flow boundary conditions of polymers, it may be particularly dangerous to work with unitedatom models, as the absence of atomic-scale corrugation may render the molecules more slippery than they really are. As a consequence, one risks drawing an erroneous (qualitative) conclusion. While it suffices to have captured the generic features of the interactions for the calculation of exponents describing critical behavior near phase transitions, one should not necessarily assume that generic models predict reliable trends for non-universal, material-specific properties.

An important problem in using generic potentials to address questions similar to the ones just mentioned, at least in a semi-quantitative fashion, is that the large number of dimensionless parameters makes it difficult for the simulator to choose adjustable parameters to be in a relevant regime. If thermal energy is the unit of energy and the lattice constant of the substrate is the unit of length, then adjustable and important parameters would be, among others, the interaction energy between monomers and (i) other monomers, (ii) wall atoms, the distance at which the (iii) non-bonded and (iv) bonded monomer-monomer as well as the (v) monomer-wall atom potential take their minima, and (vi) "typical" external pressure, i.e., hardness of the material, as well as

(vii) the stiffness of the polymer. Another proplem in using generic potentials is that they tend to generate a rather smooth dependence of the properties of interest on the model parameters. Real systems may behave differently: Changing the termination of diamond surfaces from hydrogen to deuterium lead to a quite dramatic 30% reduction in the friction forces [19], which was later attributed to the smaller chemical stability of the C-H bond compared to that of the C-D bond [6]. Thus, subtle changes in the interactions may lead to strong effects.

Having the liberty to choose interaction parameters at will is certainly one of the strengths of computer simulations, because this flexibility allows one to study the effect of each individual parameter in great detail. However, one might also argue that the values that nature or technology adopt in reality is rather narrow. Most industrial lubricants are based on poly-alpha olefins. The interaction strengths between such base oils and metallic surfaces are not likely to vary significantly from one metal to the next, relevant temperatures should range in most cases from, a few dozen degrees below the freezing point of water up to a few hundred °C, etc. This means that the relevant parameter space is relatively confined. Moreover, it is not possible to vary interaction parameters smoothly but only discrete chemical changes are possible from one (monodisperse) base oil to the next. How much do boundary conditions change during such changes is the central question of the work presented here. Specifically, we will investigate how the flow boundary condition depends on the location of a single double bond in hexene and how it changes when the double bond is eliminated altogether. This analysis will be augmented by simulations in which realistic interactions between lubricant molecules and metal atoms are replaced with Lennard Jones interactions. For all these systems, we will determine slip length and (apparent) viscosity, in order to provide mapping from molecular dynamics to continuum theories.

2. Method

In this section we report the main technical details of our molecular dynamics simulations, which were all conducted with the LAMMPS simulation package.[20, 21, 22] For the interactions between organic molecules, we used the OPLS force field,[23, 24] which, as we will show in a separate publication focusing on shearrate dependent viscosity, produces excellent values for bulk viscosities at various temperatures/pressures. The good agreement can be seen as surprising, because the OPLS force field was parameterized merely on static information. The interactions between organic molecules and wall atoms is modeled with a recently developed Buckingham potential [25] specifically optimized for tribological applications and which has similar accuracy as the OPLS force field, when compared with first-principle evaluation of forces. A feature of this force field is that most of the attractive forces between the Al and an organic molecule comes from H-Al forces as C-Al forces are mostly repulsive. There is also a small difference in the effective size of a carbon atom based on its local chemistry (whether it is participating in a single (sp³ hybridized) or double (sp²



Figure 1. Ball and stick representation of the investigated molecules (a) α -hexene (double bond on far left), (b) β -hexene (double bond one monomer in from left), (c) γ -hexene (double bond in center), and (d) hexane (no double bond).

hybridized) bond). The sp² carbons experience less repulsion in a Al-C interaction. For comparison, we also used Lennard Jones potentials for the wall-lubricant interactions, with values for the interactions taken from older literature and mixing rules rather than a direct measurement with first-principle calculations. Details will be presented in the result section.

The molecules considered were α , β , and γ -hexene, as well as hexane. Individual molecules are shown in figure 1. Their main distinguishing feature is the existence and/or location of a single double bond. 400 such oligomers are embedded between two walls leading to a separation of roughly 40 Å between the two aluminum walls.

The confining walls are (111) surfaces of fcc aluminum with the experimental lattice constant of a = 4.05 Å. The walls are either rigid or elastic. In the latter case, they are modeled with Green's function molecular dynamics (GFMD).[26, 27] The GFMD coefficients were obtained as described recently [26, 27] with the help of the fluctuation-dissipation theorem by simulating a small slab of crystal whose constituents interacted with the embedded atom method potential [28]. As the surfaces are smooth and as aluminum is much stiffer than the lubricant, elasticity of the walls did not affect the outcome of the simulations. The size of the simulation cell is 43.0 Å×44.6 Å in x and y direction, respectively, with periodic boundary conditions applied in these directions. The two walls are commensurate but the separation was sufficiently large for commensurability-effects to be irrelevant.

A time step of 1.5 fs was used in all simulations. The Coulombic interaction was computed with a particle-particle particle-mesh (PPPM) solver[29], and the temperature of the liquid was kept at 300 K (unless otherwise specified) by applying a Langevin thermostat [30, 31] along y direction only. The time constant of the Langevin thermostat was chosen to be 10 ps, which was sufficiently small to not to alter the viscosity calculations noticeably, yet large enough to maintain the desired temperature by removing the heat generated by shear flow within the stochastic noise (any change in viscosity due to the thermostat is smaller than the statistical error in the measurement and the temperature is maintained to within 0.1 K).

In all simulations, we keep the normal pressure, P_{\perp} , constant, i.e., the upper wall is allowed to fluctuate normal to the interface. Typical values for P_{\perp} used in this work lie between 10 and 200 MPa. Laterally, a constant velocity of $v_x = 5$ m/s (unless otherwise specified) is imposed on the upper wall, while the lower wall is fixed in the laboratory reference frame leading to an (apparent) shear rate in the order of 2 GHz, where the precise value depends on the separation of the walls and the slip condition. Once the system has reached steady state equilibrium, the velocity profile $v_x(z)$ of the lubricant atoms is monitored, which turned out sufficiently linear in all cases, to acquire reasonably accurate estimates of the slip length. The slope of the velocity profile, that is $\partial v_x(z)/\partial z$, is associated then with the shear rate $\dot{\gamma}$ and used in the calculation of viscosity.

3. Results

3.1. α -hexene

We will first report results on simulations that were produced by imposing normal pressures of 50 MPa and shear rates $\dot{\gamma}$ in the vicinity of 1.7 GHz. The number density of α -hexene atoms and their velocity profile are shown in figure 2. The top layer of the bottom wall is at z = 0 and the bottom layer of the top wall at z = H. A thick layer can be observed in the density profile up to a distance of almost 10 Å (z/H = 0.225) from the confining walls, at which point these effects suddenly disappear. Similarly, the velocity profile shows a cusp at distances close to 10 Å. Interestingly, the molecules appear to have a near perfect stick condition close to the walls.



Figure 2. Distribution of (a) number density ρ , (b) v_x along z direction for α -hexene confined by Al walls under realistic boundary condition, with a normal pressure of 50 MPa. On average, H = 42.0 Å.

The peculiar behavior of the α -olefins near the walls can be understood from the final molecular structure, which is shown in figure 3. (Atomic configurations are visualized using VMD[32].) Under sliding, the molecules have obviously attached with their end groups to the metal surface, thereby forming a brush-like coating on the surface. Slip is negligible between the brush and the remaining lubricant. Surprisingly, the grafted polymers do not seem to bend significantly into the shear flow, and, as we will show later, their height barely changes with pressure. Thus, the α -olefins essentially form a hard coating on the surfaces.



Figure 3. Final configuration of α -hexene confined by aluminum walls under realistic boundary condition, with a normal pressure of 50 MPa. Larger balls represent aluminum atoms, and sticks denote carbon chains; red sticks indicate double bonds, and the others are single bonds. The small gray balls are hydrogen atoms.

There are two likely explanations for the seemingly much enhanced propensity of the sp^2 double bonded carbons to stick close to the wall. The first is the geometry of the molecules. There are fewer hydrogen atoms attached to the sp^2 carbons so it may be easier for these carbons to approach the wall. However, the Al-C interaction is primarily repulsive whereas the Al-H interaction contains a much more significant attractive well so it is not obvious why fewer attached H would lead to an increased likelihood of being found near the wall. The other possibility to explain this much enhanced propensity of the sp^2 carbons appears to be the consequence of a relatively small difference [25] in the repulsion between $Al-C(sp^2)$ pairs and $Al-C(sp^3)$. Thus, a subtle change in the chemistry or model potentials may induce quite a strong effect in the ordering near the walls, which in turn produces a relatively large negative slip length that closely corresponds to the length of the molecule. To determine which of these explanations is correct we will look at Al-C interactions in Section 3.5 that are obtained from standard LJ mixing rules and not from direct first-principles measurements and so include all the molecular geometry effects but not necessarily the molecular chemical environment effect.

The question may arise if the formation of the above-mentioned rigid brushes is

related to some fortuitous coincidence or commensurability of the aluminum surface lattice and the preferred intrinsic spacing between the molecules in a liquid crystal type configuration. In order to answer this question, we investigated the structural order of the bonding sp^2 carbons in the bottom layer by calculating their in-plane structure factor and their in-plane radial distribution function. Both are shown in figure 4.



Figure 4. (a) Planar structure factor, and (b) planar pair correlation function for the 1st and the 2nd carbon atoms (C_{sp^2} atoms) in the absorbed α -hexene layers under realistic boundary condition with a normal pressure of 50 MPa. The filled columns in (a) correspond to the sharp peaks from the Al atoms in the surface layer. (c) Snapshot of the interface between absorbed α -hexene and the Al wall, only the sp² carbons (black balls) and the surface Al atoms (gray balls) are shown.

Analysis of the first two peaks in the in-plane radial distribution function reveals a (local) hexagonal ordering. This is because the ratio of the locations of the first or nearest neighbor peak and the second or next-nearest neighbor peak ($\approx 5 \text{ Å}$ and $\approx 8.5 \text{ Å}$, respectively) is approximately 1.7, which is close to the value of $\sqrt{3}$ that one would expect for an ideal hexagonal lattice. In fact, inspecting the topology of sp² bonds adhering to the surface with the help of molecular snapshots such as the one shown in figure 4(c), reveals that the anticipated lattice runs through the full simulation cell and that the lattice is highly distorted. Being a 2-dimensional structure, the brushes are probably more accurately described as a hexatic phase however we do not have access to large enough system sizes to meaningfully investigate the decay of the short-range positional order.

The nearest neighbor spacing of the aluminum atoms in the surface layer, which like the grafted molecules have hexagonal symmetry, is 2.86 Å. Thus the ratio between the nearest neighbor distance in the adsorbed and that in the substrate is approximately 1.7(4), which again is close to $\sqrt{3}$. After counting the number of adsorbed sp² bonds, it turns out that the number of adsorbed bonds per aluminum atom in the last layer is close to one over three, which could be indicative of a (commensurate) $\sqrt{3} \times \sqrt{3}$ R30 overstructure. However, the overstructure is rotated with respect to the substrate by roughly 40° , which is clearly different than the 30° rotation which would be permissible for a commensurate structure. Thus, adsorbed layer and substrate are effectively incommensurate. One would expect then, that the brush layer was not pinned to the surface which appears to be in contrast to the apparent stick condition for the overlayer. However, close examination of snapshots such as the one in figure 4(c) as a function of time shows that the brush layer does move relative to the wall However, it creeps only around 20 Å during a 30 ns run (~ 0.07 m/s) relative to the wall. The reason why the grafted layer moves so slowly relative to the substrate is that the interactions between non-bonded monomers is distinctly weaker than that between metal atoms and sp^2 carbons.

Before moving on to β -hexene, we would like to analyze how the parameters for constitutive equations, i.e., slip length and viscosity as well as shear stress depend on the (normal) pressure. Results are shown in figure 5. As the wall velocity was kept constant, we also show the shear rate, which becomes a function of slip rate and the normal pressure due to the compressibility of the lubricant.

It can be seen that the viscosity η follows a simple exponential dependence on the normal pressure. Parameters are very close to those obtained for the bulk fluid.[33]

Another important observation is the independence of the slip length on the normal pressure. This indicates that the grafted layers are essentially incompressible. Conversely, the bulk lubricant becomes compressed, which is reflected in the normal pressure dependent shear rate. The data shown is indicative of a compressibility of $d \ln \dot{\gamma}/dP_{\perp} \approx \ln(2.1/1.7)/200 \text{ MPa} = 1.3 \text{ GPa}^{-1}$, which is again close to the values that were obtained for the bulk compressibility numerically [25] and experimentally [34, 35] for the bulk compressibility.

Lastly, it is interesting to note that shear stress, τ_{xz} , and normal stress, P_{\perp} , are almost linearly related, as can be seen in figure 5. The finite value of τ_{xz} at $P_{\perp} = 0$ can be attributed to the adhesion between lubricant and wall. This "adhesive offset" is small at the tribologically relevant pressures near 200 MPa. It may thus be justified to relate the observation of a linear shear and normal force observed at the macroscopic scale (known as Amontons' law) to a similar relation at the microscopic scale. This correlation had already been identified in simulations of simple bead spring models. [17, 36, 37, 38] The small friction coefficient of 0.01, which one can deduce from figure 5(a), can be explained



Figure 5. Variation of (a) shear stress τ_{xz} , (b) slip length Λ , (c) shear rate $\dot{\gamma}$, and (d) shear viscosity η against the normal pressure applied to the top wall under realistic boundary condition.

by the atomic smoothness of the walls.

3.2. β -hexene

The same simulations as those presented in the previous section were repeated for β -hexene, except that only one state point, namely $P_{\perp} = 200$ MPa and T = 300 K, was considered. Results for number density and velocity profile are shown in figure 6. As is the case for α -hexene, a relatively large negative slip length, -7.8 Å, (i.e. large "stick") is found again. However, the layering effects show large discrepancies between the two molecules. Specifically, β -hexene molecules only exhibit one large maximum in the close vicinity of the walls and the pronounced minimum in the density occurs 6 Å from the wall for β -hexene in comparison to the 10 Å found for α -hexene.

Analyzing snapshots of the configurations, as those shown in figure 7, reveals that the structure of the adsorbed layer indeed differs for the two systems, i.e., β -hexene molecules form no dense brush-like structures. Moreover no evidence for hexagonal ordering of the "functional" groups, that is those involving sp² carbons, can be found. (The calculations for the in-plane structure factor and the radial distribution function which made us draw this conclusion were conducted in a similar fashion as in the precedent section, but their results are not explicitly shown here.) In the configurations, one can still see the occasional "oligomer tails" dangle into the shear flow. These tails appear to act as a major obstacle for the flow of the non-adsorbed molecules to a degree where the lateral motion of non-adsorbed molecules relative to the walls is arrested completely by these tails. One may conclude that the molecules involved are too rigid for the non-adsorbed β -hexene to flow through the obstacles imposed by the adsorbed



Figure 6. Distribution of (a) number density ρ , (b) v_x along z direction for β -hexene confined by Al walls under realistic boundary condition, with a normal pressure of 200 MPa. On average, H = 40.2 Å.

 β -hexene. Based on this observation, we speculate that bead spring models would have to include bending stiffnesses in order to reproduce the observed effect. This however would reduce the appealing simplicity of those models.



Figure 7. Final configuration of β -hexene confined by aluminum walls under realistic boundary condition, with a normal pressure of 200 MPa. Same color-coding as in figure 3.

3.3. γ -hexene

The calculations of the two preceding sections were repeated once more, but this time for γ -hexene, which has the double bond in the center of the molecule. This time, the molecules start to show behavior more akin of that of generic bead spring polymers, including density oscillations whose envelope smoothly damps away with increasing distance from the interface and a relatively small slip length of $\Lambda \sim -4$ Å, see figure 8. It is interesting to note the existence of a splitting of the peak closest to the walls in the density profile. This can be explained by the smaller range of repulsion of the sp²-bonded carbon atoms which can approach the wall more closely, thereby allowing the hydrogen atoms that are bonded to these sp² carbons to potentially bind more strongly to the aluminum surface.



Figure 8. Distribution of (a) number density ρ , (b) v_x along z direction for γ -hexene confined by Al walls under realistic boundary condition, with a normal pressure of 200 MPa. On average, H = 40.3 Å. Two wall velocities are shown with the scaling with the top wall velocity indicating the linearity of the slip condition.

The structures from figure 9 no longer show signs of the formation of "dilute" brushes as occurred in β -hexene. As a consequence, a regular stick condition between the first, strongly-adhering γ -hexene layer and the second layer occurs.

3.4. Hexane

In the preceding sections, it appeared as though the sp² bonded carbon units were responsible for the attraction to the aluminum walls and the stick boundary condition for the flow velocity. This observation raises the question as to what the slip length would be if no sp² carbons were present. As can be seen in the velocity profile for the aluminum-hexane system in figure 10, in this case Λ is extremely large and positive, i.e., on the order of 100 Å. A precise determination of the slip length is difficult due to extremely large times that the system needs to reach steady state. Despite these uncertainties in the calculation of the slip length, it appears that the sp³ units do not see the substrate corrugation and the friction turns out extremely small due to large slip, which leads to small dissipation.



Figure 9. Same as figure 7, except for γ -hexene instead of β -hexene.



Figure 10. Distribution of (a) number density ρ , and (b) v_x along z direction for hexane confined by Al walls under realistic boundary condition, with a normal pressure of 200 MPa. On average, H = 43.5 Å.

The large slip length implies that short paraffins are extremely easily squeezed out after a nascent aluminum surface has been exposed during machining. This in turn means that paraffins are inefficient metal working fluids and/or base oils for lubricants, as they do not prevent opposing metallic surfaces from coming into contact.

3.5. Artificial lubricant-wall interactions

In many generic simulation studies, Lennard-Jones (LJ) potentials, [39]

$$V = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right],\tag{1}$$

are used for computational convenience and the free parameters, namely the depth of the interaction (ϵ) and the LJ radius (σ) are chosen according to physical intuition or by some combination rules. While the behavior of homogeneous systems may well be rationalized with these interactions, for example, when studying the rheological properties of bulk systems consisting of linear hydrocarbons, it is not clear how much (reliable) insight can be obtained for heterogeneous systems. The reason is that the number of relevant dimensionless quantities increases very quickly with the complexity of the system and unless extreme caution is taken, as already alluded to in the introduction, is is easy to end up at irrelevant points in parameter space.

For example, when calculating the viscosity of a homogeneous system of oligomers or polymers with a fixed number of repeat units based on LJ interactions, one can use the mass of a monomer $m_{\rm m}$, the interaction strength of intramolecular monomer interaction, $\epsilon_{\rm mm}$, as well as the corresponding LJ radius, $\sigma_{\rm mm}$ to define the units of mass, length, and time, e.g., by setting them to unity. Any other parameter then needs to be expressed in terms of $m_{\rm m}$, $\epsilon_{\rm mm}$, and $\sigma_{\rm mm}$. Dimensionless variables that would then influence the viscosity of the system are the scaled temperature or thermal energy, density or pressure, and the intra-molecular bond length. The bond stiffness is a parameter in principle, but it should be sufficiently large to be close to the limit of infinite stiffness. The bending stiffness, however, will have a more dramatic effect on viscosity however ignoring this is usually rationalized based on renormalization group arguments that suggest that stiffer chains are equivalent to flexible chains with longer repeat units (distances between monomers) [40], however when other length scales are involved, such as the corrugation of our solid surface, this renormalization will no longer be possible and the stiffness can become relevant.

Once the interaction with a rigid crystalline surface of given symmetry is considered, three new parameters come into play: The lattice constant a, the interaction strength between monomers and wall atoms, $\epsilon_{\rm mw}$, and the corresponding LJ interaction radius $\sigma_{\rm mw}$, augmenting the total number of parameters to at least seven. This number would increase further if one were to distinguish sp² versus sp³ type units. Thus one needs seven to ten parameters to accurately model this system.

It is natural to doubt whether an accurate assessment of all these parameters is really all that important. In particular one might think that the differences seen in the preceding sections between the different hexene and hexane are primarily due to the molecular geometry, in particular the differences in the presence of the extra hydrogen atoms in hexane and the different locations of the unsaturated bonds in the hexene. To investigate this possibility, we examine two extreme cases of LJ interactions suggested for aluminum in the literature and then use mixing rules to obtain LJ parameters for Al-C interactions. Note that only the Al-C interaction will be changed, the other interactions remain as described earlier.

3.5.1. Smooth walls In one set of simulations, literature values for the LJ interactions between (non-bonded) aluminum ions in solution were taken [23, 24] ($\epsilon_{Al-Al} = 0.1$

kcal/mol and $\sigma_{Al-Al} = 4.05$ Å. These values are from the parameter files available from these references). Arithmetic mixing of the LJ interactions for aluminum atoms and other atoms was then used to construct new potentials for the interactions between oligomers and aluminum walls. Such simple mixing rules are frequently used in practice and are certainly justified to some degree for closed-electron shell systems. Aluminum, however, is a metal and thus one should not expect the interaction potentials - and thus the slip boundary conditions - to turn out to be realistic using these rules.

In figure 11 we show the number density and velocity profile for α -hexene using this artificially constructed LJ potential. Near the walls, the number density bears no similarity with the one that is obtained with potentials that were parametrized from first principles, i.e., there is no sign of brush formation. Also the slip length is positive and much larger than for α -hexene or another realistically-modeled hexene (which all showed stick conditions). Instead the data shows similar trends as those for hexane, although even when comparing to hexane, the slip length turns out too large by a factor of two.



Figure 11. Distribution of (a) number density ρ , (b) v_x along z direction for α -hexene confined by Al walls under artificial over-smooth boundary condition, with a normal pressure of 200 MPa. On average, H = 43.0 Å.

3.5.2. Adhesive walls The calculation in the previous section were repeated by using a different set of LJ parameters [41], i.e., one that was used to model diffusion of aluminum atoms in bulk aluminum ($\epsilon_{Al-Al} = 9.4$ kcal/mol and $\sigma_{Al-Al} = 2.551$ Å). The same mixing rules were applied as before to construct aluminum-lubricant potentials. This time, reasonable values were obtained for both slip length and adhesion, i.e., errors were less than 40%, as one can learn from table 1, which summarizes our main results on calculations done for a normal pressure of 200 MPa, in particular shear rate, viscosity, slip length, and surface energy. For the latter, we used a simple estimate: The difference in the internal energy of the composite system and that of the separate systems. We did not use more elaborate and accurate estimators for the surface energy, such as those based on Kirkwood-Buff type relations [42, 43], because of difficulties in comparing the diagonal elements of the pressure tensor when Coulomb forces were included and calculated in a slab geometry.

Table 1. Comparison of shear rate $\dot{\gamma}$, apparent viscosity η , slip length Λ , and surface energy, s, for some hydrocarbon-aluminum systems with a normal pressure of 200 MPa using different potentials. LJ1 refers to the Al-C parameters used in Subsection 3.5.1 and LJ2 to those in Subsection 3.5.2. R refers to the parameters described in Section 2.

oligomer	$\dot{\gamma}$ (GHz)	$\eta \ (mPa \cdot s)$	Λ (Å)	$s (J/m^2)$	potential
α -hexene	0.28	0.86	68	0.07	LJ1
	1.80	0.96	-5.7	0.70	LJ2
	2.14	1.03	-7.9	1.23	R
β -hexene	2.03	1.09	-7.8	0.65	R
γ -hexene	1.48	1.03	-3.4	0.63	R
hexane	0.17	0.43	120	0.28	R

Despite the semi-quantitative accuracy of the slip-boundary conditions for the second LJ potential, it needs to be recognized that the molecular structures were wrong again in that no brushes formed near the surfaces and the density profile looked very similar to the one for hexane, figure 10(a). Instead the configurations resembled those produced by γ -hexene without the characteristic hexagonal ordering of the sp² units. It thus appears as though the LJ potentials, when parametrized with mixing rules which clearly do not discriminate between the sp³ and the "functional" sp² carbon groups, do not show any signs of reproducing anything like the effects seen for the realistic potential which does. This effectively rules out the argument that these effects are due to the difference in the molecular geometry due to the location of the hydrogen atoms. The chemical environment of the carbon atoms is clearly the important factor.

4. Discussion and Conclusions

In our molecular dynamics study, we investigated flow boundary conditions of various hexene and hexane near crystalline aluminum walls with the intention to investigate the effect of small chemical changes in lubricating oligomers on slip length and related properties. We found that small changes in chemical detail, such as moving or eliminating a single double bond, can alter the slip length quite dramatically, even though surface energies change little. While we can confirm the trend that large adhesion leads to smaller slip lengths [15], we feel that the scatter in real systems is so large that this insight cannot be used as a reliable practical guideline.

The main results of this study on which we base our conclusion were summarized in table 1. One can see that α and β -hexene have essentially identical viscosities and slip lengths, but their adhesion or surface energies differ by a factor of two. Conversely, β and γ -hexene have similar adhesion but the slip length differs by a factor of two. Calculations based on LJ interactions between the oligomers and aluminum walls cover a broad range in adhesion and slip lengths, but none of them show the correct molecular structures near the walls.

As far as "trends" are concerned, we found the following: The slip length changes negligibly with pressure. Moreover, the averaged velocity profiles were linear up to the point where the velocity became identical to that of the nearest wall. This indicates to us that the presence of a (semi-confining) wall does not affect the (linear-response) viscosity. Other systems may well behave differently, although our belief is that these results should apply to most flow boundary conditions between atomically smooth metal surfaces and linear, organic oligomers.

Most coarse-graining techniques proposed for bulk homogeneous systems, such as renormalizing the bond angle stiffness away by changing the polymer repeat distance are unlikely to produce reasonable results when confronted with interactions with a metal wall. Even united-atom models, where each monomer CH_n is replaced by a single "meta-atom", are likely to underestimate the friction between the molecules and walls due to the motion of eliminated degrees of freedom. It may be possible to manipulate united-atom models to reproduce similar slip conditions but not to predict them without a-priori information. Manipulating a united atom model to get the right slip length for α -hexene is not likely to reproduce the correct trends for the other hexene or hexane. Despite the requirements for chemical details in computational models there is a vast amount of physics and chemistry [44] that can be extracted by computational methods that seek to uncover them.

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