Electronic Supplementary Material

Molecular dynamics simulation of the Stribeck curve: Boundary lubrication, mixed lubrication, and hydrodynamic lubrication on the atomistic level

Simon STEPHAN[1,*], **Sebastian SCHMITT**[1], **Hans HASSE**[1], **Herbert M. URBASSEK**[2]

[1] *Laboratory of Engineering Thermodynamics (LTD), Department of Mechanical and Process Engieering, TU Kaiserslautern, Rheinland-Pfalz 67663, Germany*

[2] *Physics Department and Research Center (OPTIMAS), TU Kaiserslautern, Rheinland-Pfalz 67663, Germany*

Supporting information to https://doi.org/10.1007/s40544-023-0745-y

1 Model for solid–fluid interactions

The solid–fluid interaction has a significant influence on tribological systems studied by molecular dynamics simulations. Therefore, it is subject of several studies [S1, S2]. There is a large variety of different interaction parameters and potentials used in the literature, even for a single substance combination of a fluid and a substrate, e.g. for systems with iron surface and alkanes as fluid [S2–S7]. Often the solid–fluid interaction is calculated based on simple mixing rules whereby the solid interaction itself is modeled by another potential, e.g. by a complex multi-body potential [S7]. Comparing the solid–fluid interaction energy modeled by Mie-type potentials yields values from $\varepsilon^* = 1.55$ [S4] up to $\varepsilon^* = 10.45$ [S2] in tribological simulations (each brought to dimensionless form by the energy parameter ε^{ff} of the respective fluid–fluid interaction). Higher solid–fluid interaction energies were used in conjunction with the Morse potential, e.g. Chang et al. [S8] used a cohesion energy of $\varepsilon^* = 28.87$.

In the present work, a model for the solid–fluid interaction was derived from quantum mechanical (QM) data that was taken from Xu et al. [S6] for the systems CH_2–Fe and CH_3–Fe. The data of the system CH_2–Fe were used for the interaction between the surface particles and the chain particles in the middle (excluding end-groups) of the Lennard–Jones (LJ) chain fluid. The solid–fluid parameters for the end-groups of the LJ chain fluid as well as for the LJ fluid were calculated from the system CH_2–Fe. Xu et al. [6] report interaction energies as well as corresponding configurational data which were used here to adjust the parameters σ and ε of a LJ 9–6 potential.

For this purpose, a single particle of each type was placed above a (100) surface of a bcc structured solid. This configuration was used to adjust the parameters σ^* and ε^* such that a single fluid particle on a surface has the same potential energy as given by Xu et al. [S6] and that the force perpendicular to the surface is zero ($F_z = 0$). This procedure follows the force matching method [S9], which has been applied for the mapping of solid–fluid interaction energies as iterative procedure with multiple QM calculations [S10] or with single QM calculations [S11] (as done in the present work in a simplified form). The LJ 9–6 potential was already used as potential for solid–fluid interactions in a previous study [S5] and was favored over the LJ 12–6 potential due to better fitting of the results. The final values used in the simulations are reported in Table S1.

* Corresponding author: Simon STEPHAN, E-mail: simon.stephan@mv.uni-kl.de

Table S1 Reduced solid–fluid interaction parameters (with respect to the fluid–fluid interaction parameters) used with the 9–6 LJ potential.

—	Methane	Decane	Decane
—	—	Middle group	End group
σ^*	0.56	0.58	0.67
ε^*	35.86	17.28	7.17

2 Force contributions

Figure S1 shows the results for the contributions to the total force on the indenter, i.e. the contribution from the indenter–substrate interactions.

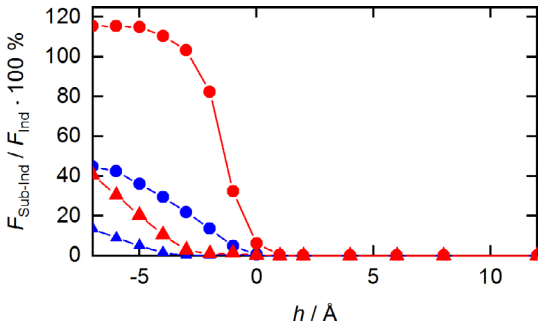

Fig. S1 Ratio of the force contribution to the forces on the indenter sampled in the quasi-stationary regime as a function of the gap heights h: Forces in z- (up-triangles) and y-direction (right-triangles). The quantity $F_{Sub-ind}/F_{Ind}$ indicates the contribution of the indenter–substrate interactions of the total force on the indenter. Results for both lubricated cases: Methane (red) and decane (blue). Lines are a guide for the eye.

3 Temperature and pressure in the lubrication gap

Figure S2 shows the results for the temperature profiles in the lubrication gap.

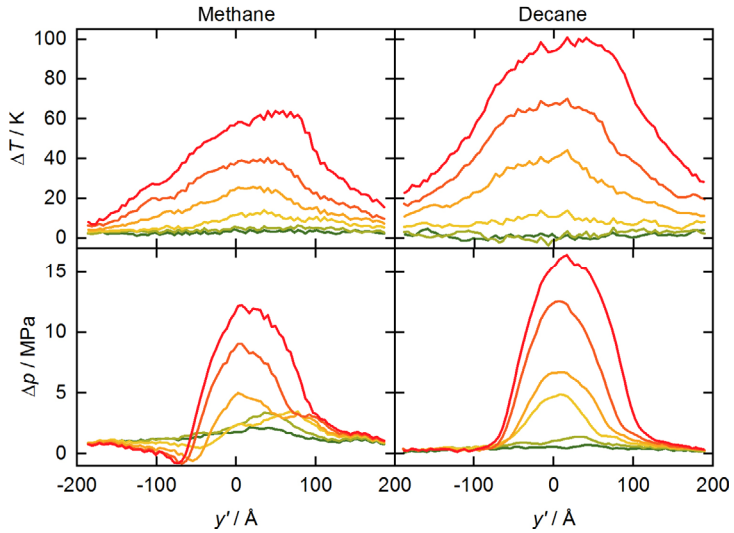

Fig. S2 Temperature and pressure profiles of the fluid in the lubrication gap with respect to the moving coordinate system (Fig. 2 in the main body of this work): Temperature profiles (top); pressure profiles (bottom). Results shown for h = −6, −4, −2, 0, 4, 8 Å (top to bottom). The left column gives the results for the methane simulations; the right column gives the results for the decane simulations. Data was sampled during the quasi-stationary phase (Fig. 4 in the main body of this work).

4 Computational aspects of simulations

The simulations were carried out on the Elwe supercomputer at the RHRK of the TU Kaiserslautern. For the simulations, Intel E5-2670 processors with a memory of 64 GB were used. Each simulation ran on 16 CPUs with 16 cores each (total: 256 cores). The simulations carried out in this work were computationally expensive due to the large number of particles and, which is also important, due to complexity of the interaction potentials. In particular, the embedded atom model (EAM) potential requires a lot of computational power. As only a single equilibration and indentation had to be carried out for each considered fluid, the bulk part of the computer time was spent on the scratching simulations. Each simulation at a given gap height, required around 22×10^3 CPUh. The decane simulations were computationally slightly more expensive due to the larger number of interaction sites and, in particular, the smaller time step. Here, each simulation required around 50×10^3 CPUh.

References

[S1] Stephan S, Dyga M, Urbassek H, Hasse H. The influence of lubrication and the solid–fluid interaction on thermodynamic properties in a nanoscopic scratching process. *Langmuir* **35**: 16948–16960 (2019)

[S2] Berro H, Fillot N, Vergne P. Molecular dynamics simulation of surface energy and ZDDP effects on friction in nano-scale lubricated contacts. *Tribol Int* **43**: 1811–1822 (2010)

[S3] Jabbarzadeh A, Atkinson J D, Tanner R I. Effect of the wall roughness on slip and rheological properties of hexadecane in molecular dynamics simulation of Couette shear flow between two sinusoidal walls. *Phys Rev E* **61**: 690–699 (2000)

[S4] Savio D, Fillot N, Vergne P, Hetzler H, Seemann W, Morales-Espejel G. A multiscale study on the wall slip effect in a ceramic–steel contact with nanometer-thick lubricant film by a nano-to-elastohydrodynamic lubrication approach. *J Tribol* **137**: 031502 (2015)

[S5] Ta T D, Tieu A K, Zhu H, Kosasih B. Adsorption of normal-alkanes on Fe (110), FeO (110), and Fe_2O_3 (0001): Influence of iron oxide surfaces. *J Phys Chem C* **119**: 12999–13010 (2015)

[S6] Xu L, Kirvassilis D, Bai Y, Mavrikakis M. Atomic and molecular adsorption on Fe (110). *Surf Sci* **667**: 54–65 (2018)

[S7] Zheng X, Zhu H, Tieu A K, Kosasih B. A molecular dynamics simulation of 3D rough lubricated contact. *Tribol Int* **67**: 217–221 (2013)

[S8] Chang W Y, Fang T H, Fang C N. Molecular dynamics on interface and nanoscratch mechanisms of alkanethiol self-assembled monolayers. *J Phys Chem B* **113**: 14994–15001 (2009)

[S9] Ercolessi F, Adams J B. Interatomic potentials from first-principles calculations: The force-matching method. *Europhys Lett* **26**: 583–588 (1994)

[S10] Kong L T, Denniston C, Müser M H, Qi Y. Non-bonded force field for the interaction between metals and organic molecules: A case study of olefins on aluminum. *Phys Chem Chem Phys* **11**: 10195–10203 (2009)

[S11] Bolton K, Bosio, Hase W L, Schneider W F, Hass K C. Comparison of explicit and united atom models for alkane chains physisorbed on α-Al_2O_3 (0001). *J Phys Chem B* **103**: 3885–3895 (1999)