Exploring Lubricant Chemistry: From Molecular Dynamics to Linear scaling DFT

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Lubricants are essential tools in enhancing efficiency and reducing machinery wear and tear. The lubricant industry's value exceeded $134.65 billion in 2022. However, understanding the intricate interplay and microscopic behavior of lubricants with additives and surfaces remains a complex challenge, often leading to a trial-and-error approach in development. Computational simulations offer a promising avenue to unravel the intricate chemistry involved, ultimately enabling the design of superior lubricants.

In this study, we employ a spectrum of simulations, starting with molecular dynamics simulations of a bulk mixture of di(2-ethylhexyl) sebacate (DEHS) and di(2-ethylhexyl) adipate (DEHA) esters and of a confined hydrocarbon, 9,10-dimethyloctadecane, a significant component of the industrially important PAO2 lubricant. These simulations are conducted between Hematite [001] slabs, investigating various operational conditions using two distinct force fields, LOPLS-AA and ReaxFF.

Subsequently, we delve into more precise yet computationally intensive quantum mechanical simulations to probe the interaction between Zinc dialkyldithiophosphates (ZDDP), a common class of lubricant additives, and a [001] Hematite surface. Our approach includes density functional methods including linear scaling DFT with ONETEP to explore phase space and nudged-elastic band calculations to identify potential reaction pathways. Our primary objective is to gain insights into the chemical behavior of this complex mixture, with a particular focus on the impact of confinement on lubricant rheological properties and the degradation patterns of ZDDP.

Our findings reveal good agreement between L-OPLS-AA molecular dynamics simulations and experimental data for both bulk and confined systems. In contrast, ReaxFF tends to overestimate viscosities but provides superior descriptions of Hematite structure and density. We posit that the computational methods and workflow outlined here hold promise for simulating combinations of lubricants, additives, and surfaces, shedding light on the intricate microscopic behavior of these technologically important yet poorly understood challenging systems.