MOLECULAR DYNAMICS OF HYDROCARBON LUBRICANTS UNDER EXTREME PRESSURES: ATOMISTIC INSIGHTS INTO THE FREE VOLUME ANSATZ

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ABSTRACT

Fluid lubrication is one of the oldest technological measures to reduce friction and wear of materials in moving contacts. Nevertheless, the properties of liquids under tribological load are still not well understood. Lubricants in tribological contacts experience extreme conditions such as high temperature and pressure, high shear rates, as well as high confinement, especially in the boundary lubrication regime. Thus the tribologically relevant lubricant properties -- in particular the viscosity -- can differ considerably from expectations based on empirical extrapolations from normal conditions. The resulting lack of predictability presents a serious obstacle for the optimization of lubricated mechanical systems with respect to lifetime and energy consumption.

In this work, we show that the pressure induced viscosity variations of oil based lubricants can be quantitatively understood by identifying the underlying molecular transport phenomena by means of molecular simulations and theoretical modelling using tools of statistical mechanics. We present a molecular dynamics simulations study of the viscosities and self-diffusion coefficients of different hydrocarbon fluids (molecular weights from 170 to 565 g/mol, Fig.1(a-e)) under extreme pressures and elevated temperatures (~1GPa and 500K). This results in a physically motivated expression for the viscosity at low shear rates as a function of density and three characteristic fluid structure parameters. The key ingredients of this model are, on the one hand, an analytical extension of the free volume approach for molecular self-diffusion [1] to complex unisotropic molecules, and on the other hand, a quantitatively predictive definition of the molecules' Stokes radius [2].
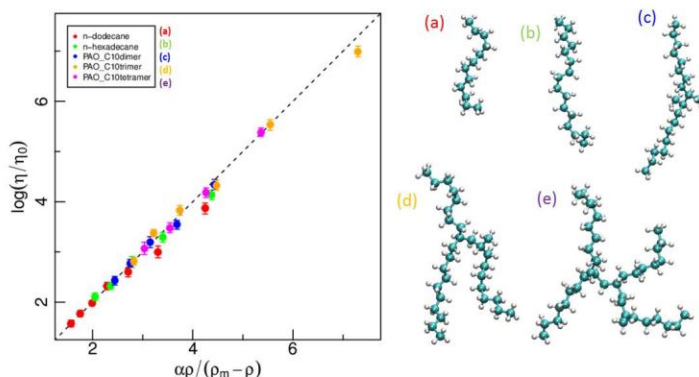

Fig.1 Scaling law for high pressure viscosities of complex hydrocarbons from molecular dynamics simulations

Based on the identified microscopic picture of the self-diffusion process, we further discuss the conditions which we expect to lead to a breakdown of either the free-volume ansatz or the Einstein-Stokes relation, and thus the limits of applicability of free-volume based viscosity models.

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