Viscosity calculation using molecular dynamics simulations – WTC 2021, Lyon

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Improved lubricants have a great potential to reduce the energy consumption in engine related industries. A limitation for the development of lubricants emerges from the missing knowledge of relevant fluid properties over the wide range of pressures and temperatures in application. Molecular dynamics simulations can play a major role in obtaining these properties, in particular the viscosity. While numerous computational methods for the viscosity calculation exist, their applicability strongly depends on the fluid composition and thermodynamic state (pressure, temperature). This study gives a comparison for the PAO4 lubricant under high pressures.

Keywords: Tribology, Lubricants, Viscosity, Green-Kubo, Stokes-Einstein

1. Introduction

Over the recent decades, molecular dynamics (MD) simulations became an established method to calculate material properties, with viscosity being a key property for the design of lubricants. Due to the short timescale of MD simulations, the viscosity calculation becomes increasingly challenging for more viscous, i.e. slower responding systems [1].
In this study, different viscosity calculation methods are examined regarding their applicability to the lubricant base oil PAO4 at high pressures.

2. Methods

2.1. Basic equations
When simulating at equilibrium (EMD), the Green-Kubo- (GK) or the Stokes-Einstein-relation (SE) can be applied for the shear viscosity computation.
While the GK equation

$$\eta_{GK} = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(t_0) P_{\alpha\beta}(t_s) \rangle dt_s$$

is based on the autocorrelation of the pressure tensor

$$P_{\alpha\beta}(t) = \frac{1}{V} \sum_{i=1}^{N} m_i v_{i,\alpha} v_{i,\beta} + \frac{1}{V} \sum_{i=1}^{N} r_{i,\alpha} f_{i,\beta}$$

the SE equation

$$\eta_{SE} = \frac{k_B T}{4\pi R_h D}$$

necessitates the computation of the self-diffusion coefficient

$$D = \lim_{t\to\infty} \left(\frac{1}{6t} \left\langle \frac{1}{N} \sum_{i=1}^{N} (r_i(t) - r_i(0))^2 \right\rangle \right)$$

and the hydrodynamic molecular radius R_h [2].
Additional methods exist for non-equilibrium molecular dynamics (NEMD) simulations. When imposing a shear rate $\dot{\gamma} = dv_x/dz$ on the liquid, the shear viscosity can be computed as

$$\eta_{NEMD} = -\frac{1}{\dot{\gamma}} \langle P_{xz} \rangle.$$

2.2. Molecular model (PAO4)
The examined base oil PAO4 consists of C_{10}-trimer, -tetramer and -pentamer molecules (Figure 1). To reduce simulation time, a slightly adapted form of the united-atom model TraPPE is used [3].

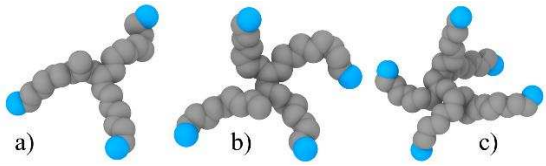

Figure 1: C_{10}-Trimer a), -tetramer b) and -pentamer c), visualized with United-atoms CH_3 (blue) and CH, CH_2 (grey).

2.3. Shear viscosity results
To reduce the variability of the results from the GK-approach, the time decomposition method is applied [4]. The same trajectory averaging is applied for the results of the Stokes-Einstein relation (Figure 2).

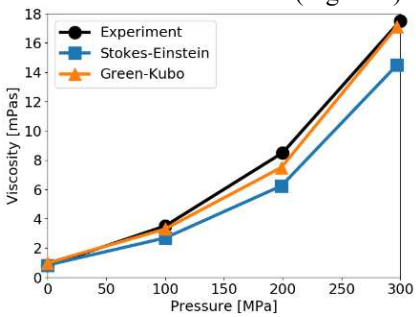

Figure 2: Results for the shear viscosity from experiment (black), SE (blue) and GK (orange) relation at a temperature of 150°C and pressures up to 300MPa.

3. Discussion

To evaluate the efficiency of the different viscosity calculation methods, their accuracy and computing time requirements are compared. With a similar time of convergence, the two EMD methods both show a good agreement with experimental results up to viscosities of 17.5 mPas. The limitations are explored for increasing viscosities due to higher pressure and lower temperature. Finally, the EMD results will also be compared to NEMD viscosity calculations.

4. References

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