Evaluation of methods for viscosity simulations of lubricants at different temperatures and pressures: a case study on PAO-2 - Supporting Information

Dimitrios Mathas\textsuperscript{1}, Walter Holweger\textsuperscript{3}, Marcus Wolf\textsuperscript{2}, Christof Bohnert\textsuperscript{2}, Vasilios Bakolas\textsuperscript{2}, Joanna Procelewska\textsuperscript{2}, Ling Wang\textsuperscript{3}, Scott Bair\textsuperscript{4}, and Chris-Kriton Skylaris\textsuperscript{1}\textsuperscript{*}

\textsuperscript{1}Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK
\textsuperscript{2}Schaeffler Technologies AG & Co. KG, Herzogenaurach, Germany
\textsuperscript{3}Mechanical Engineering Department, University of Southampton, Highfield, Southampton SO17 1BJ, UK
\textsuperscript{4}Center for High-Pressure Rheology, George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, 30332-0405, USA

\textsuperscript{*}Corresponding Author: Chris-Kriton Skylaris, Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK. Email: C.Skylaris@soton.ac.uk

Molecular Dynamics

The process of a molecular dynamics simulation is the discretized time evolution of atomic motion using Newton’s second law of motion, given inter-atomic potentials. The associated potential energy $U(\mathbf{r})$ is equal to the negative gradient of the time-varying force between atoms $F_i(t)$. This force causes an acceleration, which can be integrated with respect to time, in order
to give the velocity and the positions according to Newton’s second law of motion:

$$\mathbf{F}_i(t) = m\mathbf{\ddot{r}}_i(t) = -\frac{\partial U(r^K)}{\partial r_i}$$  \hspace{1cm} (1)

Here, $m$ is mass, $r^K$ are the positions of $K$ atoms that define the potential interactions of the system and $r_i$ is the position of each atom. Theoretically, the inter-atomic force must be calculated from the interactions of all other atoms. Unfortunately, this is very time consuming and thus a cut-off distance is employed. This distance limits the interactions to be only between the nearest neighboring atoms in the force evaluation. In order to calculate the time evolution of a system, numerical integration is used, given a timestep $\delta t$. The analytical expressions for the terms of the potential energy function (chosen in this work) are the following:

$$U_{\text{bond}} = \sum_{\text{bonds}} k_{i}^{\text{bond}} (r_i - r_0)^2$$ \hspace{1cm} (2)

$$U_{\text{angle}} = \sum_{\text{angles}} k_{i}^{\text{angle}} (\theta_i - \theta_0)^2$$ \hspace{1cm} (3)

$$U_{\text{dihedral}} = \sum_{\text{dihedrals}} k_{i}^{\text{dihedrals}} [1 + \cos (n_i \phi_i - \delta_i)]$$ \hspace{1cm} (4)

$$U_{\text{nonbond}} = \sum_{i} \sum_{j \neq i} 4 \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{i} \sum_{j \neq i} \frac{q_i q_j}{4 \pi D r_{ij}}$$ \hspace{1cm} (5)

Where $k_{i}^{\text{bond}}$, $k_{i}^{\text{angle}}$, $k_{i}^{\text{dihedrals}}$, $r_0$, $\theta_0$, $n_i$, $\delta_i$, $\epsilon_{ij}$, $\sigma_{ij}$, $q_i$ and $q_j$ are constants that depend on the molecular system examined and the chosen force field, while $D$ is the dielectric constant in vacuum. The selection of appropriate values for these parameters is of great importance, in order to describe molecular interactions, and the development of force fields is an established research field.

The LOPLS-AA force field, an all-atom force field that treats each atom explicitly, includes values for the above-mentioned force field parameters. For the LOPLS-AA force field, $U_{\text{dihedral}}$ is specified as:

$$U_{\text{dihedral}} = \frac{1}{2} K_1 [1 + \cos (\phi)] + \frac{1}{2} K_2 [1 - \cos (2 \phi)] + \frac{1}{2} K_3 [1 + \cos (3 \phi)] + \frac{1}{2} K_4 [1 - \cos (4 \phi)]$$ \hspace{1cm} (6)
Where, $K_1, K_2, K_3, K_4$ are the dihedral force constants equal to $2k_{dihe}$ and $\phi$ is the dihedral angle between four atoms.

The following tables (Table 1 - 5) show the L-OPLS-AA parameters used in this work:

Table 1: Bonding parameters 9,10-dimethyloctadecane L-OPLS-AA

| Parameter | Value ($\text{kcal mol}^{-1}$Å$^2$) | Type | $r_0$ (Å) |
|-----------|----------------------------------|------|-----------|
| $k_{\text{bond}}^1$ | 268.0 | C-C | 1.529 |
| $k_{\text{bond}}^2$ | 340.0 | C-H | 1.090 |

Table 2: Angle parameters 9,10-dimethyloctadecane L-OPLS-AA

| Parameter | Value ($\text{kcal mol}^{-1}$ rad$^2$) | Type | $\theta_0$ (deg) |
|-----------|--------------------------------------|------|-----------------|
| $k_{\text{angle}}^1$ | 58.35 | C-Ć-C | 112.7 |
| $k_{\text{angle}}^2$ | 33.00 | H-Ć-H | 107.8 |
| $k_{\text{angle}}^3$ | 37.50 | C-Ć-H | 110.7 |

Table 3: Dihedral parameters 9,10-dimethyloctadecane L-OPLS-AA

| C-C-C-C torsion | Parameter | Value (kcal/mol) |
|-----------------|-----------|-----------------|
| $K_1$ | 0.64469262386 |
| $K_2$ | -0.2143420172 |
| $K_3$ | 0.1782194073 |
| $K_4$ | 0.000 |

| C-C-C-H torsion, H-C-C-H torsion | Parameter | Value (kcal/mol) |
|----------------------------------|-----------|-----------------|
| $K_1$ | 0.000 |
| $K_2$ | 0.000 |
| $K_3$ | 0.300 |
| $K_4$ | 0.000 |
Table 4: Dihedral parameters with CH- group for 9,10-dimethyloctadecane L-OPLS-AA

| CH-C-C-C torsion,  
| C-C-CH-C torsion,  
| C-CH-CH-C torsion,  
| CH-CH-C-C torsion | Parameter | Value (kcal/mol) |
|-------------------|-----------|------------------|
|                   | $K_1$     | 1.300            |
|                   | $K_2$     | -0.050           |
|                   | $K_3$     | 0.200            |
|                   | $K_4$     | 0.000            |

Table 5: Non-bonded parameters 9,10-dimethyloctadecane L-OPLS-AA

| Atom | Description | $\varepsilon$ (kcal/mol) | $\sigma$ (Å) | $q$ (e) |
|------|-------------|--------------------------|--------------|---------|
| C    | CH$_3$      | 0.066                    | 3.50         | -0.222  |
| C    | CH$_2$      | 0.066                    | 3.50         | -0.148  |
| C    | CH           | 0.066                    | 3.50         | -0.060  |
| H    | H$_3$-C     | 0.030                    | 2.50         | 0.074   |
| H    | H$_2$-C     | 0.026                    | 2.50         | 0.074   |
| H    | H-C          | 0.030                    | 2.50         | 0.060   |

For the GAFF2-AA force field, $U_{\text{dihedral}}$ is specified as:

$$U_{\text{dihedral}} = \sum_{i=1}^{m} k_i^{\text{dih}} \left[ 1 + \cos \left( n_i \phi_i - \delta_i \right) \right]$$  \hspace{1cm} (7)

Where, $k_i^{\text{dih}}$ is the dihedral force constant ($m$ in total), $n_i$ is the multiplicity of the function and $\delta_i$ is the phase shift.

The following tables (Table 6 - 9) show the GAFF2-AA parameters used in this work:
Table 6: Bonding parameters 9,10-dimethyloctadecane GAFF2-AA

| Parameter | Value \( \text{(- kcal mol}^{-1}\text{Å}^2) \) | Type | \( r_0 \) (Å) |
|-----------|---------------------------------|------|-------------|
| \( k_{\text{bond}} \) | 232.52                          | C-C  | 1.538       |
| \( k_2^{\text{bond}} \) | 375.92                          | C-H  | 1.097       |

Table 7: Angle parameters 9,10-dimethyloctadecane GAFF2-AA

| Parameter | Value \( \text{(- kcal mol rad}^{-2}) \) | Type | \( \theta_0 \) (deg) |
|-----------|---------------------------------|------|-----------------|
| \( k_1^{\text{angle}} \) | 64.888                          | C-\( \hat{C} \)-C | 111.51          |
| \( k_2^{\text{angle}} \) | 38.960                          | H-\( \hat{C} \)-H | 107.58          |
| \( k_3^{\text{angle}} \) | 46.816                          | C-C-\( \hat{C} \) | 109.80          |

Table 8: Dihedral parameters 9,10-dimethyloctadecane GAFF2-AA

C-C-C-C torsion, \( m=3 \)

| Parameter | Value (kcal/mol) | Parameter | Value | Parameter | Value (deg) |
|-----------|------------------|-----------|-------|-----------|-------------|
| \( k_1^{\text{dihed}} \) | 0.13             | \( n_1 \) | 3     | \( \delta_1 \) | 0.0         |
| \( k_2^{\text{dihed}} \) | 0.29             | \( n_2 \) | 2     | \( \delta_2 \) | 180.0       |
| \( k_3^{\text{dihed}} \) | 0.11             | \( n_3 \) | 1     | \( \delta_3 \) | 0.0         |

C-C-C-H torsion, \( m=1 \)

| Parameter | Value (kcal/mol) | Parameter | Value | Parameter | Value (deg) |
|-----------|------------------|-----------|-------|-----------|-------------|
| \( k_1^{\text{dihed}} \) | 0.08             | \( n_1 \) | 3     | \( \delta_1 \) | 0.0         |

H-C-C-H torsion, \( m=1 \)

| Parameter | Value (kcal/mol) | Parameter | Value | Parameter | Value (deg) |
|-----------|------------------|-----------|-------|-----------|-------------|
| \( k_1^{\text{dihed}} \) | 0.12             | \( n_1 \) | 3     | \( \delta_1 \) | 0.0         |

Table 9: Non-bonded parameters 9,10-dimethyloctadecane GAFF2-AA

| Atom | \( \epsilon \) (kcal/mol) | \( \sigma \) (Å) |
|------|---------------------------|-----------------|
| C    | 0.1078                    | 3.39770953124   |
| H    | 0.0208                    | 2.60017699876   |

For GAFF2-AA the atomic charges were calculated with the semi-empirical Austin Model 1 - Bond Correction Charges (AM1-BCC) model. The following table (Table 10) shows the charges of the 9,10-dimethyloctadecane molecule.
Table 10: Atomic charges 9,10-dimethyloctadecane GAFF2-AA

| Atom | $q$ (e) | Atom | $q$ (e) |
|------|---------|------|---------|
| C1   | -0.0607 | H12  | 0.033033 |
| C2   | -0.0607 | H13  | 0.033033 |
| C3   | -0.0744 | H14  | 0.033033 |
| C4   | -0.0744 | H15  | 0.033033 |
| C5   | -0.0774 | H16  | 0.033033 |
| C6   | -0.0774 | H17  | 0.0412  |
| C7   | -0.0901 | H18  | 0.0412  |
| C8   | -0.0901 | H19  | 0.0412  |
| C9   | -0.0814 | H20  | 0.0412  |
| C10  | -0.0814 | H21  | 0.0387  |
| C11  | -0.0794 | H22  | 0.0387  |
| C12  | -0.0794 | H23  | 0.0387  |
| C13  | -0.0804 | H24  | 0.0387  |
| C14  | -0.0804 | H25  | 0.0397  |
| C15  | -0.0794 | H26  | 0.0397  |
| C16  | -0.0794 | H27  | 0.0397  |
| C17  | -0.0804 | H28  | 0.0397  |
| C18  | -0.0804 | H29  | 0.0397  |
| C19  | -0.0921 | H30  | 0.0397  |
| C20  | -0.0921 | H31  | 0.0397  |
| H1   | 0.0477  | H32  | 0.0397  |
| H2   | 0.0477  | H33  | 0.0382  |
| H3   | 0.0387  | H34  | 0.0382  |
| H4   | 0.0387  | H35  | 0.0382  |
| H5   | 0.0387  | H36  | 0.0382  |
| H6   | 0.0387  | H37  | 0.0327  |
| H7   | 0.0387  | H38  | 0.0327  |
| H8   | 0.0387  | H39  | 0.0327  |
| H9   | 0.0387  | H40  | 0.0327  |
| H10  | 0.0387  | H41  | 0.0327  |
| H11  | 0.033033| H42  | 0.0327  |

The above atoms form the following bonds: C1-C2, C1-C3, C1-C7, C2-C4, C2-C8, C4-C6, C6-C10, C10-C12, C12-C14, C14-C16, C16-C18, C18-C20, C3-C5, C5-C9, C9-C11, C11-C13, C13-C15, C15-C17, C17-C19, C1-H1, C3-H3, C3-H4, C5-H7, C5-H8, C9-H17, C9-H18, C11-H21, C11-H22, C13-H25, C13-H26, C15-H29, C15-H30, C17-H33, C17-H34, C19-H37, C19-H38, C19-H39, C7-H11, C7-H12, C7-H13, C2-H2, C8-H14, C8-H15, C8-H16, C4-H5, C4-H6, C6-H9, C6-H10, C10-H19, C10-H20, C12-H23, C12-H24, C14-H27, C14-H28, C16-H31, C16-H32, C18-H35, C18-H36, C20-H40, C20-H41.
and C\textsubscript{20}-H\textsubscript{42}.

**Calculation of Zero Shear Viscosity with Equilibrium Molecular Dynamics**

Let us define the autocorrelation function of the pressure tensor as a function of simulation time:

$$C_{\alpha\beta}(t') = \langle P_{\alpha\beta}(0) P_{\alpha\beta}(t') \rangle$$

(8)

According to the ergodic hypothesis, the correlation of $P_{\alpha\beta}$ is obtained by an ensemble average over time in the limit $t_{\text{max}} \to \infty$ ($t'$ is a time interval on which the correlation function depends):

$$C_{\alpha\beta}(t') = \frac{1}{t_{\text{max}} - t'} \int_{0}^{t_{\text{max}} - t'} P_{\alpha\beta}(t'') P_{\alpha\beta}(t'' + t') \, dt''$$

(9)

In the case of a molecular dynamics (MD) simulation, where we are dealing with discretised quantities, $t_{\text{max}}$ is the total simulation time. The discretised form of eq. 9 is:

$$C_{\alpha\beta}(t') = \frac{1}{t_{\text{max}} - (t' - \delta t)} \left( \sum_{t''=0}^{t_{\text{max}} - t'} P_{\alpha\beta}(t'') P_{\alpha\beta}(t'' + t') \right) \delta t$$

(10)

The MD simulation timestep is $\delta t$ (usually one femtosecond or less). As a result, we have that:

$$t' = N\delta t$$

(11)

$$t_{\text{max}} = N_{\text{max}} \delta t$$

(12)

Where $N$ and $N_{\text{max}}$ are integer counters of simulation time steps. As a result, eq. 10 becomes:

$$C_{\alpha\beta}(N\delta t) = \frac{1}{N_{\text{max}} - (N - 1)} \sum_{t''=0}^{(N_{\text{max}} - N)\delta t} P_{\alpha\beta}(t'') P_{\alpha\beta}(t'' + N\delta t)$$

(13)

We can divide $N_{\text{max}}$ into increasing time intervals by introducing an integer, $k$ and an autocorrelation time interval, $d\delta t$ such that $N_{\text{max}} = k_{\text{max}} d$ and $k = 0, 1, 2, \ldots, \frac{N_{\text{max}}}{d}$, as we perform autocorrelation in $kd\delta t$ time intervals, up until the value of $N_{\text{max}}$. This process checks the convergence of viscosity with time and increases the correlation time that we can sample. As a result, the ACF becomes
a function of two variables, \( N \) and \( k \):

\[
C_{\alpha\beta}(N\delta t, kd\delta t) = \frac{1}{kd - (N - 1)} \sum_{t''=0}^{(kd-N)\delta t} P_{\alpha\beta,t''}P_{\alpha\beta,t''+N\delta t} \tag{14}
\]

Finally, if we define \( s \) as the sampling rate, i.e. every how many timesteps we sample pressure tensor values (for example if \( s = 10 \) we will sample at \( 0\delta t \), \( 10\delta t \), \( 20\delta t \), etc.) for use in autocorrelation, \( d = s \, p \) and eq. 14 becomes:

\[
C_{\alpha\beta}(N\delta t, ksp\delta t) = \frac{1}{kp - (N - 1)} \sum_{t''=0}^{(kp-N)\delta t} P_{\alpha\beta,t''}P_{\alpha\beta,t''+Ns\delta t} \tag{15}
\]

Where \( N = 0, 1, 2, \ldots, (p - 1) \), \( p \) terms in total, every \( s \) number of femtoseconds, the values of the pressure tensor are used, \( p \) is the total number of autocorrelation terms and can be defined as the number of times the pressure tensor function is correlated with itself (shifted image), \( d \) is the autocorrelation time (constant number, a multiple of \( \delta t \)), which represents a fraction of the whole simulation where autocorrelation is performed, \( C_{\alpha\beta} \) is the autocorrelation term of the pressure tensor, which is a measure of self-correlation of the pressure tensor that is then used to calculate viscosity, \( N \) is the correlation term index and \( k \) is the fraction index.

**Supplementary Figures**

In Figure 1 we present a plot of the autocorrelation function of the pressure tensor \( P_{xy} \) for 9,10-dimethyloctadecane at zero shear rate, 40 °C and 0.1 MPa, during the last 0.5 ns of the EMD simulation (39.5 to 40 ns). The average value of the ACF oscillation is \( 1.01 \times 10^{-4} \) when \( t \) tends to 0.2 ns (Figure 2a) and \( 4.76 \times 10^{-5} \) when \( t \) tends to 0.5 ns (Figure 2b), which means that the integrated ACF fluctuations do not contribute significantly to the viscosity estimate.
Figure 1: Autocorrelation function example of EMD simulation for 9,10-dimethyloctadecane at zero shear rate, 40 °C and 0.1 MPa. The ACF decays quite rapidly and as a result, only a fraction of the 0.5 ns time period is shown in the plot.

Figure 2: (a) Autocorrelation function fluctuation of EMD simulation for 9,10-dimethyloctadecane at zero shear rate, 40 °C and 0.1 MPa for the period of 0.1 to 0.2 ns. (b) Fluctuations at the autocorrelation period of 0.4 to 0.5 ns.

Figure 3 shows the velocity profile of a NEMD simulation, at a chosen shear rate of $10^8$ s$^{-1}$ for 9,10-dimethyloctadecane at ambient (0.1 MPa) and elevated pressures (0.5 and 1.0 GPa). The simulation box (across $y$) is divided into twenty equally spaced regions. Then, the velocity vector component ($x$ dimension) of atoms that exist in each region at a particular timestep is averaged, and then averaged again over different time intervals every 5 ps, to improve statistics during the 40 ns production run. The resulting velocity profile is linear, as described in simple Couette flow. To maintain the same shear rate in simulations at different pressures, the applied velocity at the top edge of the simulation box has to be adjusted accordingly, so as to take into account the volume change arising from each applied pressure. This difference can be seen near
the top edge (relative gap thickness = 1), where the lowest pressure (0.1 MPa) results in the
largest simulation box, thus requiring a slightly higher velocity. Additionally, instead of equally
spaced regions but in terms of actual distances, where the centre of the simulation box is taken
as reference point, the behavior is similar and can be seen in Figure 4.

Figure 3: Velocity profile example of 9,10-dimethyloctadecane, with $\dot{\gamma}$ equal to $10^8$ s$^{-1}$, at
three different pressure values, 0.1 MPa, 0.5 GPa and 1.0 GPa.

Figure 3: Velocity profile example of 9,10-dimethyloctadecane, with $\dot{\gamma}$ equal to $10^8$ s$^{-1}$, at
three different pressure values, 0.1 MPa, 0.5 GPa and 1.0 GPa.
Figure 4: Velocity profile example of 9,10-dimethyloctadecane, with $\dot{\gamma}$ equal to $10^8$ s$^{-1}$, at three different pressure values, 0.1 MPa, 0.5 GPa and 1.0 GPa. At each pressure, the centre of the simulation box is taken as reference point.