Supplementary material for

Predicting the pressure dependence of the viscosity of 2,2,4-trimethylhexane using the SAFT coarse-grained force field

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1. Uncertainty analysis of the results

1.1 Equilibrium (GK) Pressure fluctuations simulations

We first compute the autocorrelation functions and the running integrals (viscosity vs. correlation time) for each trajectory obtained from simulations. For each trajectory, three off-diagonal elements of the pressure tensor can be used to calculate the autocorrelation function hence the running integral of viscosity based on Eq.(8) and (10) of the main paper.

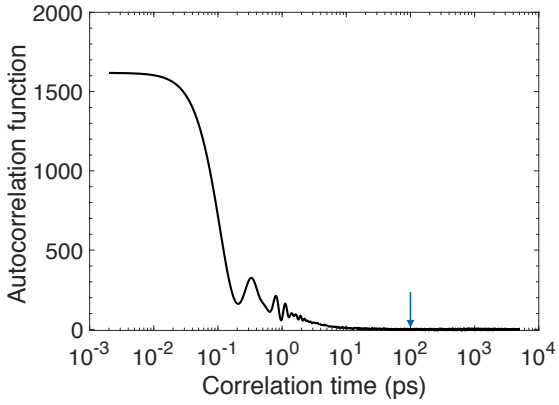


Figure S1. The averaged autocorrelation function (ACF) computed from off-diagonal elements of the pressure tensor of all trajectories using the Green-Kubo formula Eq.(10). Average pressure in this example is 150 MPa. The blue arrow marks the time after which the ACF is taken to be zero (100 ps).

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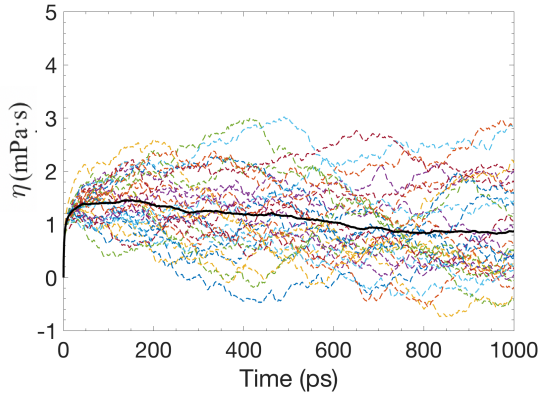


Figure S2. Viscosities (dashed colour lines) of the fluid against correlation time computed with Eq.(8), the average viscosity is represented by the black line. Average pressure in this example is 150 MPa.

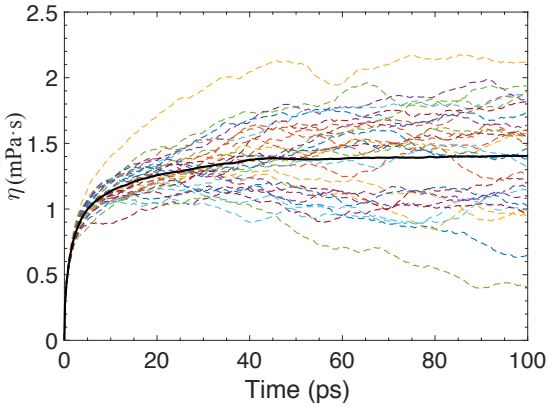


Figure S3. The running viscosity is truncated where the averaged ACF reaches zero (as indicated by the blue arrow in Fig. S1. Average pressure in this example is 150 MPa.

The averaged viscosity of all trajectories is calculated as a function of correlation time and is truncated at the point where the autocorrelation function reaches zero (see example in Fig. S1). We then fit the double-exponential function Eq. (11) and the power law function Eq. (12) respectively to the running viscosity and standard deviation.

After the fitting procedure, one obtains a curve that plateaus to a value that corresponds to the reported viscosity. The standard deviation of the measurement is obtained by fitting the standard deviations using Eq. (1) and evaluating it for the time employed in calculating the viscosity. For the 150 MPa case considered, the result is $\eta = 1.40$ mPa·s with an error of $\sigma = 0.43$ mPa·s, which corresponds to approximately 30% uncertainty.

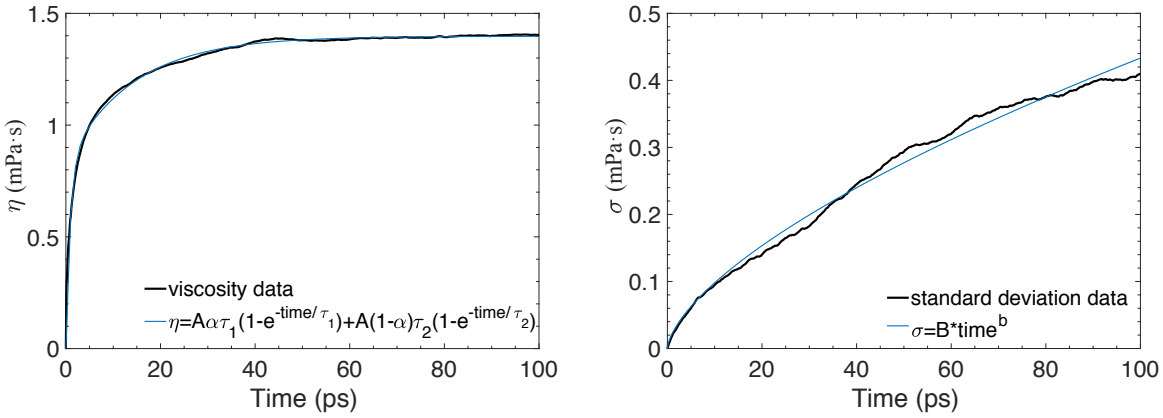


Figure S4. Post-processing scheme where Eq. (11) and (12) are fitted onto the average running viscosity (left figure) and error (right figure). For the particular example case of 150 MPa, the fitting parameters are A= 0.0513, α =17.4785, τ_1 = 0.9262, τ_2 = 14.0800. The plateau in the figure is where the final viscosity is read (η = 1.40 mPa·s) and the standard deviation (σ = 0.43 mPa·s) is read from the plot on the right at the corresponding measurement time (100 ps). For the 150 MPa case considered, the fitting parameters are B = 0.0222, b = 0.6452.

1.2. Non-equilibrium MD

At each pressure condition, we first obtain the weight factors for the data points at different cross accelerations, setting it to be inversely proportional to the GROMACS output - root mean square deviation (rmsd) of 1/η. A weighted linear fit is then applied to all the collected data points. The final viscosity read by extrapolating the linear fit to zero acceleration, i.e. equals to the intercept. The values in the final column represents the averaged standard deviation of all data points at each pressure.

Again, taking pressure at 150 MPa as an example, we obtained 3 data points at each cross acceleration ($\mathcal{A}$) for 9 different acceleration values; this is shown in Table S1. Along with 1/η, 1/η rmsd is reported from GROMACS, based on which the weight for individual data points are assigned. The raw data and its weighted linear fit are plotted in Fig. S5. We then calculate the standard deviation based for each data points according to Eq. (13), displayed again here:

$$\sigma_\eta^{\mathrm{NEMD}} = \frac{2}{s_{\max}}\sqrt{\frac{k_{\mathrm{B}}T\eta}{Vt_{\mathrm{a}}}}, \qquad \text{where} \quad s_{\max} = \mathcal{A}\frac{\rho}{\eta k}$$

From Section 3, we known that $s_{\max}$ is the maximum shear rate that can be calculated from the cross acceleration ($\mathcal{A}$), the density, the viscosity and the wave vector (k_z). Hence for the first data point in Table 3, knowing the density and box length (l_z) can be calculated as:

$$s_{\max} = \mathcal{A}\frac{\rho}{\eta k_z} = \mathcal{A}\frac{\rho}{\eta(2\pi/l_z)} = 0.001\mathrm{nm.ps}^{-2}\frac{812.764\mathrm{kg.m}^{-3}}{0.00129\mathrm{kg.ms}^{-1}(2\pi/9.228..\mathrm{nm})} = 9.255..\times 10^{-4}\ \mathrm{ps}^{-1}$$

Following which, knowing the temperature at 293.15K, system volume ($V = l_z^3$) and simulation time for each data point (t_a = 2000 ps), one can calculate the corresponding σ_η. The last two columns of Table S1 shows $s_{\max}$ and σ_η for each data points, allowing us to calculate the averaged σ_η under the pressure condition the data is collected. Using an extrapolation to zero shear acceleration, the result is η = 1.43 mPa·s, only 2% different from the viscosity obtained using GK method.

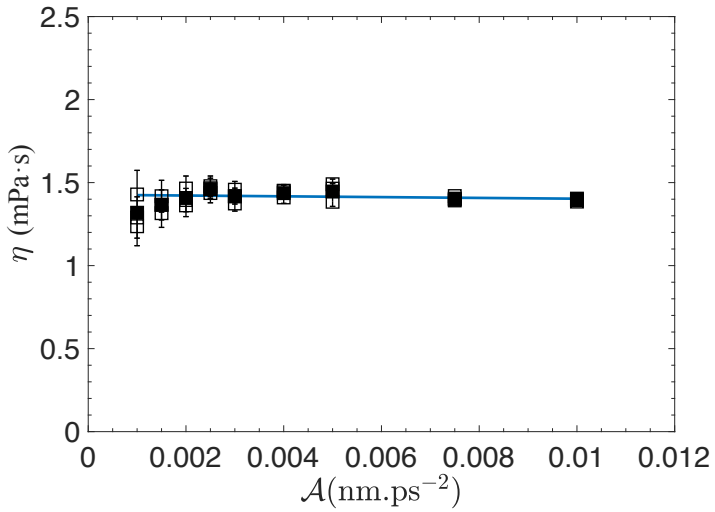


Figure S5. Viscosity (η) against shear acceleration ($\mathcal{A}$) at 150 MPa. The empty squares are the raw data, with error bars given by the values in the last column of Table 4. The filled squares are the averaged value at each shear acceleration. The raw data is linearly fitted (shown by the blue line), with the weight of each data points inversely proportional to the root mean square difference of 1/η reported from GROMACS. Viscosity is taken as the extrapolation to zero shear η = 1.43 mPa·s.

Table S1. Simulation GROMACS output, the maximum shear rate, and the calculated standard deviation for a total of 27 data points at 9 different cross accelerations under 150MPa.

$\mathcal{A}$ (nm.ps^{-2})	1/η rmsd (m.s.kg^{-1})	η (kg.m^{-1}.s^{-1})	weight	$s_{\max}$ (ps^{-1})	σ_η (kg.m^{-1}.s^{-1})
0.001	2013.170	1.29E-03	1	9.255E-04	1.245E-04
0.001	2010.280	1.43E-03	1	8.357E-04	1.451E-04
0.001	1921.950	1.24E-03	1	9.651E-04	1.170E-04
0.0015	1319.970	1.32E-03	1	1.361E-03	8.553E-05
0.0015	1406.130	1.42E-03	1	1.263E-03	9.570E-05
0.0015	1356.820	1.37E-03	1	1.311E-03	9.047E-05
0.002	1050.500	1.39E-03	2	1.712E-03	7.003E-05
0.002	1024.450	1.46E-03	2	1.631E-03	7.531E-05
0.002	1103.820	1.36E-03	2	1.752E-03	6.762E-05
0.0025	772.658	1.47E-03	2	2.036E-03	6.036E-05
0.0025	791.154	1.44E-03	2	2.077E-03	5.857E-05
0.0025	787.420	1.48E-03	2	2.018E-03	6.113E-05
0.003	669.212	1.46E-03	3	2.457E-03	4.985E-05
0.003	660.532	1.37E-03	3	2.606E-03	4.564E-05
0.003	671.869	1.42E-03	3	2.524E-03	4.789E-05
0.004	513.539	1.45E-03	4	3.298E-03	3.703E-05
0.004	478.105	1.45E-03	4	3.290E-03	3.715E-05
0.004	497.080	1.41E-03	4	3.385E-03	3.560E-05
0.005	406.980	1.38E-03	5	4.312E-03	2.769E-05
0.005	409.470	1.46E-03	5	4.078E-03	3.011E-05
0.005	414.613	1.49E-03	5	4.005E-03	3.093E-05
0.0075	260.913	1.42E-03	7	6.310E-03	1.916E-05
0.0075	277.153	1.40E-03	7	6.401E-03	1.875E-05
0.0075	274.894	1.39E-03	7	6.429E-03	1.863E-05
0.01	212.803	1.39E-03	9	8.616E-03	1.387E-05
0.01	208.763	1.40E-03	9	8.552E-03	1.402E-05

2. Process flow diagram of the simulations

<table>
<tr><td colspan="2">Fill a cubic simulation box</td></tr>
<tr><td colspan="2">Run simulation at NPT ensemble
1 million steps for equilibration run and 3 million steps for production run at 0.01ps per step
i.e. 10ns equilibration run and 30ns production run</td></tr>
<tr><td colspan="2">Select configuration
The selected configuration should have a box volume equal to the average volume during the 30 ns NPT production run.</td></tr>
<tr><td colspan="2">Run simulation at NPT ensemble
1 million steps for equilibration run at 0.01ps per step</td></tr>
<tr><td>EMD</td><td>NEMD</td></tr>
<tr><td>Run simulation at NVT ensemble
5ns production run for $P \leq 400$MPa and 10ns production run for $P > 400$MPa, all at 0.002ps per step.
Simulation repeated to obtain 10 independent trajectories.</td><td>Run simulation at NVT ensemble
2ns production run at 0.01ps per step. Simulation repeated at a minimum of 6 different cross-accelerations with values smaller than 0.1 $nm.ps^{-2}$.
At each acceleration, the simulation is ran 3 times when $P \leq 400$MPa and 6 times at $P > 400$MPa.</td></tr>
<tr><td>Collect off-diagonal pressure tensor values w.r.t. time
Obtain three tensor components (P_{xy}, P_{xz}, P_{yz}) for each trajectory and discard the first 1ns from each trajectory.</td><td>Record viscosity at each acceleration
Output “1/viscosity” values directly from g_energy feature in GROMACS.</td></tr>
<tr><td>Obtain the shear viscosity
Fit a double exponential function (Eq. 9) to the running integral and read the viscosity at time when the autocorrelation function reaches zero.</td><td>Obtain the shear viscosity
Apply a weighted linear fit to viscosity vs. acceleration diagram and read the intercept as viscosity.</td></tr>
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