

Supporting information for:
Refined Force Field for Liquid Sulfolane with
Particular Emphasis to Its Transport
Characteristics

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Determination of Gas-Phase DDEC6 Charges

Gas-phase DDEC6 charges^{S1} were obtained from single molecule quantum chemical gas-phase optimization, followed by wave-function determination, both of which were carried out in Gaussian 16.^{S2} This procedure is in contrast with the procedure used to obtain charges in ref S3. Subsequently in our procedure, charge-partitioning was carried out using Chargemol software^{S4} using the wavefunction file as input. The charges obtained were averaged over all atoms of the same atom-type to obtain average gas-phase DDEC6 charges given in Table S1.

Table S1: Single-molecule gas-phase atomic-site DDEC6 charges, $q(e)$, used in the MD run from which independent snapshots were chosen for liquid-phase DDEC6 charge calculation. These gas-phase DDEC6 charges were also used for total potential energy calculation for potential energy surfaces (PES) of the refined force field presented in Figure 2 of the main manuscript.

Atom type	q / e
SFO	1.21259
OFO	-0.62659
CS1	-0.32635
CS2	-0.12475
HC1	0.14217
HC2	0.09352

Charge Distribution Obtained in Liquid-Phase DDEC6

Charge Calculation

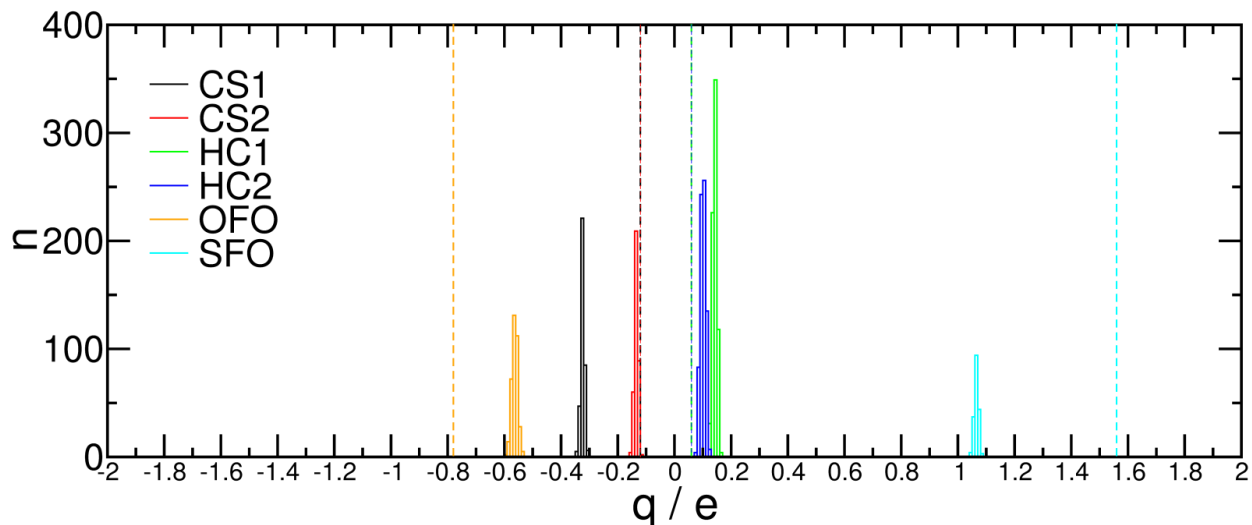


Figure S1: Distribution of charges, (q) according to atom types, obtained from seven liquid phase snapshots, energy minimized within quantum density functional theory. Subsequently, the electron density obtained thus, was used to derive atomic site charges. n is the count of a bin of width 0.01 e. Dashed lines represent the charges of the force field^{S3} from which the current force field was developed. Snapshots were chosen from the MD simulation as described in the main manuscript at temperature $T = 303$ K and pressure $p = 1$ bar. The narrow distributions of the site charges justify the use of a non-polarizable force field. Differences in the mean values of liquid phase site charges from the corresponding gas phase values indicates the need to derive charges from condensed phase simulations.

Bonded Parameters

The equilibrium values of bond lengths and angles of sulfolane were obtained from the geometry optimization of a single-molecule, at MP2/aug-cc-pvdz level of theory (see tables S2 and S3). The bond and angle force-constants were used as given in ref S3.

Table S2: Bond parameters used in the refined force field. Equilibrium bond-length r_0 (Å) and force-constant k_b (kJ·mol⁻¹·Å⁻²) of equation 1 in the main manuscript.

Bond type	r_0	k_b
SFO-OFO	1.497	10660.832
SFO-CS1	1.893	3941.328
CS1-CS2	1.534	2242.624
CS2-CS2	1.545	2242.624
CS1-HC1	1.099	2769.808
CS2-HC2	1.016	2769.808

Table S3: Angle parameters used in the refined force field. Equilibrium angle θ_0 (degree) and force-constant k_θ (kJ·mol⁻¹·rad⁻²) of equation 1 in the main manuscript.

Angle type	θ_0	k_θ
OFO-SFO-OFO	120.77	1941.38
OFO-SFO-CS1	109.34	1740.54
CS1-SFO-CS1	95.83	1631.76
CS2-CS1-SFO	104.46	1389.09
CS1-CS2-HC2	110.80	313.21
CS2-CS1-HC1	113.98	313.21
HC1-CS1-HC1	111.06	276.14
HC2-CS2-HC2	108.12	276.14
CS2-CS2-HC2	110.80	313.21
CS2-CS2-CS1	106.12	836.80
SFO-CS1-HC1	106.23	313.21

Additional MD Details

Table S4: Averaged box-sizes from NPT production from different force fields. Box-lengths for simulations using the refined force field at different temperatures and at pressure $p = 1$ bar are also reported. These box-sizes were used for NVT runs on which majority of the analyses were conducted.

Temperature	Force field	NPT averaged box-length (\AA)
303	Force field of ref S3	49.8647
303	OPLS	50.3709
303	This work	49.8082
313	This work	49.9531
323	This work	50.1071
348	This work	50.5048
373	This work	50.9340
398	This work	51.3757

Example of Block Average Calculation. Illustrated Via Density

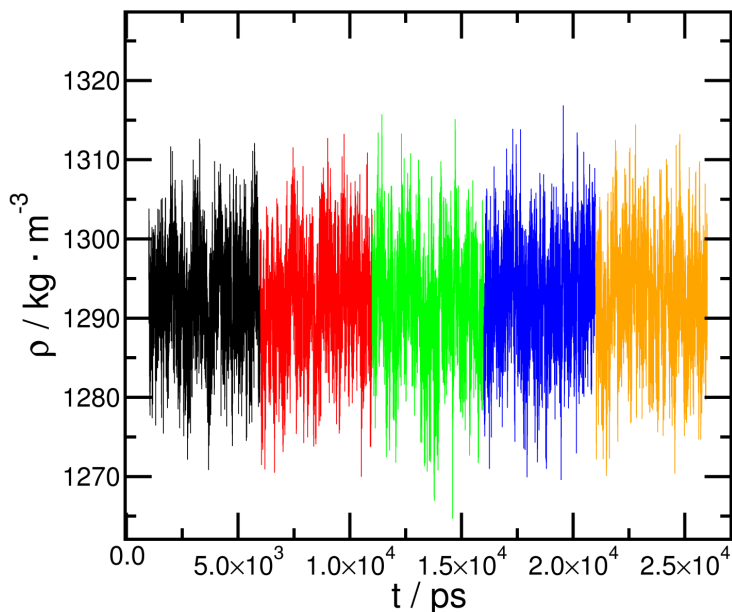


Figure S2: Density as a function of time (from 1 ns to 26 ns) of the NPT production run of the refined force field reported in this work. The run was conducted at temperature $T = 303$ K, and pressure $p = 1$ bar. Each block is represented by a different color. The blocks are assumed to be independent as in ref S5.

$$\text{Average density, } \rho = \frac{\sum_{i=1}^{N_{blocks}} \rho_{i,avg}}{N_{blocks}};$$

$$\text{Standard deviation on the average density is } U = \left(\frac{\sum_{i=1}^{N_{blocks}} (\rho_{i,avg} - \rho)^2}{N_{blocks}(N_{blocks}-1)} \right)^{1/2}$$

Here, $\rho_{i,avg}$ is the average density of block i , N_{blocks} is the number of blocks = 5 (in this case). Number of timesteps comprising each independent block, $S_{prod} = 5000$ density points (one per picosecond). ρ is the mean density averaged over individual blocks. ρ is reported along with calculated uncertainty U in an interval form in the main manuscript with a confidence level of 0.95 ($k=2$).

Additional Radial Distribution Function Plots

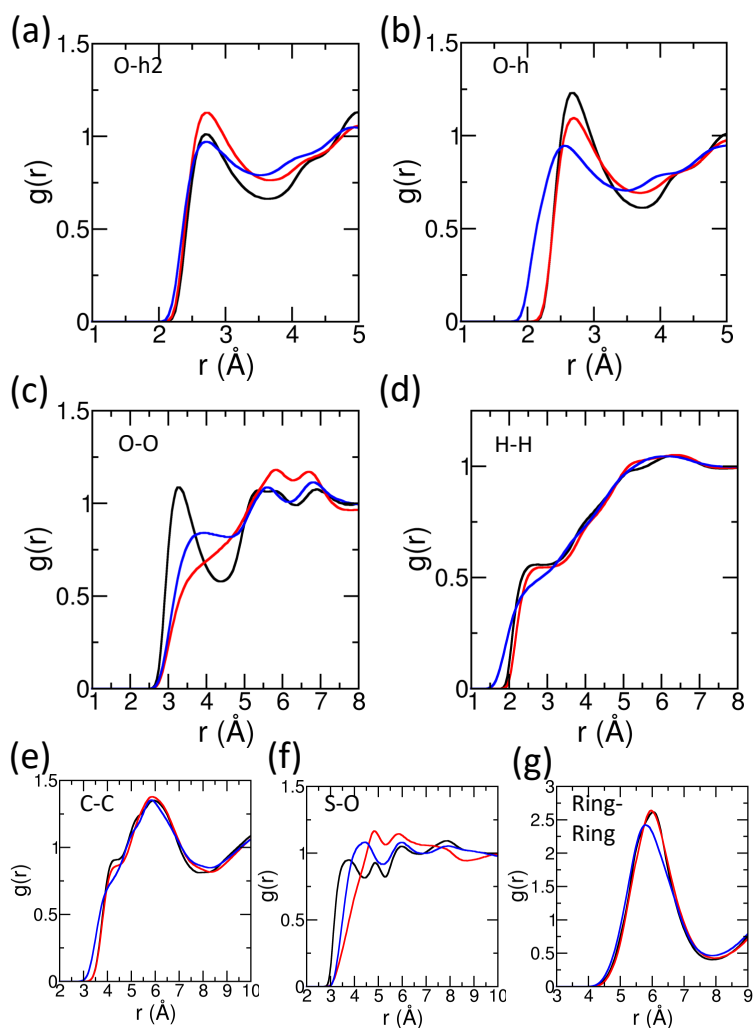


Figure S3: Intermolecular radial distribution function between the following groups of atoms - (a) OFO-HC2, (b) OFO-any H, (c) OFO-OFO, (d) any H-any H, (e) any C-any C, (f) SFO-OFO, and (g) Center of ring - Center of ring. Black - ref S3, red - OPLS, and blue - this work.

Details for Single-Molecule Volume Calculation

The volume of a single mp2/aug-cc-pvdz optimized molecule was calculated in a method similar to that in Ref. S6, i.e. a Monte-Carlo method for calculating volume was employed.

The volume calculation was carried out in the Gaussian 16^{S2} software, using the ‘volume’ keyword. The electron-density was obtained through a calculation performed using B3LYP/6-311++g(d,p) level of theory and basis-set. The convergence criterion requested was 10^{-6} for energy and 10^{-7} for RMS density. A density envelope used was 0.001 e/bohr³. Since, molecular volume of sulfolane was calculated only to obtain a rough estimate of its size, we do not report this number as a true estimate of its size.

Uncertainty Calculation for Heat of Vaporization

$$\text{Average heat of vaporization } \Delta H = \frac{\sum_{i=1}^{N_{sample}} \Delta H_{i,avg}}{N_{sample}};$$

$$\text{Standard deviation on the average heat of vaporization is } U = \left(\frac{\sum_{i=1}^{N_{sample}} (\Delta H_{i,avg} - \Delta H)^2}{N_{sample}(N_{sample}-1)} \right)^{1/2}$$

Here, $\Delta H_{i,avg}$ is the average heat of vaporization of independent run i , calculated from the average total energy of the sulfolane molecule $E_{gas,i}$ in the i^{th} run. N_{sample} is the number of independent runs = 3 (in this case). $S_{prod} = 30000$ is the number of total energy points per independent run (one every picosecond). E_{liq} , the average total energy of a sulfolane molecule in the liquid state, was obtained from a single NVT run in the respective force field and is a constant across the independent calculations of ΔH for a given force field. ΔH is the mean heat-of-vaporization averaged over three independent runs. ΔH with calculated uncertainty U is reported in an interval form in the main manuscript with a confidence level of 0.95 (k=2).

Calculation of Surface Tension - Details

To calculate surface tension, a pre-equilibrated cubic simulation box containing 800 molecules was stretched along the z-axis (150 Å) by approximately three times its size along the x or y-axis (≈ 50 Å). Surface tension was estimated from three independent NVT runs ($N_{sample} = 3$), of run length 10 ns each. i.e., $S_{prod} = 10000000$ timesteps. Three independent runs of

duration of 100 ns ($S_{prod} = 100000000$) was needed for the simulations using the force field of ref S3 to account for the time required for the various pressure components to equilibrate in this high viscosity force field. Components of the pressure tensor were saved at every timestep (1 fs). Surface tension, γ , was calculated using the relation $\gamma = l_z/4(2P_{zz} - P_{xx} - P_{yy})$ as in ref S7, where P_{xx} , P_{yy} and P_{zz} are the diagonal components of the stress tensor, and l_z is the length of the simulation box along the z -axis.

Shear Viscosity

Calculation of Shear Viscosity

The shear viscosity (η) was calculated from the Green-Kubo relation as given in ref S8 and defined in equation 1. Here, $P_{\alpha\beta}$ is the $\alpha\beta$ off-diagonal ($\alpha \neq \beta$) component of the pressure tensor. k_B is the Boltzmann constant, T is temperature, V is the volume of the system, and t time. An example for the pressure tensor correlation function is shown in Figure S4.

$$\eta(t) = \frac{V}{k_B T} \int_0^t \langle P_{\alpha\beta}(t') \cdot P_{\alpha\beta}(0) \rangle dt' \quad (1)$$

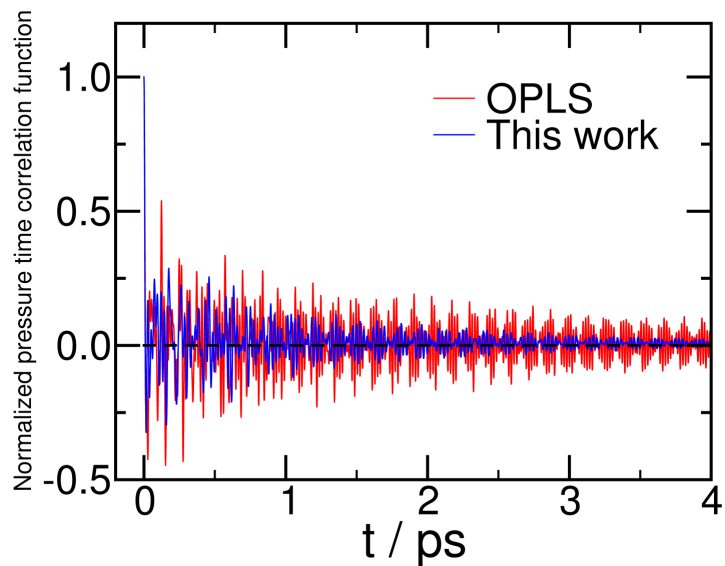


Figure S4: The pressure tensor correlation function for the OPLS force field and from this work at state point temperature $T = 303$ K, and pressure $p = 1$ bar.

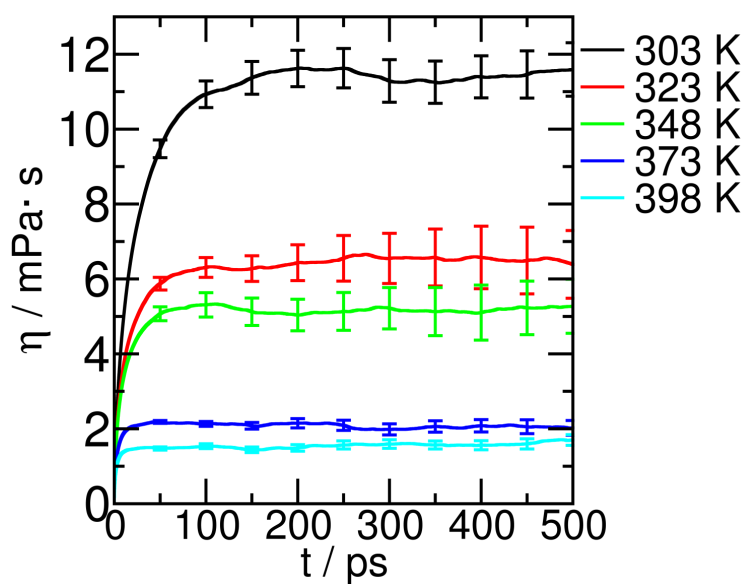


Figure S5: Graphical representation of equation 1 as a function of temperature. Data from the force field refined in this study

Calculation of Mean Shear Viscosity and Uncertainty on the mean - Details

Five independent trajectories for viscosity calculation corresponding to each force field were performed with pressure components dumped every timestep (1 fs). Each run was in turn divided into four blocks for viscosity calculation from SI equation S1, while considering each block to be independent. A total of twenty independent runs of length 5 ns each were obtained. Error bars on the running intergral obtained from averaging over twenty independent running integrals was calculated at an interval of 50 ps. To report a single value for viscosity, we consider the mean running integral of viscosity in the steady region up to 500 ps. We divide the steady portion of the running integral (200 ps to 500 ps) into three blocks ($N_{sample} = 3$) of 100 ps duration each ($S_{prod} = 100000$ steps). Through block averaging method, we arrive at the mean shear viscosity, and the uncertainty on the average, just as we did for density.

Diffusion Constant

Defining the Diffusive Regime

The mean-squared displacement ($\langle |\Delta \mathbf{r}|^2 \rangle$) grows with time-interval (t) according to a general expression: $\langle |\Delta \mathbf{r}|^2 \rangle = 6Dt^\beta$. Here, β is an exponent determining the regime of dynamics of the system, and D is the self-diffusion constant. When exponent β reaches ≈ 1 in time interval t , the system is said to have entered the diffusive regime from a sub-diffusive regime.

$$\beta(t) = \frac{d \ln(\langle |\Delta \mathbf{r}|^2 \rangle)}{d \ln(t)} \quad (2)$$

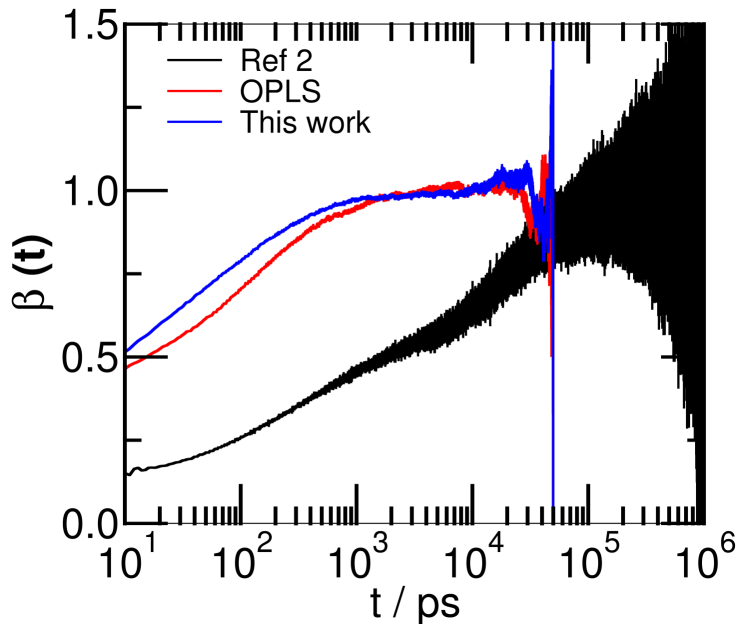


Figure S6: β as a function of time is used to determine the diffusive regime in each force field studied. Data at temperature $T = 303$ K, and pressure $p = 1$ bar.

Calculation of Mean Diffusion Constant and Uncertainty on the Mean - Details

The $\beta(t) \approx 1$ of MSD was divided into three blocks ($N_{blocks} = 3$) of duration 8 ns each ($S_{prod} = 8000$ one point per picosecond). The blocks were considered to be independent. The slope ($6Dt$) of MSD in these blocks were averaged to arrive at the self-diffusion constants D quoted in Tables 10 and 11 of the main manuscript. In the liquid modeled with the force field of ref S3, sulfolane was found to be extremely sluggish and sub-diffusive, with a nominally estimated diffusion constant which was at least two orders of magnitude less than the experimental value at 303 K. For this force field alone, a $1\mu s$ run was required to obtain a sufficient run-length in the diffusive regime for calculating the self-diffusion constant. In this case, MSD (200 ns to 500 ns) was divided into three blocks of length 100 ns each ($S_{prod} = 100000$). The calculation of uncertainty U on the block averaged diffusion constant was calculated in a manner very similar to the calculation of uncertainty for density.

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