A force field for poly(oxymethylene) dimethyl ethers (OMEn)

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Abstract

A united atom force field for the homologous series of the poly(oxymethylene) dimethyl ethers (OMEn): $\text{H}_3\text{C}-\text{O}-(\text{CH}_2\text{O})_n-\text{CH}_3$, is presented. OMEn are oxygenates and promising new synthetic fuels and solvents. The molecular geometry of the OMEn, the internal degrees of freedom and their electrostatic properties were obtained from quantum mechanical calculations. To model repulsion and dispersion, Lennard-Jones parameters were fitted to the experimental liquid densities and vapour pressures of pure OMEn ($n = 1 - 4$). The critical properties of OMEn ($n = 1 - 4$) were determined from the simulation data. Additionally, the shear viscosity of pure liquid OMEn is evaluated and compared with literature data. Finally, the solubility of CO_2 in OME2, OME3 and OME4 is predicted using a literature model for CO_2 and the Lorentz-Berthelot combining rules. The results agree well with experimental data from the literature.

1 Introduction

Poly(oxymethylene) dimethyl ethers (OMEn) are oligomers with the general structure $\text{H}_3\text{C}-\text{O}-(\text{CH}_2\text{O})_n-\text{CH}_3$. OMEn have important technological applications, e.g. as synthetic fuels,¹ promising absorbents of carbon dioxide,^{2,3} or alternatives to methanol in direct oxidation fuel cells.^{4,5} Mixtures of OMEn with $n = 3 - 5$ can be used as drop-in replacement for fossil Diesel fuel and exhibit excellent combustion properties: they reduce soot formation and also NO_x formation.^{6,7} Large scale production of OMEn is economically feasible.⁸⁻¹³ Thermodynamic properties of OMEn are thus of great interest for a range of possible technical applications.

Molecular simulation is an attractive approach for predicting thermodynamic properties of fluids. Obtaining accurate thermodynamic properties from molecular simulations requires an accurate force field. To the best of our knowledge, no force fields are available for OMEn. Parameters developed for short ethyl ethers from transferable force fields like TraPPE¹⁴ and OPLS^{15,16} can in principle be used for simulations of OMEn, but preliminary work carried out in the present work shows that this does not lead to a satisfactory description of experimental data for OMEn. Dasgupta et al.¹⁷ developed a force field for describing the internal degrees of freedom of OMEn based on ab-initio calculations but did not consider the intermolecular interactions. Therefore, in the present work, a force field for describing thermodynamic properties of OMEn ($n = 1 - 4$) was developed. As an accurate force field for OME0 (dimethyl ether) is already available in the literature,^{18,19} OME0 was not considered in this work.

Molecular models are often developed based on a fit to experimental data for liquid densities and vapour pressures.¹⁸ Two challenges arise from this fact when developing a force field for OMEn. Firstly, for OMEn, comparably few data sets on these properties are available in the literature. In the present work, for OME1, the experimental data for vapour pressures by Pan et al.²⁰ and for saturated liquid densities by Wang et al.²¹ were used for the fits. These data were retrieved from the Dortmund Data Bank.²² For OMEn ($n = 2 - 4$), experimental data by Boyd²³ for vapour pressures and by Burger et al.²⁴ for liquid densities at 1 bar

were used. Secondly, the vapour pressures, especially of the longer chain OME n , are very low at the temperatures for which this information is available from experiments. Obtaining vapour-liquid equilibria (VLE) with molecular simulations is challenging. Although simulations of VLE at such low pressures have been carried out previously,²⁵ either the chain length of the molecules was smaller or the liquid density was lower than is the case for the OME n studied in the present work. As a result, in the present work, only one data point of the vapour pressure can be used in the fit for each OME n with $n \geq 2$. For the liquid density, there is no such problem as this property can be determined easily from NpT simulations.

The united-atom approach was used for describing the CH₂ and CH₃ groups in the OME n . For simplicity, also the oxygen interaction sites are referred to as ‘groups’ throughout this paper. Repulsion and dispersion between the groups are modelled with the 12-6 Lennard-Jones (LJ) potential. For describing the intramolecular degrees of freedom, angle bending and dihedral potentials are used with parameters that were determined from quantum mechanical (QM) calculations that were carried out in the present study. The bond lengths are kept fixed. The polarity is modelled by partial charges located on the centre of mass of the LJ sites.

This paper is structured as follows: The molecular simulation methods that were used are explained in Section 2. In Section 3, the methodology for developing the OME n force field is described. The structure of the force field for OME n is presented in Section 3.1. In Sections 3.2 and 3.3, the determination of the electrostatic and structural model parameters from QM calculations is explained. The determination of the LJ parameters from a fit to experimental VLE data of pure OME n ($n = 1 - 4$) is discussed in Section 3.4. The model results are presented in Section 4. In Sections 4.1 and 4.2, simulation data obtained using the new force field are compared to correlations of experimental data. In Section 4.3, the predictions of the shear viscosity of OME n ($n = 1 - 4$) by the proposed force field are presented. In Section 4.4, we test the accuracy of the proposed force field for predicting the solubility of CO₂ in OME n ($n = 2 - 4$). Finally, conclusions are presented in Section 5.

2 Simulation Methods

The parameters for describing the internal degrees of freedom and the polarity were obtained from QM calculations. Two different calculation methods, Density Functional Theory (DFT) and Hartree-Fock (HF), were employed to evaluate the geometry and the energy of OMEn molecules. Technical details of the QM calculations are provided in Appendix A.

The VLE was simulated with Gibbs Ensemble Monte Carlo (GEMC)^{26,27} simulations with the code MedeA-Gibbs²⁸ to calculate the vapour pressures. Configurational-bias moves²⁹ were used to improve the sampling of conformations of OMEn and to increase the probability of acceptance of particle exchange moves. GEMC simulations were repeated at two state points for each OMEn with the code Cassandra.³⁰ The use of two independent MC codes enables the comparison and an assessment of the reliability of the codes and procedures, which is not trivial.^{31–33}

NpT Monte Carlo (NpT -MC) simulations were performed with MedeA-Gibbs²⁸ to calculate liquid densities at low temperatures. Here, low temperatures are those for which the vapour pressures are less than 1 bar and accurate GEMC simulations are unfeasible, unless special techniques are used to increase the acceptance probability of particle transfer moves and very long simulations are carried out.³⁴ Technical details of the GEMC and NpT -MC simulations are given in Appendix B.

For predicting the solubility of CO₂ in OMEn, pressure-composition diagrams of the mixtures were calculated in the bubble point pseudo-ensemble (BPE-MC)^{35,36} with MedeA-Gibbs.²⁸ The BPE-MC is a pseudo- NVT method. In this method, the composition of the liquid phase is fixed, whereas that of the vapour phase fluctuates. As a result, the number of molecules in the vapour phase may change. The two boxes are coupled by volume interchanges. Technical details of the BPE-MC simulations are given in Appendix B.

The evaluation of the shear viscosity was performed using GROMACS,³⁷ keeping the bond lengths fixed by using the lincs algorithm.³⁸ The shear viscosity was evaluated using the Green-Kubo formalism³⁹ through the time auto-correlation of the stress tensor components.

More details on the simulations and Green-Kubo formalism are provided in Appendix B.

Numerical values of the results of all the molecular simulations that were carried out in the present work are reported in the Supporting Information, together with estimates of the statistical uncertainties that were obtained from block averaging.

3 Development of the Force Field for OME n

3.1 Structure of OME n

Figure 1 shows the structure of OME n ($n = 1 - 4$). In the present force field two classes of CH₂ and oxygen groups are used. Depending on their position in the chain, the CH₂ and oxygen sites are classified either as ‘edge’ or as ‘central’ groups (see Figure 1). This distinction is justified by the results of the QM calculations, which are discussed in the following section.

Figure 1: Schematic representation of OME n ($n = 1 - 4$). CH₂ and oxygen groups are classified either as ‘edge’ (blue) or ‘central’ (red). They are modelled with distinct sets of parameters in the present force field. Coloured lines indicate the edge and central bonds, as explained in Section 3.3.

3.2 Electrostatic interactions

The electrostatic interactions in the OME n force field were modelled using point charges q_i , placed at the centre of mass of each LJ site i . QM calculations of OME n ($n = 1 - 5$) were carried out with DFT with the B3LYP functional^{40–42} using the conductor-like screening model (COSMO)⁴³ with the GAMESS-US^{44,45} code. Details on the QM calculations are given in Appendix A. The partial charge on each atom was calculated from a fit to the electron density data using the restrained electrostatic potential (RESP) method.⁴⁶ Finally, the point charges on CH₂ and CH₃ groups were obtained by summing up the partial charges of all atoms in each group. If a group occurs more than once in a certain OME n , the arithmetic average value was taken. Figure 2 shows the partial charge of each group for all OME n determined in this manner. Numerical values of the partial charges for all groups are given in the Supporting Information.

For the CH₃ group, the partial charge decreases as the chain length increases up to OME3 but then reaches an asymptotic value for OME n with $n \geq 3$. For the CH₂ and oxygen groups, differences are found depending on the position of the group in the chain. The charges are significantly different for the ‘edge’ and ‘central’ groups, cf. Figure 1. For the negatively charged oxygens, the magnitude of the charge is larger for the central groups than for the edge groups. The same holds for the positively charged CH₂ groups. As in the case of the CH₃ groups, there is a strong influence of the chain length on the charges of the CH₂ and oxygen groups for the small OME n . For OME n with $n \geq 3$ that influence is weaker, but a systematic trend remains: the magnitude of the charges on the CH₂ groups (positive) and the oxygens (negative) slowly decreases with increasing chain length.

Based on these findings, the following charge distribution was used in the force field: for the CH₂ and oxygen groups, a distinction was made between edge and central groups, cf. also Figure 1. In addition, individual sets of charges for each group in OME1 and OME2 are used, which are directly taken from the QM calculations. In contrast, for OME n with $n \geq 3$, the electrostatic interactions are modelled with a unique, transferable set of charges. The charges

Figure 2: Point charges of the groups of OME n determined from QM calculations. Dashed lines are guides to the eye.

on each individual group were determined by averaging the charges on that particular group from the QM calculations for OME3, OME4 and OME5. The averages were then adjusted to ensure the electro-neutrality for all OME chain lengths. Thereby, also the transferability of the force field is preserved by assigning a net zero charge to (O_{central}-CH_{2,central}) group. Table 1 shows the resulting point charges used in the present force field.

Table 1: Point charges of different groups for OME n used in the present force field. e is the elementary charge.

Site	q/e ($n = 1$)	q/e ($n = 2$)	q/e ($n \geq 3$)
CH ₃	0.2192	0.2063	0.2297
O _{edge}	-0.3462	-0.4112	-0.3392
CH _{2,edge}	0.2540	0.4090	0.3392
O _{central}	-	-0.4082	-0.4594
CH _{2,central}	-	-	0.4594

3.3 Internal degrees of freedom

In the present force field, angle bending and dihedrals are considered. As many other molecular models that are used for describing thermodynamic properties, bond stretching is not taken into account. To obtain the parameters for the internal degrees of freedom, the conformational energies of the different OME n were determined from the QM calculations described in Section 3.2. The bond lengths between different groups were calculated directly from these data for all OME n . They were then averaged according to their type for all the OME n . Table 2 shows the averaged bond lengths.

Table 2: Bond lengths for OME n used in the present force field.

Bond	length/Å
CH ₃ -O _{edge}	1.5010
O _{edge} -CH _{2,edge}	1.4513
CH _{2,edge} -O _{central}	1.4672
O _{central} -CH _{2,central}	1.4672

The bond length is slightly larger for the CH₃-O bond than for the CH₂-O bond, which agrees with previous QM calculations.¹⁷ The CH₂-O bond lengths at the edge are shorter than at the centre of the chain, differing by 0.0159 Å. On the other hand, the O-CH₂-O and CH₂-O-CH₂ angles are the same for the central and the edge groups.

The angle bending and the dihedrals were modelled independently by performing a QM geometry optimisation constraining one specific angle and dihedral type. The angle bending is modelled using a harmonic potential

$$u_b = k_b(\theta - \theta_0)^2/2, \quad (1)$$

where u_b is the bending energy, k_b is the bending constant, and θ_0 and θ are the equilibrium and the bending angle, respectively.

An angle conformational energy analysis was carried out to obtain the parameters k_b and θ_0 for each angle type, using HF calculations for OMEn. In this analysis, θ was changed to calculate the bending energy while relaxing the geometry of all the other degrees of freedom. Since the conformational energies provided by the QM calculations refer to the absolute energy of the molecule, the minimum value coming from the conformational energy analysis was set to zero for each OMEn to enable a meaningful comparison of conformational energies of different OMEn. Using this strategy, the data obtained for all the OMEn can be used in the fit of a harmonic potential to the conformational energies for each angle type. Details of the simulations are given in Appendix A, and the numerical results are provided in the Supporting Information. Table 3 shows the bending parameters.

Table 3: Bending parameters for OMEn used in the present force field.

Angle	$\theta_0/^\circ$	k_b/K
CH ₃ -O-CH ₂	115.87	81221.5
O-CH ₂ -O	105.54	131078.3
CH ₂ -O-CH ₂	116.41	77042.2

The dihedrals are described with the Ryckaert-Bellemans (RB) equation

$$u_d = \sum_{m=0}^5 C_m (\cos(\varphi))^m, \quad (2)$$

where C_m are fitting parameters and φ is the dihedral angle. In the RB equation, $\varphi = 0^\circ$ corresponds to the trans-configuration. A dihedral analysis was carried out to obtain parameters C_m of each dihedral angle. Similar to the angle bending study, HF calculations were performed for each OME n with varying values of φ and the energy was calculated. Also in this case the conformational energy was set to zero at its minimum value, allowing to fit the energies with the RB potential simultaneously for all the OME n . Details are given in Appendix A. The results of the dihedral analysis are shown in Figure 3.

Figure 3: Dihedral potential obtained from QM calculations for OME n ($n = 1 - 4$). Squares indicate the edge dihedral and triangles indicate central dihedral. Results for the different OME n are shown in different colours: OME1 (black), OME2 (green), OME3 (red) and OME4 (blue). The fitted RB potentials are shown as lines (see Eq. (2)): blue dashed line (---) for edge dihedrals, black solid line (—) central dihedrals and red dotted line ($\cdots$) is the dihedral potential for all the dihedrals from Dasgupta et al.¹⁷

Figure 3 shows that it is necessary to distinguish between two types of dihedrals in the OME n : central and edge dihedrals. However, Dasgupta et al.¹⁷ did not include this important distinction in their study. The parameters C_m calculated by fitting the conformational energies for these dihedral types are shown in Table 4 and Figure 3.

Table 4: RB dihedral potential parameters for OME*n* used in the present force field.

C_m	CH ₃ -O-CH ₂ -O (edge)	CH ₂ -O-CH ₂ -O (central)
C_0/K	528.19	293.28
C_1/K	2233.09	1393.29
C_2/K	1078.50	949.58
C_3/K	-2604.48	-1874.75
C_4/K	653.75	1171.20
C_5/K	-851.05	-820.48

The fitted dihedral potential has a global minimum at around $\varphi = 65^\circ$ and a local minimum at $\varphi = 180^\circ$, which is in agreement with the QM calculations of Dasgupta et al.¹⁷ However, regarding the potential energy of the local minimum as well as the height of the energy barrier between the two minima the results from the present work differ from those reported by Dasgupta et al.¹⁷ (see Figure 3). Some simulation codes use the Fourier equation to model dihedral potentials. Thus, we provide the equivalent parameters using the Fourier equation in the Supporting Information.

3.4 Lennard-Jones Parameters

The united-atom description is used for CH₂ and CH₃ groups, i.e. those groups are modelled with a single, unified LJ site. Each oxygen atom is also modelled with a single LJ site. The sites are positioned in the centre of mass of the corresponding group or atom. The same set of LJ parameters is used for all OME*n*.

The QM calculations showed that the fitted electrostatic charges depend on their position in the chain, see Figure 2. There are two distinct configurations, edge and central groups (see Figure 1 and Section 3.2). The same idea was adopted for the LJ sites. Thus, five types of LJ sites were considered, corresponding to the five different groups, i.e. CH₃, O_{edge}, CH_{2,edge}, O_{central}, and CH_{2,central}. As a consequence, the total number of LJ parameters to fit is ten.

In the first stage, the LJ parameters were fitted using the method of Bourasseau et al.,⁴⁷ which is based on the minimisation of the objective function F defined as

$$F(\underline{y}) = \frac{1}{N} \sum_{i=1}^N \frac{(f_i^{\text{sim}}(\underline{y}) - f_i^{\text{exp}})^2}{(s_i^{\text{sim}})^2 + (s_i^{\text{exp}})^2} \quad (3)$$

where N is the total number of reference data points, $\underline{y}$ is a set of p LJ parameters ($\underline{y} = y_1, y_2, \dots, y_p$), f_i^{sim} is the simulation result for the i -th property, f_i^{exp} is the corresponding experimental result, and s_i^{sim} and s_i^{exp} are the statistical uncertainties of the simulation data and the experimental data. The objective function $F(\underline{y})$ is locally minimised using the Gauss-Legendre least-squares estimator. Partial derivatives of a simulated property f_i^{sim} with respect to a given force field parameter y_p are calculated from statistical fluctuations.^{47–49} Further information on the method is provided in the original paper of Bourasseau et al.⁴⁷ As an initial guess for $\underline{y}$, the LJ parameters for similar groups in ethyl ethers from the TraPPE⁵⁰ force field were used.

In the second stage, when $F(\underline{y})$ is in the vicinity of its global minimum, the minimisation strategy mentioned above fails due to the limited accuracy with which the partial derivatives can be obtained. In this case, the LJ parameters were further adjusted manually. Initially, the parameters of the edge groups were fitted to minimise the objective function for OME1. Subsequently, the parameters for the $\text{O}_{\text{central}}$ group were adjusted to minimise the objective function for OME2. This does not impact OME1 as the $\text{O}_{\text{central}}$ group is present only in OME2 and longer OME n , cf. Figure 1. Finally, the parameters for the $\text{CH}_{2,\text{central}}$ group were adjusted to minimise the objective function for OME3 and OME4, without affecting OME1 and OME2. With the parameters for only one group available for adjustment, getting an excellent agreement with the experimental data for both OME3 and OME4 was not possible. Thus, a better representation of VLE properties of OME3 was prioritised over that of OME4.

The LJ parameters were fitted to experimental data for normal boiling point and liquid density at 1 bar. The experimental data for vapour pressures of OME1 were taken from Pan

et al.²⁰ and those of OME n ($n = 2 - 4$) from Boyd.²³ The experimental data for liquid densities of OME1 were taken from Wang et al.²¹ while those of OME n ($n = 2 - 4$) from Burger et al.²⁴ Most of the vapour pressure data are available in a temperature range where the vapour pressure values are less than 1 bar. However, such low vapour pressures cannot be obtained in GEMC simulations, with a statistical uncertainty low enough to perform meaningful optimisations. Therefore, only four state points for the vapour pressure of OME1 are effectively available for optimisation, and only one point each for OME n ($n = 2 - 4$). This problem does not arise for liquid densities, as they can be obtained readily from NpT -MC ensemble simulations. Thus, three state points for each OME n were used for the optimisation.

The densities for OME1 are available only at temperatures up to 388 K, while those for OME n ($n = 2 - 4$) are available only at temperatures up to 363 K. The vapour pressures for OME1 are available at temperatures up to 398 K. The vapour pressures for OME n ($n = 2 - 4$) are available up to temperatures where the vapour pressure is 1 bar. To assess the quality of the predictions by the force field over a broad temperature range, correlations of the experimental data for higher temperatures were used. These correlations were not used for fitting the LJ parameters. More information on the experimental data and the correlations are given in Appendix C.

Table 5 shows the LJ parameters that were obtained in this manner.

Table 5: Lennard-Jones parameters for OME n used in the present force field.

Site	$\sigma/\text{\AA}$	$(\varepsilon/k_B)/\text{K}$
CH ₃	3.7536	151.570
O _{edge}	2.4394	70.830
CH _{2,edge}	3.6552	35.631
O _{central}	3.4029	45.620
CH _{2,central}	3.6364	47.856

The LJ size parameter σ decreases in the order CH₃ > CH_{2,edge} $\approx$ CH_{2,central} > O_{central} > O_{edge}, which is consistent with the intuitive atomistic size sequence CH₃ > CH₂ > O. The

values of σ for central and edge CH_2 groups are similar. On the other hand, the value of σ for the edge and central oxygens are significantly different.

The value of ε follows the order $\text{CH}_3 > \text{O}_{\text{edge}} > \text{CH}_{2,\text{central}} > \text{O}_{\text{central}} > \text{CH}_{2,\text{edge}}$. The large value of ε for CH_3 and O_{edge} , and lower charges on the edge groups indicate that OME1 and OME2 have a larger relative contribution of the dispersion interactions than OME n with $n \geq 3$.

The Lorentz-Berthelot combining rules are applied for all unlike LJ interactions. LJ and electrostatic interactions within a molecule are taken into account only if the involved sites are separated by four or more bonds. For sites less than four bonds away from each other, the LJ and electrostatic interactions are excluded.

The OME n force field developed in this work has been added to the MolMod Database,¹⁹ so that it is readily available for the use in molecular simulation codes such as *ms2*,⁵¹ *ls1* *mardyn*,⁵² GROMACS³⁷ and LAMMPS.⁵³

4 Results and discussion

4.1 Vapour-liquid equilibrium

Figures 4 and 5 show the simulation results for pure OME n ($n = 1 - 4$) and their comparison to experimental data. An overview of the average deviations is given in Table 6. To the best of our knowledge, no molecular simulation results for OME n have been reported previously in the literature. The results that were obtained in the present work independently with the two codes were found to be in excellent agreement. More information on this is given in the Supporting Information.

The VLE results obtained with the present force field show good agreement with the experimental data for OME1 to OME4, with average deviations less than 1.5% for liquid densities at 1 bar and less than 5% for vapour pressures of OME n ($n = 1 - 3$). For OME4, the deviation of the vapour pressures is higher. However, this is expected as a better repre-

Figure 4: Left: Liquid densities for OMEn ($n = 1 - 4$) as a function of the temperature. The full lines are correlations of experimental data (see Appendix C). The dashed lines are extrapolations obtained from these correlations. The symbols show the molecular simulation results of the present work. A filled symbol indicates that the depicted state point was used in the development of the force field. These points indicate the liquid density at 1 bar, obtained with NpT simulations. Open symbols show the predictions using the force field. Crosses indicate the estimates of the critical properties from the literature.²⁴ Right: Corresponding deviations between the correlations of the experimental data and the molecular simulation results. Error bars are within symbol size where not indicated.

Table 6: Average absolute deviations between simulation results and experimental data, for the state points which were considered for the optimisation, in liquid densities at 1 bar and vapour pressures using the present force field for OMEn . As a result, the deviations for vapour pressures for OME1 are based on four state points, where those for OMEn ($n = 2 - 4$) are based on one state point each. The deviations for liquid densities at 1 bar are based on three state points for each OMEn .

Component	$100\Delta\rho^{\text{liq}}/\rho^{\text{liq}}$	$100\Delta p^{\text{s}}/p^{\text{s}}$
OME1	0.5	4.8
OME2	0.1	3.9
OME3	1.3	2.0
OME4	1.4	21.2

sensation of properties of OME3 was prioritised over that of OME4 (see Section 3.4). These deviations are comparable to those obtained for long alkanes using other transferable force fields, e.g. TraPPE,⁵⁰ SKS⁵⁴ and OPLS.^{55,56}

Figure 5: Left: Saturated vapour pressures for $OMEn$ ($n = 1 - 4$) as a function of the temperature. The full lines are correlations of experimental data (see Appendix C). The dashed lines are extrapolations obtained from these correlations. The symbols show the molecular simulation results of the present work. A filled symbol indicates that the depicted state point was used in the development of the force field. Open symbols show the predictions using the force field. Crosses indicate the estimates of the critical properties from the literature.²⁴ Right: Corresponding deviations between the correlations of the experimental data and the molecular simulation results. Error bars are within symbol size where not indicated.

It is instructive to compare the extrapolations from the correlations of experimental data to the predictions obtained from the present force field for the properties of $OMEn$ at higher temperatures. For the liquid density, no systematic trend is observed. With the exception of one point for OME4 at very high temperature, the extrapolations and the predictions by molecular simulations agree within 2%. Taking into account that the experimental data are extrapolated over a range of about 200 K, this agreement is excellent. However, for the pressure both data sets show different trends. The molecular simulation results suggest that the vapour pressure curve is steeper than that estimated from extrapolating the experimental data, at least for the longer $OMEn$. Here, the uncertainty associated with extrapolating the experimental data over a wide temperature range seems to play an important role. Moreover, the uncertainty in the experimental data for the low vapour pressures of $OMEn$ ($n = 2 - 4$) is probably high and it is unfortunately not specified in the original paper.²³

4.2 Critical properties

The critical temperature T_c and density ρ_c of OME n ($n = 1 - 4$) were calculated by fitting the vapour and liquid densities (ρ^{vap} and ρ^{liq} , respectively) obtained in the simulations to the density scaling law and the law of rectilinear diameters^{57,58}

$$\rho^{\text{liq}} - \rho^{\text{vap}} = B(T - T_c)^\beta \quad (4)$$

$$\frac{\rho^{\text{liq}} - \rho^{\text{vap}}}{2} = \rho_c + A(T - T_c) \quad (5)$$

where A and B are fit parameters. The exponent β was set to 0.325, as found for a 3-dimensional Ising-type fluid.^{59,60}

The extended Antoine equation was fitted to the simulation data for the vapour pressures of OME n ($n = 1 - 4$) as described in Appendix C. The critical pressure p_c was calculated from that equation using the number for T_c that was determined as described above.

Table 7 shows the results for T_c , ρ_c and p_c obtained in this manner. In the literature, an estimate based on experimental data is only available for the critical temperature of OME1.⁶¹ For OME n ($n = 2 - 4$), only estimates of T_c from a group contribution approach are available.²⁴ These estimates and the results of the present force field for T_c show a consistent offset of about 5% for all OME n ($n = 1 - 4$).

Table 7: Critical properties of OME estimated from the molecular simulation results compared with literature values.

Component	Simulations			Literature
	T_c/K	$\rho_c/\text{kg m}^{-3}$	p_c/bar	T_c/K
OME1	497.3	309.2	48.8	480.6 ^a
OME2	568.0	321.4	38.2	552.2 ^b
OME3	621.5	322.1	30.2	603.4 ^b
OME4	679.3	318.8	25.0	646.9 ^b

^a Estimate based on experimental data.⁶¹

^b Estimate from group contribution method.²⁴

The critical temperatures of OME n increase with the chain length, while the critical pressure reduces. The critical densities of the OME n do not increase monotonously with the chain length: a maximum is predicted for OME3. The same behaviour of T_c and ρ_c as a function of the chain length has been found for alkanes using molecular simulations^{54,62} and experiments.⁶³ In the case of alkanes, the maximum ρ_c is obtained for octane; and then ρ_c decreases monotonically for longer chains. In the case of OME n , the maximum ρ_c is obtained for OME3, which contains nine carbons and oxygens.

4.3 Shear viscosity of OME

In Figure 6, the simulation data from the present work for the shear viscosity of OME n ($n = 1 - 4$) are compared to experimental data.^{64,65} The predictions underestimate the shear viscosity for all OME n . The average deviations are 14.1%, 13.4%, 18.3%, and 9.5% for OME1, OME2, OME3, and OME4 respectively. These deviations lie in the range of what is expected for predictions of the shear viscosity data with force fields.⁶⁶⁻⁶⁸ The temperature dependence of the viscosity is predicted well for all studied OME n .

Figure 6: Shear viscosity of OME1-4 for different temperatures. Circles indicate experimental results from Zheng et al.⁶⁴ for OME1 and Kang et al.⁶⁵ for OME n ($n = 2 - 4$). Squares indicate simulation results from this work. Lines are guides to the eye.

4.4 Solubility of CO₂ in OME

The solubility of CO₂ in OME n was studied using BPE-MC simulations. The solubility is reported here in terms of the total pressure as a function of the mole fraction of CO₂ in the liquid phase. The CO₂ model by Merker et al.⁶⁹ was taken from the MolMod Database.¹⁹ It consists of three LJ sites and three-point charges, which represent the quadrupole moment of CO₂.

As in the literature,^{70,71} the modified Lorentz-Berthelot combining rules were applied for describing the unlike LJ interactions between CO₂ and the OME n . An adjustable binary parameter ξ is introduced in the Berthelot rule for the unlike energy parameters:

$$\varepsilon_{\text{OME}n, \text{CO}_2} = \xi \sqrt{\varepsilon_{\text{OME}n, \text{OME}n} \varepsilon_{\text{CO}_2, \text{CO}_2}} \quad (6)$$

The universal parameter ξ is used for the unlike LJ interactions between all sites on CO₂

and on OME n . It has the same value $\xi = 1.035$ for all OME n .

Figure 7 shows the solubility of CO₂ in OME n ($n = 2, 3, 4$) using $\xi = 1.035$ at 353.15 K. The average deviations of the total pressure of all simulated state points with respect to the experimental values are 8.3%, 3.8%, and 5.7% for OME2, OME3, and OME4 respectively. The experimental data for the solubility of CO₂ in OME n ($n = 2 - 4$) were taken from Schappals et al.³ No experimental data for the solubility of CO₂ in OME1 are available, to the best of the authors' knowledge.

Good agreement between the simulation and the experimental values for the solubility of CO₂ in OME n is obtained. The simulation results show hardly any dependence of the chain length of OME n on the solubility. This is in line with the experimental results, which show only a weak influence of the chain length on the solubility.

When $\xi = 1.0$ is used, the solubility of CO₂ in all the three considered OME n is underestimated, i.e. for a given CO₂ mole fraction in the liquid phase, the total pressure is overestimated. Moreover, the dependence of chain length of OME n on the solubility is not predicted correctly, i.e. the solubility decreases with an increase in the chain length of OME n .

Figure 7: Solubility of CO_2 at 353.15 K in OMEn ($n = 2 - 4$). Circles indicate the experimental results of Schappals et al.³ Squares indicate the simulation results from this work. Lines are guides to the eye.

5 Conclusions

A united atom force field for OMEn was developed. The bond lengths and angles, dihedral potential, and point charges were obtained from QM calculations. Results of the QM calculations show that edge effects are important for modelling OMEn because edge and central groups differ in their electrostatic and dihedral potential. The LJ parameters were fitted to the VLE data of OMEn ($n = 1 - 4$). The force field reproduces the VLE properties of OMEn ($n = 1 - 3$) well, with average absolute deviations of 1.3% for the liquid density 5% for the vapour pressure; whereas for OME4 , these values are 1.4% and 21.2% respectively. While assessing the relatively large deviation in the vapour pressure of OME4 , it should be considered that the parameters of only one LJ site were available for fitting the vapour pressures of OME3 and OME4 , and a better representation of OME3 was prioritised. Moreover, only a single experimental data point was available for fitting the vapour pressures of OMEn

($n = 2 - 4$). A further improvement in the force field may be possible, but a more comprehensive experimental database would be required for such an attempt. Other properties of OMEn should probably be included in such an endeavour. The estimates of the critical properties of OMEn were obtained from the simulation results. The critical properties of OMEn follow the same trends as those of alkanes: with increasing length of the chain, T_c increases while p_c decreases monotonically, whereas ρ_c shows a maximum for OME3. The force field was also used to predict the shear viscosity of OMEn, which is slightly underestimated. Finally, also the solubility of CO₂ in OMEn ($n = 2 - 4$) was studied. After the adjustment of a single universal state-independent parameter in the combining rule of the unlike dispersive interactions, a good agreement between the simulation results for the solubility and the experimental data was obtained. Thus, the proposed force field enables predictions of thermodynamic data of pure OMEn as well as mixtures of OMEn with other components. The force field has also been added to the MolMod database, which makes it easily available for molecular simulations with many widely used simulation codes.

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Supporting Information Available

The Supporting Information contains results of the QM calculations, bond lengths and angles for individual OME n , numerical results of all the simulations reported in this work, and parameters for the dihedral potential using the Fourier equation.

A QM calculations

QM calculations were carried out with GAMESS-US.^{44,45} Two methods were used for two different purposes. First, Density Functional Theory (DFT) with the B3LYP functional^{40–42} was applied to calculate the bond lengths, angles, and point charges. Second, the Hartree-Fock (HF) method was used to calculate the bending energy and dihedral energy. In both methods, the 6-311G^{**} basis set was applied.

The DFT calculations were combined with the conductor-like screening model (COSMO) to determine the partial charge of each atom. COSMO takes into account the dielectric continuum that surrounds the molecule to model the electrostatic interaction with a solvent. The solvent is treated as continuum represented by a permittivity ϵ_r . The electrostatic potential was calculated over an isosurface constructed of van der Waals spheres that surrounds every single atom.⁴³ Then, the partial charge of each atom was obtained by fitting the electrostatic potential of the electric potential isosurface using the restrained electrostatic potential (RESP) method.⁴⁶ Detailed results are available in the Supporting Information.

The angle and dihedral energies were calculated for an isolated OME n molecule using the HF method. The conformational energy was calculated for each angle and dihedral in OME n ($n = 1 - 4$). The energy of each angle was obtained by changing the angle with a step of 0.2° for all the angle types, and a subsequent geometry optimisation was performed to relax the energy of all the other internal degrees of freedom (details are provided in the Supporting Information). Each dihedral was systematically varied from 0° to 360° with an increment of 5°, and the geometry optimisation was carried out for each specific dihedral

angle, to obtain the dihedral energy (details are provided in the Supporting Information).

B Molecular Simulation Details

B.1 GEMC simulations

In GEMC simulations, the probabilities for particle exchange and volume exchange were fixed at 48 % and 2 %, respectively. The remaining 50 % were equally divided between translation, rotation, and internal regrowth moves. The maximum amplitudes for translation, rotation, and volume exchange moves were set to 40 % acceptance. Configurational bias moves were carried out using five trial configurations for inserting the first united-atom group and 10 trial configurations for inserting each consequent group in the chain.

LJ interactions were truncated at 14 Å, and analytical tail corrections were applied. The minimum allowable distance between two united-atom groups was set to 1 Å. If the distance between two particles was observed to be smaller than this, the move was rejected. Ewald summations were used to calculate the electrostatic interactions.

GEMC simulations were carried out using 240 particles. The volumes of the two boxes were selected to yield about 40 particles in the vapour phase and 200 particles in the liquid phase. The boxes were created by random molecule insertions using configurational bias regrowth. Both boxes were initially allowed to equilibrate without volume and particle exchanges for 3,000 MC cycles, where the number of MC moves in one cycle is equal to the number of united-atom groups. In addition, the system was equilibrated in the Gibbs ensemble for 40,000 cycles for OME1 and OME2 and 80,000 cycles for OME3 and OME4. A Gibbs Ensemble production run of 600,000 cycles was used to compute the property averages for OME1, whereas 900,000 cycles were used for OME n ($n = 2 - 4$). Statistical uncertainties were computed by block averaging.

B.2 NpT -MC simulations

In NpT -MC simulations, the probability for volume interchanges was set at 4%. The remaining 96% were equally divided between translation, rotation and internal regrowth moves. The maximum amplitudes for translation, rotation and volume exchange moves were set to 40% acceptance. Configurational bias moves for internal regrowth were carried out using five trial configurations for inserting the first united-atom group and 10 trial configurations for each subsequent group in the chain.

Similar to GEMC simulations, LJ interactions were truncated at 14 Å, and analytical tail corrections were applied. The minimum allowable distance between two united-atom groups was set to 1 Å. If the distance between two particles was observed to be smaller than this, the move was rejected. Ewald summations were used to calculate the electrostatic interactions.

NpT simulations were carried out using 200 molecules, inserted randomly in the box using configurational bias regrowth at the beginning of the simulation. Initially, the box was allowed to equilibrate for 2000 NVT cycles, where the number of MC moves in each cycle is equal to the number of molecules. NpT simulations consisted of 20,000 equilibration cycles and 100,000 production cycles. Statistical uncertainties were calculated by block averaging.

B.3 BPE-MC simulations for the OME n -CO $_2$ mixtures

The composition of the liquid phase was chosen according to the experimental data points available in Schappals et al.³ The total number of molecules in the liquid phase was set to 500. A total of 210,000 MC cycles were carried out. The first 10,000 MC cycles were discarded. The probabilities for the BPE-MC move (pseudo particle exchange between the boxes) and volume exchange were fixed at 39.5 % and 0.5 %, respectively. The probability for translation, rotation, and internal regrowth was 20 % for each move. The maximum acceptance for translation, rotation, and volume exchange moves was set to 40 %. Configurational-bias parameters were the same as those in the GEMC simulations. A cutoff radius of 14 Å was used for LJ interactions, and analytical tail corrections were applied. The minimum distance

between two particles was set to 1 Å. Ewald sums were used to calculate the electrostatic interactions.

B.4 Calculation of the shear viscosity

The Green-Kubo formalism³⁹ was used to calculate the shear viscosity η by sampling the time auto-correlation of the virial stress tensor components:

$$\eta = \frac{1}{5Vk_B T} \int_0^\infty \sum_{k=1}^5 \langle J_k(t) \cdot J_k(0) \rangle dt \quad (7)$$

where k_B is the Boltzmann constant, V is the volume of the simulation box, and T denotes the temperature. Each single term $J_k(t)$ in Eq. (7) represents the components of the virial stress tensor, $(J_{xx} - J_{yy})/2$, $(J_{yy} - J_{zz})/2$, J_{xy} , J_{yz} , J_{zx} . The calculation of the stress components rely on the virial theorem:^{72,73}

$$J_{\alpha\beta} = \sum_{i=1}^N m_i v_{i\alpha} v_{i\beta} - \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N r_{ij\alpha} \frac{\partial u_{ij}}{\partial r_{ij\beta}}. \quad (8)$$

Here, α and β represent the spatial vector components (x, y, z) , N is the total number of particles, m_i denotes the mass of the i^{th} particle, $v_{i\alpha}$ and $v_{i\beta}$ indicate the velocity of the i^{th} particle along directions α and β , $r_{ij\alpha}$ is the distance between the i^{th} and the j^{th} particles along direction α , u_{ij} is the potential energy interaction between the i^{th} and the j^{th} particles.

Long simulation runs are required to obtain convergence of the auto-correlation function. Therefore, a 30 ns long molecular dynamics simulation was performed to calculate the shear viscosity. The virial stress tensor components ($J_{\alpha\beta}$) were dumped each timestep, and a post-processing analysis with the Eq. (7) was carried out to estimate the shear viscosity.

The timestep used for these molecular simulations was 1 fs, and a cut-off radius of 1.4 nm for Lennard-Jones interactions was employed. The Particle Mesh Ewald (PME) Method was used to model the electrostatic interactions⁷⁴ using a cut-off radius of 1.4 nm, with a

PME order of 6, and a Fourier spacing of 0.16 nm. The lincs constraint algorithm³⁸ was used to freeze the bond length with an order of 12, and 4000 molecules were used to perform the molecular simulations, for each state point. In the first step, an equilibration run using NpT ensemble at 1 bar for 10 million of timesteps at one specific state point was performed to calculate the liquid density for each OME. Then, in the second step, a production run using a NVT ensemble for 30 million timesteps was carried out to calculate the shear viscosity.

C Correlations of the experimental data

The liquid density at 1 bar was correlated using the Racket equation.²⁴

$$\rho^{\text{liq}}/(\text{mol L}^{-1}) = \frac{A}{B\left(1+(1-\frac{T}{T_c})^D\right)} \quad (9)$$

The parameters A , B and D were obtained by fitting the experimental density values from Wang et al.²¹ for OME1. The parameters as well as the experimental density values for OME n ($n = 2 - 4$) were obtained from Burger et al.²⁴ The parameters A , B , and D as well as the critical temperatures T_c are given in Table 8.

Table 8: Parameters of the correlation of the liquid density at 1 bar of OME n , see Eq. (9).

Component	A	B	D	T_c/K
OME1	1.663	0.324	0.383	480.6
OME2	0.900	0.277	0.285	552.2
OME3	0.703	0.272	0.285	603.4
OME4	0.550	0.262	0.285	646.9

The experimental vapour pressure was correlated by the extended Antoine equation.²⁴

$$\ln(p^s/\text{bar}) = A + \frac{B}{T/\text{K} + C} + D \ln(T/\text{K}) \quad (10)$$

The values of A , B , C and D are given in Table 9. The parameters were obtained by fitting

the vapour pressure values of OME1 from Pan et al.²⁰ and for OME n ($n = 2 - 4$) from Boyd et al.²³

Table 9: Parameters of the correlation of the vapour pressure of OME n , see Eq. (10).

Component	A	B	C	D
OME1	9.241	−2413.00	−53.84	0.0
OME2	8.924	−2697.00	−74.86	0.0
OME3	57.740	−7730.00	0.0	−6.548
OME4	80.080	−9950.00	0.0	−9.59

References

- (1) Lump, B.; Rothe, D.; Pastötter, C.; Lämmermann, R.; Jacob, E. Oxymethylene ethers as diesel fuel additives of the future. *MTZ Worldwide* **2011**, *72*, 34–38.
- (2) Burger, J.; Papaioannou, V.; Gopinath, S.; Jackson, G.; Galindo, A.; Adjiman, C. S. A hierarchical method to integrated solvent and process design of physical CO₂ absorption using the SAFT- γ Mie approach. *AIChE J.* **2015**, *61*, 3249–3269.
- (3) Schappals, M.; Breug-Nissen, T.; Langenbach, K.; Burger, J.; Hasse, H. Solubility of carbon dioxide in poly(oxymethylene) dimethyl ethers. *J. Chem. Eng. Data* **2017**, *62*, 4027–4031.
- (4) Devaux, D.; Yano, H.; Uchida, H.; Dubois, J.-L.; Watanabe, M. Electro-oxidation of hydrolysed poly-oxymethylene-dimethylether on PtRu supported catalysts. *Electrochim. Acta* **2011**, *56*, 1460–1465.
- (5) Baranton, S.; Uchida, H.; Tryk, D. A.; Dubois, J. L.; Watanabe, M. Hydrolyzed poly-oxymethylenedimethylethers as liquid fuels for direct oxidation fuel cells. *Electrochim. Acta* **2013**, *108*, 350–355.

- (6) Feiling, A.; Münz, M.; Beidl, C. Potential of the synthetic fuel OME_{1b} for the soot-free diesel engine. *ATZextra Worldwide* **2016**, *21*, 16–21.
- (7) Iannuzzi, S. E.; Barro, C.; Boulouchos, K.; Burger, J. POMDME-diesel blends: Evaluation of performance and exhaust emissions in a single cylinder heavy-duty diesel engine. *Fuel* **2017**, *203*, 57–67.
- (8) Schmitz, N.; Burger, J.; Ströfer, E.; Hasse, H. From methanol to the oxygenated diesel fuel poly(oxymethylene) dimethyl ether: An assessment of the production costs. *Fuel* **2016**, *185*, 67–72.
- (9) Burger, J.; Siegert, M.; Ströfer, E.; Hasse, H. Poly(oxymethylene) dimethyl ethers as components of tailored diesel fuel: Properties, synthesis and purification concepts. *Fuel* **2010**, *89*, 3315–3319.
- (10) Breitzkreuz, C. F.; Schmitz, N.; Ströfer, E.; Burger, J.; Hasse, H. Design of a production process for poly(oxymethylene) dimethyl ethers from dimethyl ether and trioxane. *Chem. Ing. Tech.* **2018**, *90*, 1489–1496.
- (11) Schmitz, N.; Ströfer, E.; Burger, J.; Hasse, H. Conceptual design of a novel process for the production of poly(oxymethylene) dimethyl ethers from formaldehyde and methanol. *Ind. Eng. Chem. Res.* **2017**, *56*, 11519–11530.
- (12) Schmitz, N.; Breitzkreuz, C. F.; Ströfer, E.; Burger, J.; Hasse, H. Vapor–liquid equilibrium and distillation of mixtures containing formaldehyde and poly(oxymethylene) dimethyl ethers. *Chem. Eng. Process.* **2018**, *131*, 116–124.
- (13) Burger, J.; Ströfer, E.; Hasse, H. Chemical equilibrium and reaction kinetics of the heterogeneously catalyzed formation of poly(oxymethylene) dimethyl ethers from methylal and trioxane. *Ind. Eng. Chem. Res.* **2012**, *51*, 12751–12761.

- (14) Stubbs, J. M.; Potoff, J. J.; Siepmann, J. I. Transferable potentials for phase equilibria. 6. United-atom description for ethers, glycols, ketones, and aldehydes. *J. Phys. Chem. B* **2004**, *108*, 17596–17605.
- (15) Briggs, J. M.; Matsui, T.; Jorgensen, W. L. Monte Carlo simulations of liquid alkyl ethers with the OPLS potential functions. *J. Comput. Chem.* **1990**, *11*, 958–971.
- (16) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- (17) Dasgupta, S.; Smith, K. A.; Goddard III, W. A. Polyoxymethylene: the Hessian biased force field for molecular dynamics simulations. *J. Phys. Chem.* **1993**, *97*, 10891–10902.
- (18) Eckl, B.; Vrabec, J.; Hasse, H. Set of molecular models based on quantum mechanical ab initio calculations and thermodynamic data. *J. Phys. Chem. B* **2008**, *112*, 12710–12721.
- (19) Stephan, S.; Horsch, M. T.; Vrabec, J.; Hasse, H. MolMod—an open access database of force fields for molecular simulations of fluids. *Mol. Simul.* **2019**, 1–9.
- (20) Pan, J.; Wu, J.; Liu, Z. Vapor pressure of dimethoxymethane and 1, 1, 1, 3, 3-pentafluoropropane. *J. Chem. Eng. Data* **2006**, *51*, 186–189.
- (21) Wang, X.; Pan, J.; Wu, J.; Liu, Z. Surface tension of dimethoxymethane and methyl *tert*-butyl ether. *J. Chem. Eng. Data* **2006**, *51*, 1394–1397.
- (22) Dortmund Data Bank. www.ddbst.com, 2018.
- (23) Boyd, R. H. Some physical properties of polyoxymethylene dimethyl ethers. *J. Polym. Sci.* **1961**, *50*, 133–141.

- (24) Burger, J.; Ströfer, E.; Hasse, H. Production process for diesel fuel components poly(oxymethylene) dimethyl ethers from methane-based products by hierarchical optimization with varying model depth. *Chem. Eng. Res. Des.* **2013**, *91*, 2648–2662.
- (25) Eggimann, B. L.; Sun, Y.; DeJaco, R. F.; Singh, R.; Ahsan, M.; Josephson, T. R.; Siepmann, J. I. Assessing the Quality of Molecular Simulations for Vapor–Liquid Equilibria: An Analysis of the TraPPE Database. *Journal of Chemical & Engineering Data* **2019**,
- (26) Panagiotopoulos, A. Z.; Quirke, N.; Stapleton, M.; Tildesley, D. Phase equilibria by simulation in the Gibbs ensemble. *Mol. Phys.* **1988**, *63*, 527–545.
- (27) Panagiotopoulos, A. Z. Direct determination of phase coexistence properties of fluids by Monte Carlo simulation in a new ensemble. *Mol. Phys.* **1987**, *61*, 813–826.
- (28) Yiannourakou, M.; Ungerer, P.; Leblanc, B.; Ferrando, N.; Teuler, J.-M. Overview of Medea®-GIBBS capabilities for thermodynamic property calculation and VLE behaviour description of pure compounds and mixtures: application to polar compounds generated from ligno-cellulosic biomass. *Mol. Simul.* **2013**, *39*, 1165–1211.
- (29) Siepmann, J. I.; Frenkel, D. Configurational bias Monte Carlo: a new sampling scheme for flexible chains. *Mol. Phys.* **1992**, *75*, 59–70.
- (30) Shah, J. K.; Marin-Rimoldi, E.; Mullen, R. G.; Keene, B. P.; Khan, S.; Paluch, A. S.; Rai, N.; Romanielo, L. L.; Rosch, T. W.; Yoo, B.; Maginn, E. J. Cassandra: An open source Monte Carlo package for molecular simulation. *J. Comput. Chem.* **2017**, *38*, 1727–1739.
- (31) Schappals, M.; Mecklenfeld, A.; Kröger, L.; Botan, V.; Köster, A.; Stephan, S.; García, E. J.; Rutkai, G.; Raabe, G.; Klein, P.; Leonhard, K.; Glass, C. W.; Lenhard, J.; Vrabec, J.; Hasse, H. Round Robin study: Molecular simulation of thermodynamic

- properties from models with internal degrees of freedom. *J. Chem. Theory Comput.* **2017**, *13*, 4270–4280.
- (32) Stephan, S.; Thol, M.; Vrabec, J.; Hasse, H. Thermophysical properties of the Lennard-Jones fluid: Database and data assessment. *J. Chem. Inf. Model.* **2019**,
- (33) Nezbeda, I. Simulations of vapor–liquid equilibria: Routine versus thoroughness. *J. Chem. Eng. Data* **2016**, *61*, 3964–3969.
- (34) Chen, Q. P.; Chu, J. D.; DeJaco, R. F.; Lodge, T. P.; Siepmann, J. I. Molecular simulation of olefin oligomer blend phase behavior. *Macromolecules* **2016**, *49*, 3975–3985.
- (35) Ungerer, P.; Boutin, A.; Fuchs, A. H. Direct calculation of bubble points by Monte Carlo simulation. *Mol. Phys.* **1999**, *97*, 523–539.
- (36) Ungerer, P.; Boutin, A.; Fuchs, A. Direct calculation of bubble points for alkane mixtures by molecular simulation. *Mol. Phys.* **2001**, *99*, 1423–1434.
- (37) Berendsen, H.; van der Spoel, D.; van Drunen, R. GROMACS: A message-passing parallel molecular dynamics implementation. *Comput. Phys. Commun.* **1995**, *91*, 43–56.
- (38) Hess, B.; Bekker, H.; Berendsen, H. J. C.; Fraaije, J. G. E. M. LINCS: A linear constraint solver for molecular simulations. *J. Comput. Chem.* **1997**, *18*, 1463–1472.
- (39) Alfè, D.; Gillan, M. J. First-principles calculation of transport coefficients. *Phys. Rev. Lett.* **1998**, *81*, 5161–5164.
- (40) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (41) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785.

- (42) Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, *105*, 9982–9985.
- (43) Klamt, A.; Schüürmann, G. COSMO: A new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799–805.
- (44) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery Jr, J. A. General atomic and molecular electronic structure system. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (45) Gordon, M. S.; Schmidt, M. W. *Theory and applications of computational chemistry*; Elsevier, 2005; pp 1167–1189.
- (46) Bayly, C. I.; Cieplak, P.; Cornell, W.; Kollman, P. A. A well-behaved electrostatic potential based method using charge restraints for deriving atomic charges: the RESP model. *J. Phys. Chem.* **1993**, *97*, 10269–10280.
- (47) Bourasseau, E.; Haboudou, M.; Boutin, A.; Fuchs, A. H.; Ungerer, P. New optimization method for intermolecular potentials: Optimization of a new anisotropic united atoms potential for olefins: Prediction of equilibrium properties. *J. Chem. Phys.* **2003**, *118*, 3020–3034.
- (48) Hill, T. L. *An introduction to statistical thermodynamics*; Courier Corporation, 1986.
- (49) Lagache, M.; Ungerer, P.; Boutin, A.; Fuchs, A. Prediction of thermodynamic derivative properties of fluids by Monte Carlo simulation. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4333–4339.
- (50) Martin, M. G.; Siepmann, J. I. Transferable potentials for phase equilibria. 1. United-atom description of n-alkanes. *J. Phys. Chem. B* **1998**, *102*, 2569–2577.

- (51) Rutkai, G.; Köster, A.; Guevara-Carrion, G.; Janzen, T.; Schappals, M.; Glass, C. W.; Bernreuther, M.; Wafai, A.; Stephan, S.; Kohns, M.; Reiser, S.; Deublein, S.; Horsch, M.; Hasse, H.; Vrabec, J. *ms2: A molecular simulation tool for thermodynamic properties*, release 3.0. *Comput. Phys. Commun.* **2017**, *221*, 343–351.
- (52) Niethammer, C.; Becker, S.; Bernreuther, M.; Buchholz, M.; Eckhardt, W.; Heinicke, A.; Werth, S.; Bungartz, H.-J.; Glass, C. W.; Hasse, H.; Vrabec, J.; Horsch, M. *ls1 mardyn: The massively parallel molecular dynamics code for large systems*. *J. Chem. Theory Comput.* **2014**, *10*, 4455–4464.
- (53) Plimpton, S. Fast parallel algorithms for short-range molecular dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.
- (54) Siepmann, J. I.; Karaborni, S.; Smit, B. Simulating the critical behaviour of complex fluids. *Nature* **1993**, *365*, 330.
- (55) Jorgensen, W. L.; Madura, J. D.; Swenson, C. J. Optimized intermolecular potential functions for liquid hydrocarbons. *J. Am. Chem. Soc.* **1984**, *106*, 6638–6646.
- (56) Siu, S. W.; Pluhackova, K.; Böckmann, R. A. Optimization of the OPLS-AA force field for long hydrocarbons. *J. Chem. Theory Comput.* **2012**, *8*, 1459–1470.
- (57) Rowlinson, J. S.; Swinton, F. L. *Liquids and liquid mixtures: Butterworths monographs in chemistry*; Butterworth-Heinemann, 2013.
- (58) Rowlinson, J. S.; Widom, B. *Molecular theory of capillarity*; Courier Corporation, 2013.
- (59) Ferrenberg, A. M.; Landau, D. Critical behavior of the three-dimensional Ising model: A high-resolution Monte Carlo study. *Phys. Rev. B* **1991**, *44*, 5081.
- (60) Wilding, N. B. Critical-point and coexistence-curve properties of the Lennard-Jones fluid: A finite-size scaling study. *Phys. Rev. E* **1995**, *52*, 602.

- (61) Kobe, K. A.; Mathews, J. F. Critical properties and vapor pressures of some organic nitrogen and oxygen compounds. *J. Chem. Eng. Data* **1970**, *15*, 182–186.
- (62) Errington, J. R.; Panagiotopoulos, A. Z. A new intermolecular potential model for the n-alkane homologous series. *J. Phys. Chem. B* **1999**, *103*, 6314–6322.
- (63) Anselme, M. J.; Gude, M.; Teja, A. S. The critical temperatures and densities of the n-alkanes from pentane to octadecane. *Fluid Phase Equilib.* **1990**, *57*, 317–326.
- (64) Zheng, P.; Meng, X.; Wu, J.; Liu, Z. Density and viscosity measurements of dimethoxymethane and 1,2-dimethoxyethane from 243 K to 373 K up to 20 MPa. *Int. J. Thermophys.* **2008**, *29*, 1244–1256.
- (65) Kang, M.; Song, H.; Jin, F.; Chen, J. Synthesis and physicochemical characterization of polyoxymethylene dimethyl ethers. *J. Fuel Chem. Technol.* **2017**, *45*, 837–845.
- (66) Zhang, Y.; Otani, A.; Maginn, E. J. Reliable viscosity calculation from equilibrium molecular dynamics simulations: A time decomposition method. *J. Chem. Theory Comput.* **2015**, *11*, 3537–3546.
- (67) Rowley, D. R. W. R. L. Shear viscosity of polar liquid mixtures via non-equilibrium molecular dynamics: Water, methanol, and acetone. *Mol. Phys.* **1998**, *94*, 555–564.
- (68) Guevara-Carrion, G.; Nieto-Draghi, C.; Vrabec, J.; Hasse, H. Prediction of transport properties by molecular simulation: Methanol and ethanol and their mixture. *J. Phys. Chem. B* **2008**, *112*, 16664–16674.
- (69) Merker, T.; Engin, C.; Vrabec, J.; Hasse, H. Molecular model for carbon dioxide optimized to vapor-liquid equilibria. *J. Chem. Phys.* **2010**, *132*, 234512.
- (70) Schnabel, T.; Vrabec, J.; Hasse, H. Henry’s law constants of methane, nitrogen, oxygen and carbon dioxide in ethanol from 273 to 498 K: Prediction from molecular simulation. *Fluid Phase Equilib.* **2005**, *233*, 134–143.

- (71) Vrabec, J.; Stoll, J.; Hasse, H. Molecular models of unlike interactions in fluid mixtures. *Mol. Simul.* **2005**, *31*, 215–221.
- (72) Tsai, D. H. The virial theorem and stress calculation in molecular dynamics. *J. Chem. Phys.* **1979**, *70*, 1375–1382.
- (73) Swenson, R. J. Comments on virial theorems for bounded systems. *Am. J. Phys.* **1983**, *51*, 940–942.
- (74) Darden, T.; York, D.; Pedersen, L. Particle mesh Ewald: An $N \cdot \log(N)$ method for Ewald sums in large systems. *J. Chem. Phys.* **1993**, *98*, 10089–10092.

Figure 8: Graphical abstract