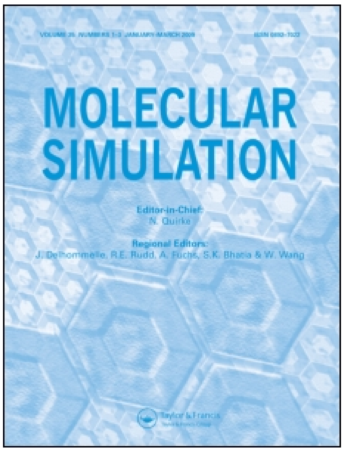

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AN ALL-ATOM FORCE FIELD FOR LIQUID ETHANOL – PROPERTIES OF ETHANOL–WATER MIXTURES

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An all-atom model of ethanol is presented. It describes a number of properties of liquid ethanol in good agreement with experiment. It has also been tested in conjunction with the simple-point-charge (SPC) water model. The calculated bulk properties of ethanol-water mixtures show reasonable agreement with experimental data where available.

Keywords: Ethanol; ethanol-water mixtures; molecular dynamics simulations.

1. INTRODUCTION

Ethanol is a common solvent in chemistry. Therefore, I was surprised not to find ethanol models in abundance in the literature. A united-atom model has been given by Jorgensen [1]. However, the limitations of united-atom models in the simulation of polymer membranes (my area of work) have been demonstrated before [2]. It was the intention to develop an all-atom ethanol force field which can also be used in connection with the SPC water model [3]. Therefore, it has been designed to be compatible with this water model. The purpose of this short note is to report the new all-atom force field for liquid ethanol for further reference and to analyse its performance for a number of properties of liquid ethanol and, in addition, mixtures of ethanol and water.

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2. FORCE FIELD AND SIMULATION DETAILS

Most intramolecular force field parameters are either relatively uncritical for the calculation of bulk liquid properties or can be easily compensated for by small changes in other parameters. In order to reduce the optimisation space, I have taken parameters for bond lengths (treated as rigid constraints) and bond angles that I used before without further adaptation (Table I). Similarly, for the rotation of the methyl group, I used a threefold cosine potential with a barrier height typical for liquid alkanes. However, the orientation of the OH group is more crucial, since it contributes to the orientation of the molecular dipole and determines the possibility of forming hydrogen bonds. I have calculated the potential energy curve along the H-O-C-C dihedral angle in the gas phase by ab initio methods (not shown). A Hartree-Fock (HF) calculation using the 6-31G** basis set gives trans (180°) as the most stable conformation and gauche ($\pm 64°$) as a second minimum with a potential energy of $+0.42$ kJ/mol with respect to trans. The rotational barriers come out as 7.4 kJ/mol (cis, 0°) and 5.3 kJ/mol (120°). A mixed HF and density-functional calculation (B3LYP) in the same basis finds gauche ($\pm 64°$) more stable than trans by -1.4 kJ/mol, with rotation barriers of 5.7 kJ/mol (cis) and 4.5 kJ/mol (120°). The gas-phase dipole moments of the gauche and trans conformers are similar (1.7 and 1.8 Debyes for trans and gauche in HF; 1.5 and 1.6 Debyes in B3LYP), so a significant shift in their relative energies by a polarisable solvent is not to be expected. In my experience (e.g. ref. 4.), B3LYP is to be trusted more for relative energy differences among local minima, whereas HF tends to be more correct for rotational barrier heights. I therefore chose heights of 6 kJ/mol for both the cis and the trans-gauche barriers. In order to reproduce the gauche-trans energy difference, I also introduced a small charge (-0.029 e) on the methyl carbon exclusively for the Coulombic interaction between this carbon and the hydroxyl H.

Starting points for the atomic Lennard-Jones parameters ε and σ were values used before for poly(ethylene oxide) [5,6] and SPC water [3]. The hydroxyl H has no Lennard-Jones interactions. They are compensated by larger parameters for the oxygen atom. This description of polar hydrogens is identical to that of SPC water [3], the previous united-atom force field for ethanol [1], and the GROMOS force field [7,8]. Since one goal of the ethanol force field is compatibility with SPC water, I opted for the same sort of model for the hydroxyl group. The choice of atomic charges was guided by the principle that there should be no charge separation along aliphatic C-H and C-C bonds, since these are small enough for being

TABLE I Parameters for the all-atom force field for ethanol

Nonbonded interactions[a]	$E_{pot}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0}\left(\frac{1}{r_{ij}} - \frac{\varepsilon_{RF}-1}{2\varepsilon_{RF}+1}\frac{r_{ij}^2}{r_{cutoff}}\right)$			
Atoms	*m/a.m.u.*[b]	$\varepsilon/kJ\ mol^{-1}$[c]	σ/nm[c]	*q/e*
H(OH)	1.00787	0	0	0.4
O	15.9949	0.65	0.317	−0.7
$C(CH_2)$	12	0.336	0.35	0.3
$C(CH_3)$	12	0.336	0.35	0
$H(CH_2,CH_3)$	1.00787	0.21	0.257	0
Bond constraints	*d/nm*			
H-O	0.097			
C-O	0.1431			
C-C	0.153			
C-H	0.11			
Bond angles	$E_{pot}(\phi) = \frac{k_\phi}{2}(\phi - \phi_0)^2$			
	$\phi_0/degrees$	$k_\phi/kJ\ mol^{-1}\ rad^{-2}$		
H-O-C	105	320		
O-C-C	107.8	460		
O-C-H	108	350		
C-C-H	110	367		
H-C-H	108	306		
Dihedral angles	$E_{pot}(\tau) = \frac{k_\tau}{2}[1 - \cos 3(\tau - \tau_0)]$			
	$\tau_0/degrees$[d]	$k_\tau/kJ\ mol^{-1}$		
H-O-C-C	180	6		
O-C-C-H	180	11.5		

[a] There are no nonbonded interactions between atoms separated by one or two bonds (first and second neighbours). For the nonbonded third neighbour interaction $H(OH) - C(CH_3)$, the charge on carbon is adjusted to $-0.029\ e$.

[b] Atomic masses are those of the most abundant isotopes.

[c] The Lorentz-Berthelot combination rules are used for mixed interactions:

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}, \quad \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$$

[d] The cis conformation corresponds to $\tau = 0°$.

absorbed into the Lennard-Jones interactions. For the O-H bond a charge separation of 0.4 e was assumed, similar to SPC water (0.41 e), whereas for C-O a charge separation of 0.3 e was taken. This leads to the atomic charges in Table I. These charges are in line with charges derived by electrostatic potential fits to the HF/6-31G** charge density of the trans conformer, if one collapses the charges of the aliphatic hydrogens into their carbon atoms: + 0.41 e(H), − 0.70 e(O), + 0.33(CH_2), − 0.04(CH_3). Various changes in nonbonded parameters and their combinations were attempted, before I arrived at the values reported in Table I. In particular, the σ parameters of the aliphatic hydrogens were adjusted in order to reproduce the density of liquid ethanol.

For water, the simple point charge (SPC) model was used in its original parametrisation [3] which was recently shown to need no improvement if used at room temperature and ambient pressure [9].

Molecular dynamics calculations were carried out with the YASP program [10]. The time step was 2 fs. Temperature T and pressure p were kept constant at 293.15 K (20°C) and 101.3 kPa (1 atm), resp., by the weak-coupling scheme [11], the coupling times were 0.1 ps(T) and 2.0 ps(p). All bond lengths were kept rigid by the SHAKE procedure [12]. An atomic neighbour list was used which was updated every 15 time steps and which included all pairs within 1.1 nm. The cut-off for nonbonded interactions was 1.0 nm with a reaction field correction [10]. The choice of the effective dielectric constant (relative permittivity) ε_{RF} used in the reaction-field treatment is not very crucial, once it is above, say 10. For the mixtures, it was combined from the dielectric constants of water (80) and Ethanol (24.3) by weighting them with the corresponding mole fractions. Simulation times of the various systems are listed in Table II.

3. PROPERTIES OF NEAT ETHANOL

A number of liquid properties of pure ethanol have been calculated as part of the evaluation of the new model. These are listed in Table II along with experimental values where available [13,14]. The mass density ρ which was used in the parametrisation comes out within 0.6% of the experimental value. The heat of vaporisation ΔH_{vap} was estimated as

$$\Delta H_{vap} = -E_{pot}(\text{inter}),$$

where E_{pot}(inter) is the contribution of all *inter*molecular nonbonded interactions to the potential energy. This definition disregards contributions

TABLE II Calculated properties of ethanol-water mixtures at 20°C and 1 atm[(a)]

x_{EtOH}	N_{EtOH}/N_{H_2O}	t (ns)	ρ (kg/m^3)	ΔH_{vap} (kJ/mol)	ΔH_M (J/mol)	κ $(10^{-10}$ $Pa^{-1})$	D_{H_2O} $(10^{-5}$ $cm^2/s)$	D_{EtOH} $(10^{-5}$ $cm^2/s)$	ε_r
0	0/432	2.5	978.6 (7.2)	41.49 (0.20)	0	1.74 (0.12)	3.32 (0.32)	-	117 (18)
0.0787	34/398	2.4	924.6 (81.9)	41.43 (0.99)	246	399 (220)	2.99 (0.07)	1.44 (0.12)	72 (1.6)
0.199	43/173	6.3	904.6 (8.5)	41.95 (0.37)	18.0	1.95 (0.13)	1.60 (0.25)	0.763 (0.11)	63 (5.0)
0.398	86/130	2.4	862.0 (7.0)	42.42 (0.39)	29.2	1.95 (0.12)	1.12 (0.12)	0.698 (0.13)	55 (16)
0.602	130/86	2.6	833.2 (6.0)	42.93 (0.42)	1.73	1.95 (0.35)	0.690 (0.17)	0.601 (0.045)	40 (8.7)
0.801	173/43	1.8	813.0 (5.8)	43.52 (0.44)	−103	2.15 (0.29)	0.816 (0.16)	0.567 (0.062)	31 (3.0)
1	216	1.8	794.4 (5.3)	43.89 (0.43)	0	2.06 (0.51)	-	0.642 (0.079)	21 (7.2)
exper. pure EtOH [13,14]			789.3	42.32		11.1		0.89-0.93	24.3

[(a)] x_{EtOH}: mole fraction ethanol;

t: simulated time;

ρ : mass density, root-mean-square (RMS) fluctuations in parentheses;

ΔH_{vap}: heat of vaporisation, RMS fluctuations in parentheses;

ΔH_M: enthalpy of mixing;

κ : isothermal compressibility, in parentheses standard deviation between different subtrajectories (usually of length 200 ps);

D_{H_2O}, D_{EtOH}: tracer diffusion coefficients of water and ethanol, respectively, in parentheses standard deviation of x, y and z components;

ε_r : relative permittivity (dielectric constant), in parentheses standard deviations between values calculated from fluctuations of individual Cartesian components of the total dipole moment vector.

from *intra*molecular degrees of freedom to the heat of vaporisation as well as from volume work and quantum corrections. The thus estimated ΔH_{vap} is 1.6 kJ/mol larger than the experimental value. The isothermal compressibility κ was estimated for an isothermal-isobaric ensemble from the fluctuations ΔV of the box volume V

$$\kappa = \langle \Delta V^2 \rangle / (V k_B T),$$

where k_B is Boltzmann's constant. The calculated compressibility comes out too small by a factor of 5. A disagreement of this sort is not all that untypical in liquid force fields. In part it is a consequence of the steep repulsive part r^{-12} of the Lennard-Jones potential.

The diffusion coefficient D has been calculated from the slope of the centre-of-mass mean-square displacement, taking averages over all molecules and all time origins. It should be noted that all diffusion coefficients calculated in this work are tracer diffusion coefficients, not to be confused with binary diffusion coefficients not to be confused with binary diffusion coefficients which measure the change in concentration. The calculated tracer diffusion coefficient for ethanol comes out too small by some 30%, which again is not untypical for liquid force fields.

The static relative permittivity ε_r of liquid ethanol has been calculated from the fluctuations of the total dipole moment $\mathbf{M}$ of the simulation cell

$$(\varepsilon_r - 1)\left(\frac{2\,\varepsilon_{\mathrm{RF}} + 1}{2\,\varepsilon_{\mathrm{RF}} + \varepsilon_r}\right) = \frac{\langle M^2\rangle - \langle M\rangle^2}{3\,\varepsilon_0\, V k_B T},$$

where $\varepsilon_{\mathrm{RF}}$ is the relative permittivity used in the reaction field treatment (see above) and ε_0 is the vacuum permittivity. The standard deviation between permittivities calculated separately from the fluctuations of the components M_x, M_y and M_z is used as an error estimate. The experimental permittivity is within the error bars of the calculation. The calculation only yields the contribution to the permittivity by the reorientation of molecular dipoles, not the smaller contribution from the electronic polarisability of the molecules. The importance of the latter can be crudely estimated from the refractive index $n_D = 1.36$ [13] of ethanol at the sodium D line (589 nm)

$$\varepsilon_{r,D} = n_D^2 = 1.85.$$

Visible light of this wavelength has a period of approximately 2×10^{-2} fs, orders of magnitude shorter than the fastest molecular motion. Hence, it will only probe the electronic contribution to the permittivity. Taking $\varepsilon_{r,D}$ as the missing contribution of the electronic polarisability also at zero frequency brings the calculated ε_r to 22.9, that is within 6% of the experimental value. As an aside: Using the refractive index to estimate the electronic part of ε_r seems to hold in other cases as well. For example, in a recent MD study of chloroform [15], ε_r was calculated to be 2.4, compared to an experimental value of 4.81. From the refractive index, the electronic contribution would amount to 2.1, bringing experiment and calculation into close agreement. In the case of a model for dimethyl sulfoxide [16], however, the discrepancy between calculation (30) and experiment (46) was too large to be accounted for by the electronic contribution (2.2).

4. ETHANOL-WATER MIXTURES

The properties of ethanol-water mixtures have also been calculated. I normally used a total of 216 molecules except for pure water and the $x_{\mathrm{EtOH}} = 0.0787$ system which would otherwise have been too small for the cut-off used. For these two systems, a total of 432 molecules was used. The calculated properties are given in Table II. For comparison with experiment, however, there are also plots of these data.

The density ρ of the water-ethanol system is shown in Figure 1 together with experimental values [14]. Both sets agree to within a few percent over the whole range. The agreement varies, however. It is best on the ethanol end (0.7 % deviation) and becomes worse at higher water contents. At

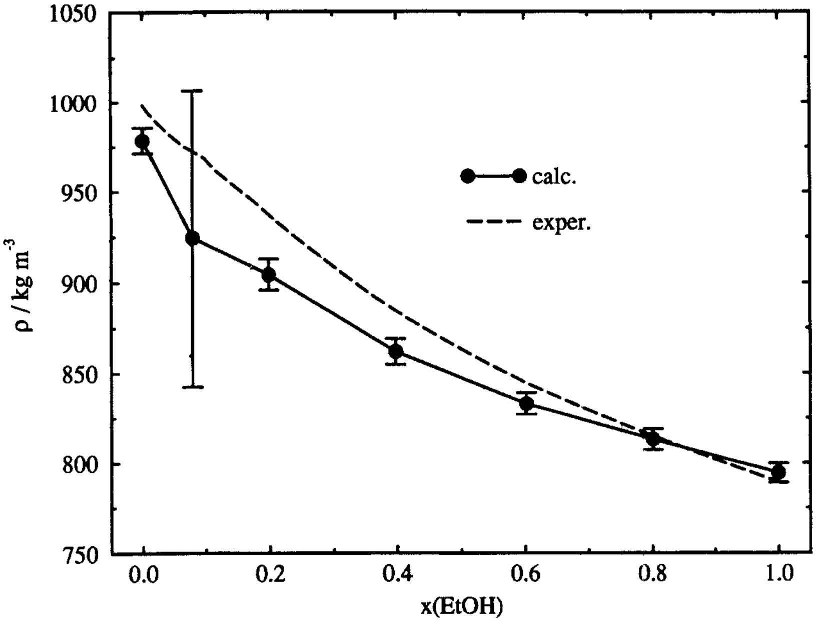

FIGURE 1 Mass density ρ of ethanol-water mixtures at 20°C and 1 atm. Error bars indicate the size of the RMS fluctuations.

$x_{\text{EtOH}} = 0.0787$, the mixture undergoes large density fluctuations for which no solid explanation has been found also upon closer inspection of the structures. At the moment, I would speculate that this is a size effect.

The molar enthalpy of mixing ΔH_M is defined as

$$\Delta H_M = \Delta H_{\text{vap}}\,(\text{mixture}) - x_{\text{EtOH}}\,\Delta H_{\text{vap}}(\text{EtOH}) - (1 - x_{\text{EtOH}})\,\Delta H_{\text{vap}}(\text{H}_2\text{O}).$$

The volume change upon mixing ΔV_M has also been calculated. It is, however, so small that the $p\Delta V_M$ contribution to ΔH_M can be neglected. The enthalpy of mixing is shown in Figure 2. The calculation shows that ΔH_M is essentially zero over the whole range. Experimentally, a small negative ΔH_M is found (-0.83 kJ/mol at most) [14]. Given that ΔH_M is calculated as the small difference of large numbers, the agreement is reasonable. It would appear, though, that in order to produce a better agreement with experiment, force field parameters for certain interactions between ethanol and water molecules would have to be tuned. This is commonly done in other force fields (*e.g.*, ref. 7) for Lennard-Jones parameters for interactions of water with aliphatic groups.

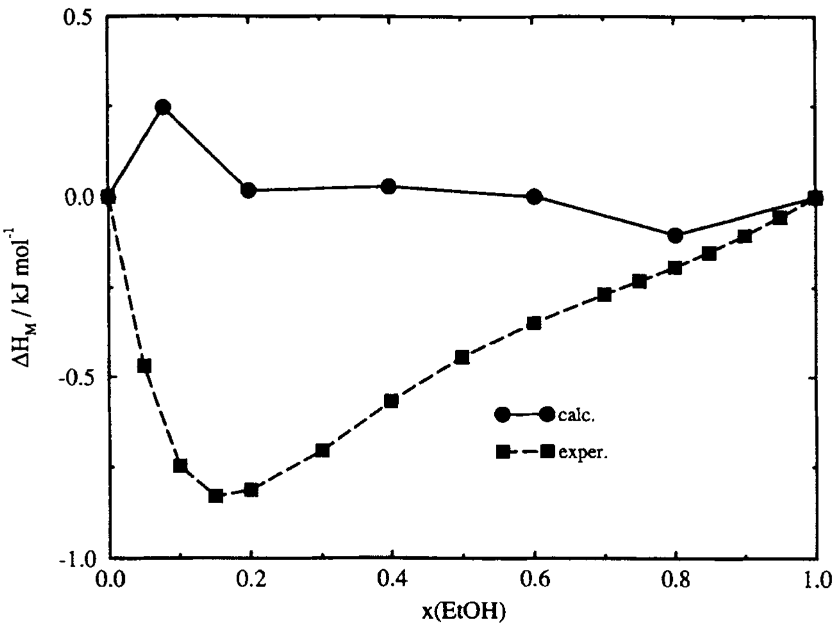

FIGURE 2 Enthalpy of mixing ΔH_M of ethanol-water mixtures at 20 C and 1 atm.

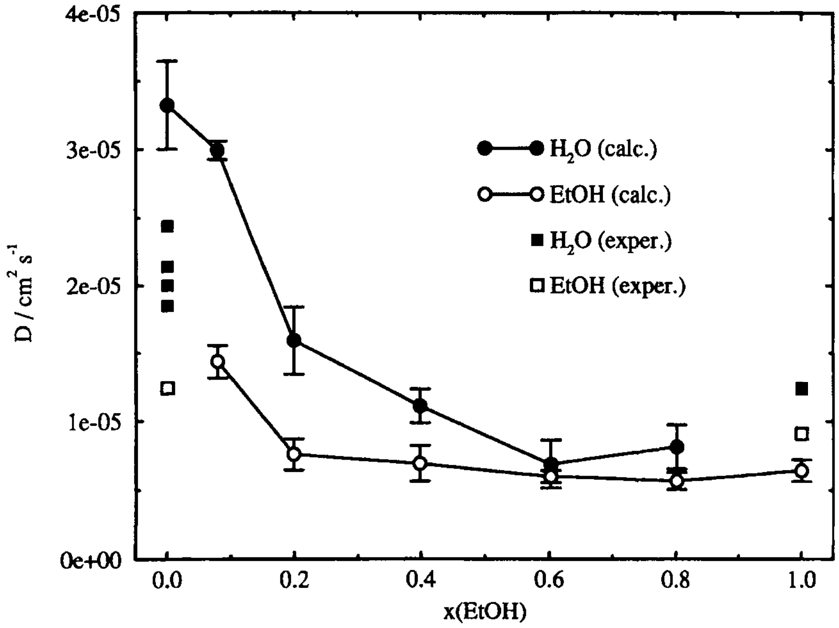

FIGURE 3 Tracer diffusion coefficients D of ethanol and water in ethanol-water mixtures at 20°C and 1 atm. Error bars denote the standard deviations of the three diagonal elements of the diffusion tensor (D_{xx}, D_{yy}, D_{zz}).

Tracer diffusion coefficients D of both ethanol and water have been calculated over the whole range of compositions (Fig. 3). Experimental tracer diffusion coefficients could only be found for (almost) pure systems, that is for water in pure water and traces of ethanol in water (infinite dilution), and vice versa. The calculated diffusion coefficients extrapolate well to these limits with the exception of the diffusion coefficient of pure water which is overestimated by a small amount, a well-known feature of the SPC water model. The ethanol model, on the other hand, appears to do well on both ends of the concentration range.

The relative permittivity ε_r of ethanol-water mixtures, in general, reproduces the experiment well over the whole concentration range (Fig. 4). The agreement is certainly good enough for the ethanol-water models to be used as solvents in the simulation of solutions of polar or ionic solutes. However, dielectric properties are known to be sensitive to the particulars of the treatment of the Coulombic interactions (cut-off distance, reaction-field correction or not, Ewald sums or not, etc.). Hence, they could come out differently for

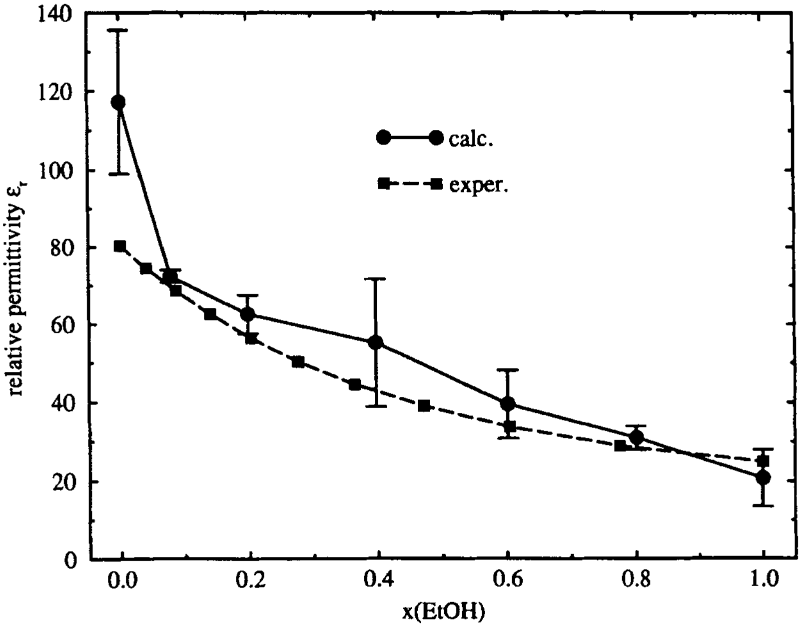

FIGURE 4 Relative permittivity ε_r for ethanol-water mixtures at 20°C and 1 atm. Error bars denote the standard deviations of relative permittivities calculated from fluctuations of individual Cartesian components of the vector of the total dipole moment.

this model if those settings were different. An example of this is the dielectric constant of pure water which, in this work, is calculated to be 117, whereas a simulation of 512 SPC water molecules at 300 K and using a cut-off of 0.9 nm and $\varepsilon_{RF} = \infty$ found a value of 54 [17].

5. SUMMARY

An all-atom force field for ethanol has been parametrised. It is of standard analytical form. In spite of its simplicity it describes well the bulk properties not only of neat liquid ethanol but also of ethanol-water mixtures where the water is modelled by the SPC force field. Although it fails to reproduce small details in the thermodynamic properties (*e.g.* enthalpy of mixing) it does surprisingly well for transport and response properties (diffusion coefficients and relative permittivity).

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