

Force Field Benchmark of Organic Liquids: Density, Enthalpy of Vaporization, Heat Capacities, Surface Tension, Isothermal Compressibility, Volumetric Expansion Coefficient, and Dielectric Constant

Carl Caleman,[†] Paul J. van Maaren,[‡] Minyan Hong,[‡] Jochen S. Hub,[‡] Luciano T. Costa,[§] and David van der Spoel^{*,‡}

[†]Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron Notkestraße 85, DE-22607 Hamburg, Germany

[‡]Department of Cell and Molecular Biology, Uppsala University, Husargatan 3, Box 596, SE-75124 Uppsala, Sweden

[§]Departamento de Ciências Exatas, Federal University of Alfenas—MG Rua Gabriel Monteiro da Silva, 700 Alfenas—MG CEP: 37130-000, Brazil

S Supporting Information

ABSTRACT: The chemical composition of small organic molecules is often very similar to amino acid side chains or the bases in nucleic acids, and hence there is no a priori reason why a molecular mechanics force field could not describe both organic liquids and biomolecules with a single parameter set. Here, we devise a benchmark for force fields in order to test the ability of existing force fields to reproduce some key properties of organic liquids, namely, the density, enthalpy of vaporization, the surface tension, the heat capacity at constant volume and pressure, the isothermal compressibility, the volumetric expansion coefficient, and the static dielectric constant. Well over 1200 experimental measurements were used for comparison to the simulations of 146 organic liquids. Novel polynomial interpolations of the dielectric constant (32 molecules), heat capacity at constant pressure (three molecules), and the isothermal compressibility (53 molecules) as a function of the temperature have been made, based on experimental data, in order to be able to compare simulation results to them. To compute the heat capacities, we applied the two phase thermodynamics method (Lin et al. *J. Chem. Phys.* **2003**, *119*, 11792), which allows one to compute thermodynamic properties on the basis of the density of states as derived from the velocity autocorrelation function. The method is implemented in a new utility within the GROMACS molecular simulation package, named `g_dos`, and a detailed exposé of the underlying equations is presented. The purpose of this work is to establish the state of the art of two popular force fields, OPLS/AA (all-atom optimized potential for liquid simulation) and GAFF (generalized Amber force field), to find common bottlenecks, i.e., particularly difficult molecules, and to serve as a reference point for future force field development. To make for a fair playing field, all molecules were evaluated with the same parameter settings, such as thermostats and barostats, treatment of electrostatic interactions, and system size (1000 molecules). The densities and enthalpy of vaporization from an independent data set based on simulations using the CHARMM General Force Field (CGenFF) presented by Vanommeslaeghe et al. (*J. Comput. Chem.* **2010**, *31*, 671) are included for comparison. We find that, overall, the OPLS/AA force field performs somewhat better than GAFF, but there are significant issues with reproduction of the surface tension and dielectric constants for both force fields.

1. INTRODUCTION

Parameters in most force fields have been derived incrementally, that is, building on previous work by adding support for different chemical moieties in a sequential fashion. While the focus of many force fields is on biomolecules, the chemical basis lies in organic molecules. Of the major force fields available today OPLS/AA (optimized parameters for liquid simulations, all atoms) is one of the few that “specializes” in simple liquids.¹ The generalized Amber force field (GAFF) was introduced recently² (together with the Antechamber set of programs³) to aid in the derivation of force field parameters for small molecules that are often involved in binding to biomolecules. Accurate parameters are crucial for predicting, for instance, the Gibbs energy of ligand binding, a key property in drug design.⁴ The GAFF parameters for small molecules are intended to be combined with the Amber force field⁵ although there are studies of proteins using GAFF parameters as well.⁶

A critical component in force field development is generation of partial charges. The method for deriving partial charges by

optimizing their values to reproduce the electrostatic potential (ESP) was introduced in the 1980s by Kollman et al.^{7,8} The electron density taken from a quantum chemistry calculation, together with the nuclear charges, generates an electrostatic potential around the molecule. Typically, the set of partial charges for a molecule, for use in force field calculations, is determined by minimizing the (square) difference between the ESP generated by the partial charges and the ESP generated by the quantum chemistry calculation. A set of partial charges (or indeed any atom-centered set of spherically distributed charges) can never completely reproduce the ESP due to the fact that electron density is not completely spherically symmetric around the nuclei (for instance, due to p and higher orbitals). A further issue is due to the fact that the fitting points are highly correlated, and hence atoms far from the ESP data points (e.g., the buried

Received: October 18, 2011

Published: December 07, 2011

carbon in isobutanol) may end up being a sink for the fit^{9,10} and get arbitrary values. An ad hoc refinement of the ESP method to overcome this problem is the restrained ESP (RESP) method.¹¹ The RESP method does the same fit, however with an added penalty on the absolute value of the charge. The RESP method is an integral part of the Antechamber package,^{2,3} which relies on either quantum calculations or empirical methods, such as AM1-BCC,^{12,13} to provide the partial charges.

Mobley et al. tested the performance of GAFF parameters for Gibbs energies of hydration using two different water models.^{14,15} They paid particular attention to the way the partial charges were determined and found that the final results are related to the level of theory used, something that was corroborated by Wallin et al., who did a similar study of charge schemes for ligand binding.¹⁶ The CM1 charge model for OPLS/AA,¹⁷ used in the study of Wallin et al.,¹⁶ performs well,^{18,19} although some degradation for conformational energetics is expected. The differences are generally considered to be minor.¹ There are some drawbacks with these studies however. First, they involve complex systems, where a subset of the parameters was changed and the “quality” of the charges evaluated on the basis of a single number, the free energy, hereby ignoring the interdependency between Lennard-Jones parameters and point charges. Second, free energy calculations depend critically on the amount of the sampling that was used, although it is possible to ascertain that the errors due to sampling are small.²⁰ In order to test the validity of force field, it would be good to take one step back and evaluate the performance for simple systems first, in order to avoid systematic errors due to water model and/or protein force fields. A recent review by Jorgensen and Tirado-Rives provides further background information on the topic of force field development.¹

To assess the state of the art of GAFF and OPLS/AA force fields, we provide a comprehensive benchmark of the liquid properties of molecules in each of the GAFF and OPLS/AA force fields. Previous simulations of mixtures of alcohol and water^{21,22} using the OPLS/AA force field showed that many properties of the pure liquids are reproduced faithfully, but the heat of mixing and the density of mixing are slightly, but significantly, off. Similar comparisons of force fields for water models are numerous in the literature (see for example, refs 23–29), while for organic liquids there are some papers by Kaminski and Jorgensen,^{30,31} and a recent paper by Wang and Tingjun,³² which we discuss in the Discussion section.

Liquid properties are usually known experimentally with high accuracy, and their calculation is most often straightforward. Rather, the time goes into the preparation and equilibration of the systems. A total of 146 molecular liquids was prepared and simulated using these force fields in the GROMACS molecular simulation package,^{33–36} and from these molecular dynamics simulations, we extract the density ρ (from constant pressure simulations), the enthalpy of vaporization ΔH_{vap} , the heat capacities at constant pressure c_p and volume c_v , the volumetric expansion coefficient α_p , the isothermal compressibility κ_T , the surface tension γ , and the static dielectric constant $\epsilon(0)$. Although, in principle, more observables could be computed, this set includes the most important thermodynamic properties of the liquids, including temperature derivatives of energy and volume. The intention of this work is to supply a large number of tests for further force field development. To this end, the topologies and structures have been made available on a dedicated Web site at <http://virtualchemistry.org>, while the simulation parameters are available as Supporting Information to this paper. These topologies and structure files may be useful for simulations of

biomolecules in organic liquids as well. The recently presented all atom CHARMM general force field (CGenFF)³⁷ would be an equally well suited candidate for inclusion in this comparison, but we have chosen to limit our simulations to two force fields only. However, to allow the reader to compare OPLS/AA and GAFF to a similar study based on CGenFF, we have included results on density and enthalpy of vaporization from that paper.³⁷

2. METHODS

2.1. Energy Function. Most force fields use the same functional form for the intermolecular part of the interaction function, based on the Coulomb potential and the Lennard-Jones potential:

$$V_{\text{nb}}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

where r_{ij} is the distance between two atoms i and j , q_i and q_j are the partial charges on the atoms, ϵ_0 is the permittivity of vacuum, σ_{ij} is the van der Waals radius, and ϵ_{ij} is the well-depth for this atom pair. In most force fields, the parameters σ_{ij} and ϵ_{ij} are derived from the atomic values σ_i and ϵ_i using a simple equation (the combination rule). Suffice to say that we have applied the standard combination rules for GAFF (Lorentz–Berthelot³⁸) and for OPLS/AA ($\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$ and $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$)³⁹ in this work.

2.2. Molecule Selection and Preparation. A set of organic molecules was selected for which both enthalpy of vaporization and density are known at room temperature. Models for these molecules were built using either PRODRG⁴⁰ or Molden.⁴¹ These molecules were optimized using the Gaussian 03 suite of programs⁴² at the Hartree–Fock level with the 6-311G** basis set.^{43–47}

2.2.1. OPLS/AA Topologies. The OpenBabel (<http://openbabel.org>) code was used to extract a coordinate file including connectivity information from the Gaussian output files, and this file was used to generate an initial topology using the GROMACS tools³⁵ for the OPLS/AA force field.^{1,39} The topologies were checked manually for correctness before using them, making sure that the total charge of the molecule is zero, and also that the atom types were correct. For molecules containing linear groups (e.g., nitriles), a virtual site construction was added to the topologies preserving the moment of inertia and the total mass, in order to keep the groups perfectly linear.⁴⁸

2.2.2. GAFF Topologies. For the simulations where GAFF² was used, the Antechamber software^{2,3} was employed to generate the topologies from the coordinate files (which were generated as explained above). Gaussian 03⁴² at the Hartree–Fock level with the 6-311G** basis set^{43–47} (as provided by the Basis Set Exchange Web site^{49,50}) and Merz–Singh–Kollman (MK) scheme⁷ were used to determine the partial charges in Gaussian. This particular basis set was used because it is very similar to the 6/31G* basis set,⁵¹ which is the default for GAFF, while simultaneously supporting a larger number of elements (e.g., I). The MK radius for I is not implemented in Antechamber, we used $R_I = 2.15$ Å. The `amb2gmx.pl` script⁵² was used to convert the AMBER topologies into the GROMACS format (this script is available online at <http://ffamber.cns.msu.edu/>). The final partial charges were calculated using the RESP method¹¹ as implemented in Antechamber, and we manually checked that the charges were sane. Note that RESP can be used with any QM method producing electrostatics, not just with HF/6-311G**.

Table 1. Simulation Characteristics for the Different Simulation Types

name	length	# molecules	ensemble	constraints	electrostatics
LIQ	10 ns	1000	NPT	all bonds	PME
GAS	100 ns	1	NVT	all bonds	all interactions
SURF	10 ns	1000	NVT	all bonds	PME
DOS	100 ps	1000	NVT	none	PME

No modifications for linear group were made for the GAFF topologies, where the Antechamber software³ generates a near-linear angle term instead.

2.2.3. Liquid Simulation Box Preparation. To generate liquid simulation boxes, we first made a $2 \times 2 \times 2 \text{ nm}^3$ box containing a single molecule. From 125 such single molecule boxes, we built up a $10 \times 10 \times 10 \text{ nm}^3$ box. These boxes were simulated under high pressure (100 bar) to force the molecules into the liquid phase, and finally we let the systems relax under normal pressure (1 bar) to reach an equilibrated system. For the equilibration simulations, we used Berendsen's coupling algorithm⁵³ because of its efficient relaxation properties.⁵⁴ To generate our final simulation boxes, we stacked $2 \times 2 \times 2$ of the 125 molecule boxes and ran an additional equilibration simulation. The absolute drift in total energy was automatically checked in the equilibration and production simulations, and the simulations were continued until the drift was below 0.5 J/mol/ns per degree of freedom, which is a very strict criterion but which is necessary to accurately compute fluctuation properties.

2.3. Simulation Parameters. The GROMACS suite of programs was used for all simulations.^{33–36} Following previous simulations of alcohol water mixtures^{21,22} using the OPLS/AA force field,^{1,39} we employed a 1.1 nm cutoff for Lennard-Jones interactions and the same distance as the switching distance for the particle mesh Ewald (PME) algorithm for computing Coulomb interactions.^{54,55} Although the OPLS/AA force field was not developed for use with PME, extensive studies on water models⁵⁶ and proteins in water⁵⁷ have shown that correspondence of simulation results with experimental data improves considerably when long-range interactions are taken into account explicitly—irrespective of the force field used. Analytic corrections to pressure and potential energies were made to compensate for the truncation of the Lennard-Jones interactions.³⁸ In the production simulations, we used the Nosé–Hoover algorithm for temperature coupling,^{58,59} in order to provide correct fluctuations, which is necessary to compute fluctuation properties. A time constant for coupling of 1 ps (corresponding to a mass parameter Q of 7.6 ps at room temperature) was used, which is in the range of time scales for intermolecular collisions, as recommended by Holian et al.⁶⁰ For production simulations at constant pressure, the Parrinello–Rahman pressure coupling⁶¹ algorithm was used with compressibility set to $5 \times 10^{-5} \text{ bar}^{-1}$ and a time constant of 5 ps. The temperatures of the simulations were selected to fit the experimental data available. In most simulations, the bonds were constrained using the LINCS algorithm^{62,63} for all molecules, applying two iterations in order to obtain good energy conservation. Periodic boundary conditions were used in all liquid phase simulations.

Four types of production run simulations were performed according to Table 1. The density of states (DOS) production simulations were performed under constant volume conditions, but they were preceded by equilibration simulations

under NPT (without constraints) in order to obtain the equilibrium density at $P = 1 \text{ bar}$ for the subsequent DOS simulations. In the DOS simulations, slightly stricter energy conservation parameters were used: a neighbor list buffer of 0.3 nm, combined with a switched Lennard-Jones and short-range electrostatics term (1.0–1.1 nm), see reference 56 for a description of the functional form.

The GAS simulations were done using a stochastic dynamics (SD) integrator, which adds a friction and a noise term to Newton's equation of motion:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -m_i \xi_i \frac{d\mathbf{r}_i}{dt} + \mathbf{F}_i(\mathbf{r}) + \rho_i \quad (2)$$

where m_i is the mass of atom i , ξ_i is a friction constant, and $\rho(t)$ is a noise process with

$$\langle \rho_i(t) \rho_j(t+s) \rangle = 2m_i \xi_i k_B T \delta(s) \delta_{ij} \quad (3)$$

where k_B is Boltzmann's constant, T is the temperature, $\delta(s)$ is the Dirac δ function, and δ_{ij} is the Kronecker δ function. A leapfrog algorithm adapted for SD simulations⁶⁴ was used to integrate eq 2. When $1/\xi_i$ is large compared to the time scales present in the system, SD functions like molecular dynamics with stochastic temperature-coupling. One of the benefits with SD as compared to MD is that when simulating a system in a vacuum there is no accumulation of errors for the overall translational and rotational degrees of freedom, making sampling of different configuration states more accurate. SURF and LIQ simulations were done using a conventional MD leapfrog integrator.⁶⁵ To enable replication of our simulations and detailed scrutiny of the data, we provide all simulation parameters for each type of run, as well as starting structures and topologies. These files, in GROMACS format, are available for downloading at <http://virtualchemistry.org>.

To ensure that our liquid systems did not freeze during the simulations, we monitored the changes in diffusion constant ΔD as derived from the mean square displacement during the simulations, defined as

$$\Delta D = \frac{2(D_{\text{end}} - D_{\text{begin}})}{D_{\text{end}} + D_{\text{begin}}} \quad (4)$$

The subscript “begin” means the value is an average over the 1000–1500 ps of the simulation, and “end” means over 8500–9000 ps. $|\Delta D|$ is close to zero for most simulations, indicating that D is approximately the same in the beginning and at the end of the simulation. We also verified that $D > 0$ for all simulations. For the simulations where $|\Delta D| \geq 0.5$, we ensured that the systems indeed were not frozen, by inspecting the full mean square displacement curve and the trajectory of the simulations. In the Supporting Information (Figure S1), we show ΔD for all of the liquid simulations.

2.4. Analysis. The density ρ in a constant pressure simulation follows trivially from the mass M of the system divided by the volume V :

$$\rho = \frac{M}{\langle V \rangle} \quad (5)$$

The enthalpy of vaporization can be computed from

$$\Delta H_{\text{vap}} = (E_{\text{intra}}(\text{g}) + k_B T) - (E_{\text{intra}}(\text{l}) + E_{\text{inter}}(\text{l})) \quad (6)$$

where E_{intra} is the intramolecular energy in either the gas (g) phase or the liquid (l) phase and E_{inter} represents the intermolecular energy of the system. In practice, we can simply evaluate

$$\Delta H_{\text{vap}} = (E_{\text{pot}}(\text{g}) + k_{\text{B}}T) - E_{\text{pot}}(\text{l}) \quad (7)$$

ρ was determined from LIQ simulations and ΔH_{vap} from LIQ and GAS simulations.

The SURF simulations were done using liquid boxes, the size of which in the z direction was extended by a factor of 3, generating a simulation box with two liquid–vacuum interfaces. The surface tension γ then follows from

$$\gamma(t) = \frac{L_z}{2} \left(P_z(t) - \frac{P_x(t) + P_y(t)}{2} \right) \quad (8)$$

where P_n is the pressure component in direction n and L_z is the length of the box in the z direction (perpendicular to the surfaces).

Static dielectric constants $\epsilon(0)$ were computed on the basis of the fluctuations of the total dipole moment \mathbf{M} of the simulation box^{66,67} in the LIQ simulations:

$$\epsilon(0) = 1 + \frac{4\pi}{3} \frac{\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2}{Vk_{\text{B}}T} \quad (9)$$

where V is the volume of the simulation box. Errors were estimated by block-averaging over 10 blocks of 1 ns. In order to verify the validity of eq 9, we computed the autocorrelation time τ_{M} of the total dipole moment \mathbf{M} in the simulation boxes (from the integral of the autocorrelation function). In order for fluctuations to be well-defined, τ_{M} should be at least an order of magnitude shorter than the simulation length. Henceforth, we omitted the dielectric constants for those systems where τ_{M} was longer than 1 ns. For those systems where this was the case, longer simulations of 50 ns were performed, in most cases without any improvement.

The fluctuation properties α_{p} (the volumetric thermal expansion coefficient) and κ_{T} (the isothermal compressibility) are computed from the LIQ simulations according to³⁸

$$\langle \delta V \delta H \rangle = k_{\text{B}}T^2 \langle V \rangle \alpha_{\text{p}} \quad (10)$$

where H is the enthalpy and δ indicates the fluctuations, and

$$\langle \delta V^2 \rangle = k_{\text{B}}T \langle V \rangle \kappa_{\text{T}} \quad (11)$$

These two properties can be related to the difference between heat capacities at constant pressure and constant volume through

$$\Delta c = c_{\text{p}} - c_{\text{v}} = VT \frac{\alpha_{\text{p}}^2}{\kappa_{\text{T}}} \quad (12)$$

where V is the molecular volume. We can take advantage of this relation in two ways, first by computing α_{p} and κ_{T} from our simulations and then computing the constant pressure heat capacity based on the constant volume heat capacity. By using experimental data for α_{p} and κ_{T} , we can also establish “experimental” constant volume heat capacities, which are difficult to measure directly. In this work, we have done both, as detailed in the Results and Discussion sections.

The classical—that is, without any quantum corrections—heat capacity $c_{\text{p}}^{\text{class}}$ can be obtained from the fluctuations in the

Table 2. Statistics of a Linear Fit of Calculated to Experimental Values According to $y = ax + b^a$

force field	N	a	b	RMSD	% dev.	R^2
ρ (g/l)						
GAFF	235	0.96	58.5	82.9	4	97%
OPLS/AA	235	0.98	20.9	40.4	2	99%
CGenFF ³⁷	111	1.03	−36.0	26.0	2	99%
OPLS/AA ⁷⁰	9	1.01	−24.0	45.3	4	96%
ΔH_{vap} (kJ/mol)						
GAFF	231	1.07	0.8	10.6	17	83%
OPLS/AA	231	0.96	3.4	6.5	11	89%
CGenFF ³⁷	95	0.94	2.4	4.7	7	84%
γ (10^{-3} N/m)						
GAFF	155	0.75	0.9	8.6	23	70%
OPLS/AA	155	0.97	−5.5	7.3	22	89%
$\epsilon(0)$						
GAFF	163	0.27	0.4	15.7	35	55%
OPLS/AA	176	0.16	0.7	15.9	43	55%
α_{p} (10^{-3} /K)						
GAFF	221	0.90	0.3	0.3	24	67%
OPLS/AA	221	0.91	0.3	0.3	21	75%
OPLS/AA ⁷⁰	9	0.53	0.8	0.7	42	39%
κ_{T} (1/GPa)						
GAFF	103	0.66	0.0	0.3	27	74%
OPLS/AA	103	0.76	0.1	0.3	19	85%
OPLS/AA ⁷⁰	8	0.93	0.0	1.1	59	84%
c_{p} (J/mol K)						
GAFF	130	1.08	−30.9	19.8	10	98%
OPLS/AA	132	1.10	−30.2	18.2	10	97%
OPLS/AA ⁷⁰	9	0.94	3.5	10.4	7	94%
c_{v} (J/mol K)						
GAFF	72	1.02	−17.6	18.8	10	97%
OPLS/AA	72	1.04	−17.9	18.3	9	95%
OPLS/AA ⁷⁰	8	1.01	−5.4	10.8	7	95%
$c_{\text{p}}^{\text{class}}$ (J/mol K)						
GAFF	214	1.77	−21.6	148.3	77	87%
OPLS/AA	214	1.98	−52.8	147.0	73	93%

^aUncertainties in the simulation results are used as weights in the fit. The number of (experimental) data points N is given for each property. Root mean square deviation (RMSD) from experimental values, average relative deviation in percent, and the correlation coefficient R^2 are given. OPLS/AA results from ref 70 and CGenFF results from ref 37 (using the so called CHARMM generalized force field) are also listed for comparison.

enthalpy:³⁸

$$k_{\text{B}}T^2 c_{\text{p}}^{\text{class}} = \langle \delta H^2 \rangle \quad (13)$$

Although this is straightforward to calculate, the numbers obtained in this manner are a factor of 2 too high (Table 2). Therefore, we have determined the heat capacities c_{p} and c_{v} on the basis of the two phase thermodynamic method^{68–70} (described in the Supporting Information), which is based on the convolution of the density of states with a weighting function based on

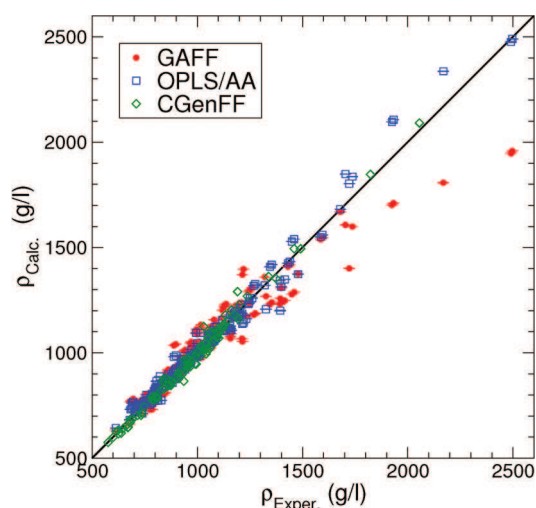


Figure 1. Correlation between densities (ρ) calculated by MD simulation using GAFF, OPLS/AA, CGenFF, and experimental results. The CGenFF data were adopted from Vanommeslaeghe et al.³⁷ and are based on a different (but similar) set of molecules, including 111 molecules. For a full list of the CGenFF data, we refer to the reference and the supplemental files therein.

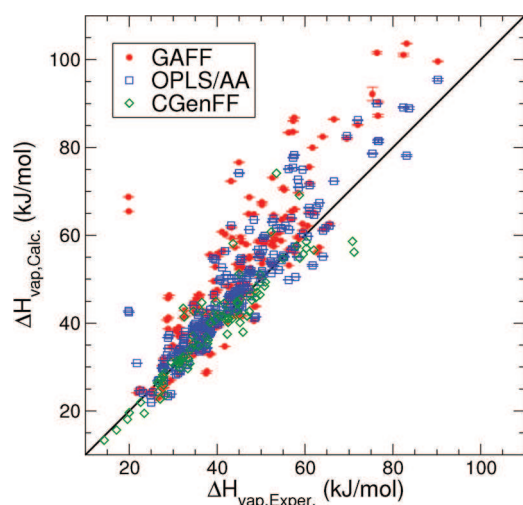


Figure 2. Correlation between enthalpy of vaporization (ΔH_{vap}) calculated using GAFF, OPLS/AA, CGenFF, and experimental results. The CGenFF data were adopted from Vanommeslaeghe et al.³⁷ and are based on a different (but similar) set of molecules, including 95 molecules. For a full list of the CGenFF data, we refer to the reference and the supplemental files therein.

quantum harmonic oscillators, as introduced originally by Berens et al.⁷¹ The final expression yielding the heat capacity c_V is

$$c_V = k_B \int_0^\infty [\text{DoS}_{\text{gas}}(\nu) W_{\text{gas}}^{\text{cv}}(\nu) + \text{DoS}_{\text{solid}}(\nu) W_{\text{solid}}^{\text{cv}}(\nu)] d\nu \quad (14)$$

DoS_{gas} and $\text{DoS}_{\text{solid}}$ denote the density of states in a gas and a solid, $W_{\text{gas}}^{\text{cv}}(\nu)$ and $W_{\text{solid}}^{\text{cv}}(\nu)$ are weighting factors for the same, and c_P can be obtained by combining eq 12 and eq 14. For all details and a complete derivation, we refer the reader to the Supporting Information.

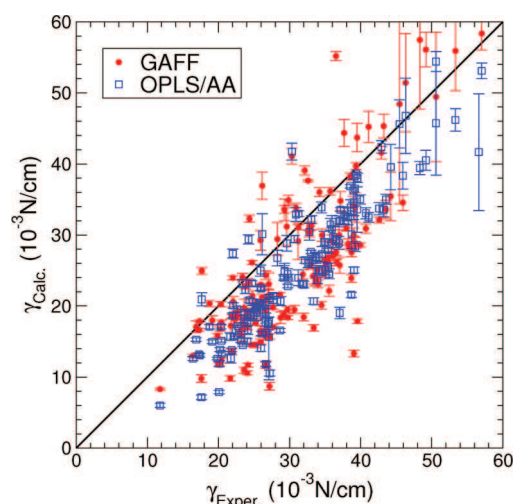


Figure 3. Correlation between surface tension (γ) calculated using the GAFF and the OPLS/AA force fields and experimental results.

The properties investigated fall into two categories: those that follow directly from the ensemble average of a property (energy, pressure, volume) and those based on fluctuations (heat capacities, compressibility, and expansion coefficient). For the first category, error estimates were based on a block averaging procedure that automatically takes the autocorrelation of the property under investigation into account.⁷² Properties like potential energy and density usually have relatively short autocorrelation times. The surface tension fluctuates significantly but also has a short autocorrelation time. For the second category, we have used a different approach when estimating the error. By dividing the entire simulation trajectory into nine, in time, equally long parts, we get nine values for each property, from which we can estimate the total error. In the case of c_V , we used five blocks of 20 ps for error estimation instead.

We calculated c_P on the basis of eq 12 and estimated the error δc_P from the errors in c_V (δc_V), α_P ($\delta \alpha_P$), and κ_T ($\delta \kappa_T$) as

$$\delta c_P^2 = \delta c_V^2 + \left(\frac{2VT\alpha_P}{\kappa_T} \right)^2 \delta \alpha_P^2 + \left(\frac{VT\alpha_P^2}{\kappa_T^2} \right)^2 \delta \kappa_T^2 \quad (15)$$

or, expressed in Δc (eq 12):

$$\delta c_P^2 = \delta c_V^2 + (\Delta c)^2 \left(2 \frac{\delta \alpha_P^2}{\alpha_P^2} + \frac{\delta \kappa_T^2}{\kappa_T^2} \right) \quad (16)$$

3. RESULTS

Correlations between experimental data and simulations for observables and derived quantities are plotted in Figures 1–8. The statistics for linear fits to the data ($y_{\text{calcd}} = ay_{\text{exptl}} + b$) are given in Table 2 for each of the observables and the two force fields, plus similar data from refs 37 and 70. To identify which specific molecule generated a certain value in the figures, we refer to Tables S2–S10 in the Supporting Information. An overview of the names of the molecules, their formula, molecular weight, CAS number, and ChemSpider ID is given in Table S1 (Supporting Information). For many molecules, results at different

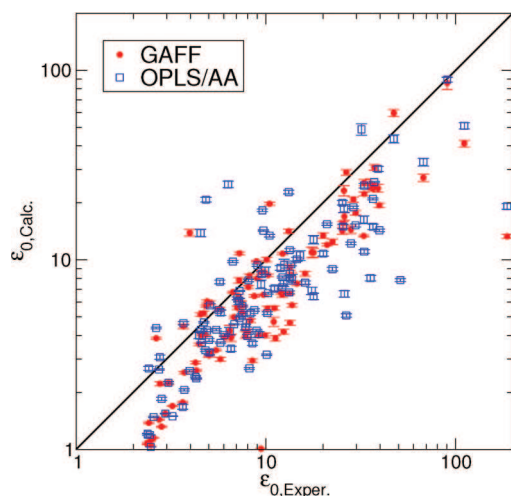


Figure 4. Correlation between dielectric constant (ϵ_0) calculated using the GAFF and the OPLS/AA force fields and experimental results. Note the logarithmic axes.

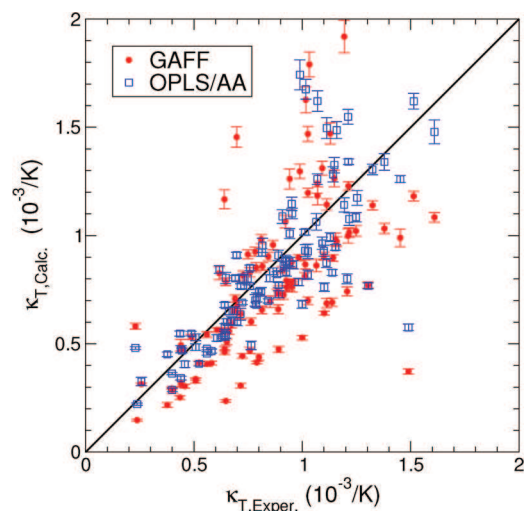


Figure 6. Correlation between isothermal compressibility (κ_T) calculated using the GAFF and the OPLS/AA force fields and experimental results.

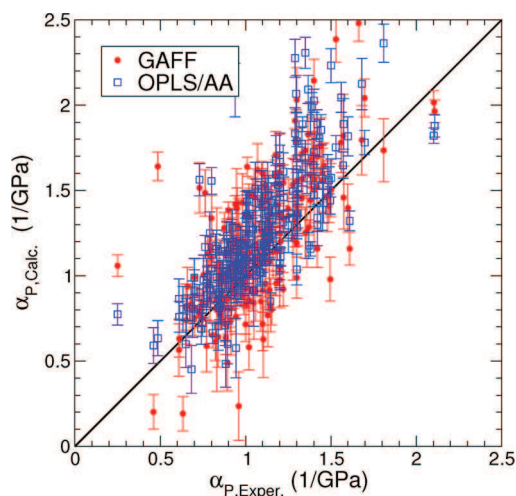


Figure 5. Correlation between volumetric expansion coefficient (α_p) calculated using the GAFF and the OPLS/AA force fields and experimental results.

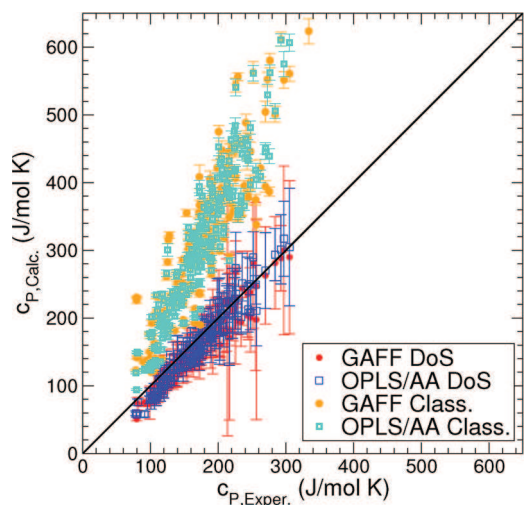


Figure 7. Correlation between measured heat capacity at constant pressure (c_p) and computed using the GAFF and the OPLS/AA force fields based on either the density of states (DoS) method, which includes quantum corrections and a Δc correction based on simulations, or based on a purely classical treatment (c_p^{class} , Class.).

temperatures were generated, and hence the number of data points may be larger than the number of molecules. For densities, heats of vaporization, surface tensions, and dielectric constants, some of the experimental values were generated from analytical functions of temperature based on experimental data, the parameters of which are given in the Handbook of Chemistry and Physics,⁷³ the Landolt-Bornstein database,⁷⁴ and Yaws' book on Thermophysical Properties of Chemicals and Hydrocarbons.⁷⁵ In addition, we parametrized the dielectric constant, heat capacity at constant pressure, and isothermal compressibility as a function of the temperature for some molecules (see below).

3.1. Statistics. In the following, we discuss general trends in all properties first; outliers are described separately below. A comparison of the values in Table 2 shows that OPLS/AA is slightly better than GAFF at reproducing experimental data for most observables, with both lower RMSD and higher correlation coefficients R^2 .

3.1.1. Density. The density ρ (Figure 1, Table S2) of virtually all liquids is reproduced very well, with $R^2 = 97\%$ (GAFF) and

99% (OPLS/AA) (Table 2). For GAFF, the densities are systematically slightly underestimated ($a = 0.96$), while for OPLS/AA, $a = 0.98$, very close to 1, and both have an R^2 close to 100%. In a recent publication, Vanommeslaeghe et al. presented the CHARMM general force field (CGenFF).³⁷ They calculated densities for a set of 111 drug-like molecules, using boxes of 216 molecules. Their reported densities are also very accurate with $a = 1.03$ and $R^2 = 99\%$, see Figure 1 and Table S2.

3.1.2. Enthalpy of Vaporization. ΔH_{vap} (Figure 2, Table S4) correlates very well with experimental data in most cases, with $R^2 = 83\%$ (GAFF) and 89% (OPLS/AA) (Table 2). The GAFF overestimates ΔH_{vap} with slope $a = 1.07$, while OPLS/AA underestimates a slightly at 0.96. These deviations cannot just be attributed to a small number of outliers, as may be evident from Figure 2. Vanommeslaeghe et al.³⁷ calculated enthalpy of

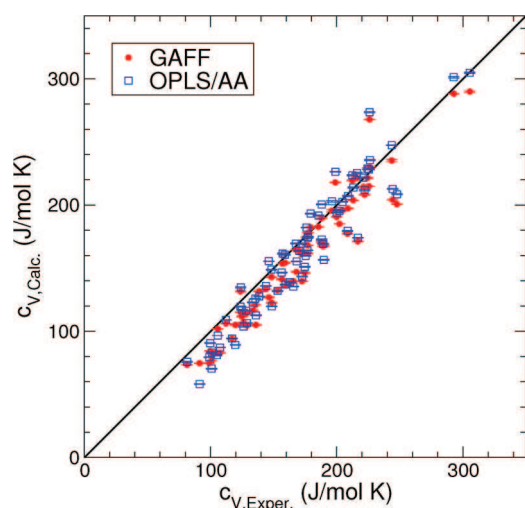


Figure 8. Correlation between measured heat capacity at constant volume (c_v) and computed using the GAFF and the OPLS/AA force fields based on the density of states method, which includes quantum corrections.

vaporization for a set of 95 small molecules. Like for OPLS/AA, ΔH_{vap} is underestimated in CGenFF calculations with a slope of $a = 0.94$. The correlation between experiments and simulation is similar to the two force fields studied here, $R^2 = 84\%$. The CGenFF data set is based on a comparable but different set of molecules than what has been analyzed here (37 molecules overlap between the two studies). To simplify a comparison between OPLS/AA, GAFF, and CGenFF, we have listed the CGenFF ΔH_{vap} values from the study by Vanommeslaeghe et al. next to OPLS/AA and GAFF values in Table S3, and we have plotted them in Figure 2.

3.1.3. Surface Tension. The surface tension γ (Figure 3, Table S4) seems to be underestimated systematically in both force fields with slope $a = 0.75$ (GAFF) and 0.97 (OPLS/AA, Table 2). The interactions between molecules on the surface are not sufficiently strong, a well known problem with nonpolarizable force fields.^{21,25,76} The values are spread around the diagonal for both GAFF ($R^2 = 70\%$) and OPLS/AA ($R^2 = 89\%$), and here again OPLS/AA performs slightly better than GAFF.

3.1.4. Dielectric Constant. For 32 molecules, a novel parametrization of the temperature dependence of the dielectric constant was made on the basis of experimental values predominantly from the Landolt-Bornstein database.⁷⁷ The parametrization is to a polynomial of second or third order (as is used in the Handbook of Chemistry and Physics⁷³), and the resulting coefficients are given in Table 3. Interpolations of these polynomials were used in order to compare the simulations to experimental data, and the fits are presented in Figure S3 of the Supporting Information.

The dielectric constant $\epsilon(0)$ (Figure 4, Table S5) appears to be the most difficult property to reproduce in our simulations, with slopes $a < 0.5$ and $R^2 \leq 60\%$ for both force fields (Table 2). Apart from lacking explicit polarization, limited sampling (1000 molecules for 10 ns were used in all cases) may be one of the causes; another contributing factor is the high viscosity of molecules containing alcohol or amine groups, further aggravated by the fact that some of these molecules were simulated at temperatures close to the melting temperature.

Some liquids have extremely large dielectric constants, e.g., methanamide ($\epsilon(0) = 109$) and *N*-methylformamide ($\epsilon(0) = 190$).

For these molecules, GAFF predicts 41 and 14, respectively, while OPLS/AA predicts 51 and 19. Xie et al. report a simulated dielectric constant of 200 for *N*-methylformamide, using a polarizable model, with only 256 molecules and 1 ns of simulation, but the authors state that “The dielectric constants have only been averaged for 1 ns of simulation time, and they are almost certain not yet converged.” Indeed, Whitfield et al. had previously concluded that very long times (50 ns) may be needed to obtain converged dielectric constants of molecules like *N*-methylacetamide because they tend to form long linear chains.⁷⁸ Such chains can in periodic simulation systems become “infinite”, which may contribute to the long relaxation time. It should be noted, however, that for most molecules in our study, the values are well converged, as witnessed by small error bars. Deviations from experimental results are therefore due predominantly to a lack of polarization and too low mobility of molecules. Interestingly, GAFF is somewhat better at predicting $\epsilon(0)$ than OPLS/AA (Table 2), most likely because the partial charges are somewhat higher for most molecules.

3.1.5. Volumetric Expansion Coefficient. The volumetric expansion coefficient α_p is plotted in Figure 5 and tabulated in Table S6. The slope of the correlation plots is slightly less than 1 for both GAFF ($a = 0.9$) and OPLS/AA ($a = 0.91$), and there is a large spread around the $y = x$ line for both OPLS/AA and GAFF with a RMSD of 0.3/GPa in both cases.

3.1.6. Isothermal Compressibility. For 53 molecules, an interpolation of experimental values of the isothermal compressibility κ_T as a function of the temperature was performed (Table 4 and Figure S3). The simulated κ_T 's are plotted versus the experimental values in Figure 6 and tabulated in Table S8. Like for α_p , the spread in numbers is large, and the slope of the correlation plots is significantly less than 1 (GAFF, 0.66; OPLS/AA, 0.76, Table 2). In general, it seems that fluctuation properties are more difficult to predict than simple linear averages. Although we applied a very strict convergence criterion for the total energy of 0.5 J/mol/ns per degree of freedom, it may be that even longer equilibration times and production simulations are needed.

3.1.7. Heat Capacities. For three molecules, an interpolation of experimental numbers is presented in Table 5 and Figure S4. The heat capacity is a difficult property to calculate due to significant quantum effects. The simple eq 7 produces numbers (c_p^{class}) that are twice too high (Table 2). Since the energy taken up by vibrations in a classical harmonic oscillator is much higher than for a quantum harmonic oscillator at the same frequency, the c_p^{class} values are too high. Introducing quantum corrections, in the manner proposed by Berens et al.,⁷¹ on which the two phase thermodynamics (2PT) method^{68–70} is based, presupposes that the frequencies in the classical simulation are correct: this is often the case since most force constants have been derived from spectroscopic experiments. It should be noted that there is no *a priori* reason to assume that the intermolecular degrees of freedom behave harmonically, as they are determined by Coulomb and van der Waals interactions. Despite these theoretical shortcomings, the 2PT method produces reasonable results for c_p (see Figure 7, Table 2, and Table S8)—much closer to experiment than c_p^{class} on any account. In order to compute c_p , it is necessary to add a correction Δc (eq 12) to the heat capacity at constant volume c_v that is produced by the density of states analysis. Δc is underestimated by classical force field calculations; however, c_p still is estimated reasonably, with $a = 1.08$ for GAFF and $a = 1.02$ for OPLS/AA with correlation coefficients $R^2 = 98\%$ and 97% , respectively. If we compare just c_v from our simulations (i.e., without adding in Δc) and subtract the experimental

Table 3. Parameterization of Temperature Dependence of Dielectric Constants in a Polynomial Form $\epsilon(0) = A + BT + CT^2 + DT^3$, Which Is the Same Form Used in the Handbook of Chemistry and Physics^{73a}

molecule	<i>N</i>	χ^2	T_{\min}	T_{\max}	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
bromomethane	12	0.7	194.60	275.70	52.59	−2.812e−01	4.565e−04	0
methanol	92	1.0	175.62	337.75	226.69	−1.319e+00	2.937e−03	−2.359e−06
1,1,1,2,2-pentachloroethane	9	0.0	245.15	338.15	13.81	−5.527e−02	7.186e−05	0
1,1,2,2-tetrachloroethane	14	0.2	231.15	318.15	71.61	−3.630e−01	5.010e−04	0
1,2-dibromoethane	39	0.1	288.15	353.15	10.31	−3.114e−02	4.200e−05	0
1,1-dichloroethane	8	0.2	288.15	323.15	36.77	−1.300e−01	1.361e−04	0
2-chloroethanol	30	3.1	263.15	401.75	105.36	−3.245e−01	3.619e−05	5.019e−07
ethanamide	7	0.3	358.15	448.20	−200.55	1.551e+00	−2.239e−03	0
methylsulfonylmethane	6	0.0	293.15	323.15	53.55	−2.539e−01	3.571e−04	0
2-aminoethanol	7	0.4	283.65	298.15	166.68	−7.576e−01	1.018e−03	0
1,3-dioxolan-2-one	24	0.5	309.46	364.15	223.34	−4.560e−01	9.143e−05	0
1,3-dioxolane	31	0.2	175.93	303.15	40.61	−2.507e−01	6.323e−04	−5.695e−07
dimethoxymethane	5	0.0	170.65	298.15	2.59	−9.298e−04	3.847e−06	0
ethylsulfonylethane	6	0.1	293.15	323.15	11.68	−1.994e−02	0.000e+00	0
2-methylpropan-2-amine	4	0.0	291.15	303.15	294.70	−1.887e+00	3.060e−03	0
thiophene	14	0.1	252.65	333.15	2.32	5.071e−03	−1.232e−05	0
furan	31	0.2	198.15	303.15	6.69	−2.044e−02	2.644e−05	0
pentane-2,4-dione	9	2.0	291.15	323.15	−532.57	3.658e+00	−5.982e−03	0
3-methylpyridine	6	1.0	293.15	333.00	35.54	−9.303e−02	4.307e−05	0
benzenethiol	6	0.3	293.15	358.15	5.72	−7.033e−03	7.362e−06	0
(E)-hex-2-ene	6	0.0	157.00	295.00	2.43	−1.132e−03	−1.372e−06	0
1-methoxy-2-(2-methoxyethoxy)ethane	5	0.0	298.15	333.15	32.07	−1.359e−01	1.766e−04	0
diethyl propanedioate	7	0.2	293.15	343.15	19.98	−5.034e−02	3.345e−05	0
2,4,6-trimethylpyridine	10	0.1	293.15	358.15	16.67	−3.036e−02	2.361e−06	0
triethyl phosphate	6	0.1	294.15	333.15	−1.59	1.317e−01	−2.780e−04	0
phenylmethanol	26	0.2	278.15	363.15	105.48	−5.130e−01	6.802e−04	0
tetrahydrothiophene 1,1-dioxide	57	0.4	300.75	398.15	488.81	−3.732e+00	1.055e−02	−1.017e−05
2,4,6-trimethylpyridine	10	0.1	293.15	358.15	16.67	−3.036e−02	2.361e−06	0
dimethoxymethane	5	0.0	170.65	298.15	2.92	−4.106e−03	1.126e−05	0
1,3-dichloropropane	5	0.1	298.15	333.15	−61.39	4.818e−01	−8.107e−04	0
methylsulfonylmethane	6	0.2	273.30	310.48	23.41	−8.896e−02	1.076e−04	0
1,2-ethanedithiol	3	0.0	293.15	333.15	11.23	−1.350e−02	0.000e+00	0

^a T_{\min} and T_{\max} (K) indicate the validity range of the parameterization. *N* indicates the number of points in the fit; χ^2 is the root mean square deviation. See the Supporting Information for details.

Δc from the measured c_p , we find a very good correlation (GAFF, $a = 1.02$, $R^2 = 97\%$; OPLS/AA, $a = 1.04$, $R^2 = 95\%$), see Figure 8 and Table 2. Although correlation between experimental results and calculations can by no means validate the underlying theoretical model, it nevertheless indicates that the results are meaningful, because we have approximately 70 experimental c_V values to which to compare. Indeed, although the root-mean-square deviation (RMSD) from experimental results is similar for c_V and c_p , the fit to experimental results is much better (slope a close to 1) for both OPLS/AA and GAFF. The DOS simulations were performed without constraints, and the heat capacities depend directly on the intra- and intermolecular vibrations. Deviations from the experimental heat capacities could therefore indicate problems with the force constants for intramolecular motions.

3.2. Outliers Per Force Field. Table 6 shows how the molecular models of the individual molecules perform relative to the force field as a whole. The average relative deviations in σ and averaged over 1–8 data points (depending on the availability of experimental data) signals how well the force field performs for each molecule. The properties used were density, enthalpy of

vaporization, surface tension, dielectric constant, volumetric expansion coefficient, isothermal compressibility, and the heat capacity at constant volume.

Some types of molecules are problematic in both of the force fields considered here. Small molecules containing more than one Cl or Br atom generally have both density and enthalpy of vaporization values that deviate significantly from experimental reference. This is not the case for molecules containing only one of these atoms, or molecules where there is a spacer (e.g., a CH_2 group) between them. It could therefore be that the differences are caused by overlapping atoms. By introducing a new atom type of Br and Cl for the case where there are two such atoms next to each other on the carbon chain, these problems might be resolved.

The density and enthalpy of vaporization of methanoic acid (formic acid) were particularly hard to reproduce, as was noted previously by Jedlovsky and Turi, who constructed a specific potential for this molecule.⁷⁹ The main feature responsible for the improved model in this case was a higher charge ($\approx 0.1e$) on the C–H atom than is used in either OPLS/AA (0) or GAFF (0.04). Methanoic acid forms very strong linear chains, which are

Table 4. Parameterization of Temperature Dependence of Isothermal Compressibility Constants in a Polynomial Form $\kappa_T = A + BT + CT^{2a}$

molecule	<i>N</i>	χ^2	T_{\min}	T_{\max}	<i>A</i>	<i>B</i>	<i>C</i>
dichloromethane	3	0.000	293.15	303.15	-1.709e+01	1.144e-01	-1.800e-04
methanamide	5	0.008	288.15	323.15	1.352e-01	9.161e-04	0
nitromethane	4	0.020	298.15	323.15	-1.253e+00	6.666e-03	0
methanol	24	0.014	213.15	333.15	1.004e+00	-6.791e-03	2.557e-05
acetonitrile	5	0.000	298.15	318.15	3.174e+00	-2.209e-02	5.114e-05
1,1,2,2-tetrachloroethane	2	0.000	293.15	303.15	-4.962e-01	3.900e-03	0
1,1,2-trichloroethane	7	0.002	288.15	318.15	-7.213e-01	4.937e-03	0
bromoethane	5	0.010	273.15	323.15	9.748e+00	-6.685e-02	1.287e-04
N-methylformamide	4	0.011	288.15	313.15	6.378e-03	1.968e-03	0
nitroethane	3	0.015	298.15	323.15	-9.873e-01	6.004e-03	0
ethanol	16	0.007	203.15	363.15	1.280e+00	-8.946e-03	2.857e-05
methylsulfinylmethane	7	0.030	293.15	353.15	5.206e-01	-3.136e-03	1.052e-05
2-aminoethanol	6	0.000	278.15	333.15	7.273e-01	-4.276e-03	1.051e-05
1,3-dichloropropane	6	0.000	283.15	323.15	6.932e-01	-4.785e-03	1.678e-05
propan-2-one	10	0.010	293.15	328.15	-3.053e+00	1.468e-02	0
methyl acetate	8	0.012	293.15	328.15	-2.562e+00	1.249e-02	0
1,3-dioxolane	2	0.000	293.15	313.15	-1.317e+00	6.960e-03	0
1-bromopropane	7	0.003	288.15	318.15	-1.264e+00	8.037e-03	0
N,N-dimethylformamide	18	0.018	288.15	333.20	1.748e+00	-1.073e-02	2.367e-05
1-nitropropane	3	0.004	298.15	323.15	-1.111e+00	6.420e-03	0
2-nitropropane	3	0.020	298.15	323.15	-1.060e+00	6.604e-03	0
1,4-dichlorobutane	5	0.004	288.15	318.15	-8.725e-01	5.246e-03	0
propane-1,2,3-triol	19	0.003	293.15	473.15	8.358e-01	-4.323e-03	7.862e-06
propan-1-amine	6	0.036	293.15	323.15	-2.469e+00	1.238e-02	0
N,N-dimethylacetamide	5	0.015	288.15	318.15	-5.890e-01	4.142e-03	0
butan-1-ol	15	0.021	293.15	393.15	1.307e+00	-8.833e-03	2.543e-05
N-ethylethanamine	5	0.002	298.15	318.15	7.548e+00	-5.536e-02	1.188e-04
butan-1-amine	8	0.003	298.15	328.15	2.330e+00	-1.702e-02	4.371e-05
ethyl acetate	9	0.012	298.15	350.30	5.084e+00	-3.567e-02	7.598e-05
oxolane	5	0.001	278.15	323.15	-9.434e-01	4.999e-03	4.886e-06
1-bromobutane	12	0.000	298.15	333.15	2.650e+00	-1.860e-02	4.413e-05
1-chlorobutane	10	0.029	293.15	318.15	-2.399e+00	1.205e-02	0
pentanenitrile	5	0.005	283.15	323.15	8.811e-01	-7.004e-03	2.429e-05
ethyl propanoate	15	0.022	278.15	338.15	6.964e-01	-7.128e-03	2.882e-05
2-methylbutan-2-ol	2	0.000	293.15	298.15	-1.495e+00	8.600e-03	0
pentan-1-ol	8	0.010	293.15	333.15	3.158e+00	-2.044e-02	4.292e-05
pentan-3-ol	10	0.003	293.15	368.15	4.952e+00	-3.315e-02	6.587e-05
nitrobenzene	5	0.009	298.15	323.15	-3.337e-01	2.832e-03	0
cyclohexanone	5	0.021	298.15	308.15	-9.399e-01	5.421e-03	0
hexan-2-one	8	0.022	278.15	338.15	-1.451e+00	8.315e-03	0
1-methoxy-2-(2-methoxyethoxy)ethane	6	0.001	298.15	318.15	-8.794e-01	5.105e-03	0
N,N-diethylethanamine	8	0.006	298.15	328.15	4.400e+00	-3.405e-02	8.064e-05
N-propan-2-ylpropan-2-amine	7	0.001	298.15	328.15	9.459e+00	-6.732e-02	1.357e-04
methoxybenzene	5	0.043	298.15	338.15	-1.520e+00	7.287e-03	0
3-methylphenol	6	0.041	298.15	413.15	1.744e+00	-1.029e-02	2.104e-05
toluene	50	0.006	288.15	333.15	2.342e+00	-1.627e-02	3.853e-05
diethyl propanedioate	7	0.000	298.15	328.15	2.164e+00	-1.397e-02	3.048e-05
heptan-2-one	2	0.000	293.15	298.15	-8.915e-01	6.200e-03	0
ethylbenzene	7	0.008	293.15	333.15	2.524e+00	-1.652e-02	3.683e-05
1,2-dimethylbenzene	10	0.022	273.15	417.50	-2.914e-01	1.846e-03	6.429e-06
octan-1-ol	16	0.033	293.15	413.15	2.242e+00	-1.449e-02	3.206e-05
quinoline	2	0.000	333.15	373.15	-5.477e-01	3.320e-03	0
(1-methylethyl)benzene	3	0.003	293.15	298.15	-6.340e-01	5.110e-03	0

^a T_{\min} and T_{\max} (K) indicate the validity range of the parameterization. *N* indicates the number of points in the fit; χ^2 is the root mean square deviation. See the Supporting Information for details.

Table 5. Parameterization of Temperature Dependence of Heat Capacity at Constant Pressure in a Polynomial Form $c_p = A + BT^a$

molecule	N	χ^2	T_{\min}	T_{\max}	A	B
1,3-dioxolane	9	0.187	288.15	328.15	4.371e+01	2.613e-01
1,2,3,4-tetrafluorobenzene	41	0.145	235.47	319.79	1.158e+02	2.491e-01
1,2,3,5-tetrafluorobenzene	25	0.343	229.32	311.18	1.186e+02	2.400e-01

^a T_{\min} and T_{\max} (K) indicate the validity range of the parameterization. N indicates the number of points in the fit; χ^2 is the root mean square deviation. See the Supporting Information for details.

difficult to break. This leads to long correlation times for the system dipoles and to dielectric constants that are far from the experimental values (Table S5).

Benzaldehyde and furan are also problematic in both force fields. Even if they both generate decent densities and enthalpies of vaporization, the other properties (surface tension, dielectric constant, and thermal expansion coefficient) are far from the experimental values.

Molecules containing a nitro group (specially nitromethane, 1-nitropropane, and 2-nitropropane) stick out as a problematic group in GAFF. The charges on nitro groups are high, leading to high density and enthalpy of vaporization.

The standard OPLS/AA parameterization of alcohols has been reported to perform poorly for octan-1-ol. MacCallum and Tieleman⁸⁰ therefore derived a specific united atom potential of the molecule where they used modified charges on the headgroup. The OPLS/AA parametrization investigated here gives both too high a density and too high an enthalpy of vaporization, and therefore the other properties investigated for this molecules also deviate from experimental results. Methyl-2-methylprop-2-enoate shows similar problems, and this could probably be corrected in a similar way. It should be noted that, compared to GAFF, the charges on the headgroup in these two molecules are relatively high in OPLS/AA.

4. DISCUSSION

The development of force fields for molecular simulation is critically dependent on the availability of good reference data, preferably from experimental sources. All force fields, be they empirical, purely derived from quantum-mechanics, or a combination of the two, will eventually have to face the test of comparing predicted to measured values. There is a large amount of literature on force field testing for proteins and peptides,^{57,81–87} nucleic acids,^{88–91} carbohydrates,⁹² specific organic molecules or protein fragments,^{20,26,93–97} and ions,^{98–101} to list but a few. In addition, there are indirect force field tests, for instance of the binding energy in protein–ligand complexes,^{16,102} protein structure prediction,¹⁰³ or of force-field-based docking codes.^{104–106} It is interesting to mention the industrial fluid properties simulation challenges, which are stimulating modelers to predict properties of liquids by any means, including molecular simulation.^{107,108}

Here, we have introduced a benchmark set of 146 liquids in order to assess two popular all atom force fields, OPLS/AA and GAFF, and to set a standard for future force fields. For comparison, we have included an independent density and enthalpy of vaporization data set computed using CGenFF, based on a similar set of molecules.³⁷ Calculated density, enthalpy of vaporization, heat capacities, surface tension, dielectric constants,

Table 6. Average Relative Deviation (σ) from Experimental Values, in Brackets, the Number of Observables^a

name	CGenFF	GAFF	OPLS/AA
1. chloroform		2.1(6)	3.0(7)
2. dichloro(fluoro)methane		1.0(4)	1.3(4)
3. dibromomethane		2.9(6)	1.7(7)
4. dichloromethane		1.7(7)	3.6(7)
5. methanal		0.3(4)	0.3(4)
6. methanoic acid		4.5(6)	2.6(7)
7. bromomethane		1.4(3)	0.4(3)
8. methanamide	0.0(1)	1.2(7)	0.4(6)
9. nitromethane		2.0(7)	0.8(7)
10. methanol	0.0(2)	0.8(7)	0.8(7)
11. 1,1,1,2-pentachloroethane		0.5(4)	0.8(4)
12. 1,1,2,2-tetrachloroethane		1.7(7)	1.7(7)
13. 1,1-dichloroethene		1.7(4)	0.8(4)
14. 1,1,2-trichloroethane		1.2(7)	0.9(7)
15. acetonitrile	0.0(1)	1.1(7)	2.2(7)
16. 1,2-dibromoethane		2.6(7)	4.0(7)
17. 1,1-dichloroethane	0.0(1)	0.7(7)	1.7(7)
18. 1,2-dichloroethane		1.6(7)	1.2(7)
19. methyl formate		0.9(4)	0.8(5)
20. bromoethane	0.0(1)	2.2(7)	0.6(7)
21. chloroethane	0.0(1)	0.8(5)	1.3(5)
22. 2-chloroethanol		0.4(4)	0.5(4)
23. ethanamide		0.2(4)	0.8(5)
24. N-methylformamide		1.4(7)	1.4(7)
25. nitroethane		1.5(7)	0.7(7)
26. methoxymethane		0.5(5)	1.3(5)
27. ethanol	0.0(2)	1.0(7)	0.7(6)
28. 1,2-ethanedithiol		0.6(3)	0.1(3)
29. methylsulfanylmethane	0.1(2)	1.2(5)	1.6(5)
30. methylsulfanylmethane	0.1(1)	1.0(7)	0.6(7)
31. methylsulfanylmethane		1.4(5)	1.2(5)
32. 2-aminoethanol		1.2(5)	1.3(6)
33. ethane-1,2-diamine		1.2(7)	1.9(7)
34. prop-2-enenitrile		1.0(5)	1.2(5)
35. 1,3-dioxolan-2-one		0.5(5)	0.2(4)
36. propanenitrile		1.1(7)	1.9(7)
37. 1,2-dibromopropane		1.1(5)	0.6(4)
38. 1,3-dichloropropane		0.9(7)	1.0(7)
39. (2R)-2-methyloxirane		0.0(2)	0.1(2)
40. propan-2-one	0.0(2)	1.0(7)	0.7(7)
41. methyl acetate	0.0(2)	1.3(7)	0.9(7)
42. 1,3-dioxolane	0.0(1)	1.2(4)	0.6(4)
43. 2-iodopropane		0.7(5)	1.1(5)
44. 1-bromopropane		1.3(7)	0.6(7)
45. N,N-dimethylformamide		0.7(6)	0.5(6)
46. N-methylacetamide	0.0(1)	0.4(4)	0.2(4)
47. 1-nitropropane		1.6(7)	1.2(7)
48. 2-nitropropane		1.6(7)	0.9(7)
49. dimethoxymethane		0.8(5)	0.9(5)
50. propane-1,2,3-triol		1.3(6)	0.8(6)
51. propan-1-amine		1.1(7)	1.5(7)
52. propan-2-amine		0.7(5)	0.6(4)
53. 2-methylpropane	0.0(1)	0.8(5)	1.1(5)

Table 6. Continued

name	CGenFF	GAFF	OPLS/AA
54. ethylsulfanylethane		0.6(5)	0.7(5)
55. butane-1-thiol		0.9(5)	0.5(5)
56. butan-1-ol		1.1(7)	0.9(7)
57. 2-methylpropan-2-ol		0.4(2)	0.1(2)
58. butane-1,4-diol		0.9(6)	0.4(6)
59. (2-hydroxyethoxy)ethan-2-ol		1.2(4)	1.1(5)
60. N-ethylethanamine		1.1(7)	1.2(7)
61. butan-1-amine		1.1(7)	0.9(7)
62. 2-methylpropan-2-amine		1.0(5)	0.8(5)
63. 2-(2-hydroxyethylamino)ethanol		0.5(4)	0.4(4)
64. pyrimidine	0.0(2)	0.7(4)	0.6(4)
65. furan	0.2(2)	1.9(5)	1.9(5)
66. thiophene	0.0(2)	0.7(4)	0.3(5)
67. 1H-pyrrole	0.1(1)	1.3(7)	1.1(7)
68. ethenyl acetate		0.5(4)	0.8(4)
69. oxolan-2-one		0.3(3)	0.3(4)
70. acetyl acetate		1.2(4)	1.2(4)
71. 1,4-dichlorobutane		0.6(7)	0.8(7)
72. oxolane		0.6(6)	1.3(7)
73. ethoxyethene		0.3(3)	0.2(3)
74. ethyl acetate	0.0(2)	1.2(7)	1.1(7)
75. tetrahydrothiophene 1,1-dioxide		0.8(4)	0.9(4)
76. thiolane		0.5(4)	0.4(4)
77. 1-bromobutane		1.1(7)	0.7(7)
78. 1-chlorobutane		1.4(7)	1.8(7)
79. pyrrolidine	0.1(1)	1.3(7)	1.3(7)
80. N,N-dimethylacetamide		1.0(7)	0.9(7)
81. morpholine		0.8(5)	0.9(5)
82. pyridine	0.1(2)	0.6(6)	0.9(7)
83. cyclopentanone		0.8(5)	0.6(5)
84. 1-cyclopropylethanone		0.2(2)	0.1(2)
85. pentane-2,4-dione		0.9(5)	1.3(5)
86. methyl 2-methylprop-2-enoate		0.8(5)	3.6(5)
87. pentanenitrile		0.6(6)	1.6(7)
88. ethyl propanoate		1.3(7)	1.1(7)
89. diethyl carbonate		2.1(7)	0.7(6)
90. pentan-1-ol		1.0(7)	0.9(7)
91. pentan-3-ol		1.0(7)	1.1(7)
92. 2-methylbutan-2-ol		1.1(5)	0.5(5)
93. pentane-1,5-diol		0.8(6)	0.6(6)
94. pentan-3-amine		0.5(4)	0.6(4)
95. 1,2,3,4-tetrafluorobenzene		0.2(2)	0.1(2)
96. 1,2,3,5-tetrafluorobenzene		0.2(2)	0.1(2)
97. 1,3-difluorobenzene	0.2(2)	0.7(4)	1.3(5)
98. 1,2-difluorobenzene		0.7(4)	1.0(5)
99. fluorobenzene	0.1(2)	1.6(7)	0.5(6)
100. nitrobenzene	0.0(2)	1.1(7)	1.1(7)
101. 2-chloroaniline		0.9(4)	0.6(4)
102. phenol		0.8(4)	0.9(5)
103. benzenethiol		1.4(5)	1.3(5)
104. 2-methylpyridine		0.3(4)	0.9(5)
105. 3-methylpyridine	0.1(2)	0.8(5)	0.6(5)
106. 4-methylpyridine	0.0(2)	1.1(7)	0.4(6)
107. cyclohexanone		1.0(7)	0.9(7)
108. (E)-hex-2-ene	0.0(2)	0.0(2)	0.0(2)

Table 6. Continued

name	CGenFF	GAFF	OPLS/AA
109. hexan-2-one		0.8(6)	0.9(7)
110. 2,4,6-trimethyl-1,3,5-trioxane		1.6(4)	1.0(4)
111. cyclohexanamine		0.8(5)	0.7(5)
112. 2-propan-2-yloxypropane		3.3(7)	0.9(7)
113. 1-methoxy-2-(2-methoxyethoxy)ethane		1.5(7)	1.1(7)
114. triethyl phosphate		2.8(6)	2.2(6)
115. N,N-diethylethanamine		1.2(7)	1.0(7)
116. N-propan-2-ylpropan-2-amine		0.8(6)	0.6(6)
117. trifluoromethylbenzene		0.8(5)	0.5(4)
118. benzonitrile		1.0(5)	1.0(5)
119. benzaldehyde	0.2(2)	5.7(7)	3.7(6)
120. toluene	0.1(2)	1.6(7)	1.3(7)
121. methoxybenzene	0.1(2)	1.2(7)	1.1(7)
122. phenylmethanol		1.0(5)	0.8(5)
123. 2-methylphenol		0.9(5)	0.8(5)
124. 3-methylphenol		1.0(5)	0.9(5)
125. 4-methylphenol	0.1(1)	1.2(5)	0.7(5)
126. diethyl propanedioate		1.1(4)	0.8(4)
127. 2,4-dimethylpentan-3-one		0.6(4)	0.4(4)
128. heptan-2-one		1.1(7)	0.7(7)
129. ethenylbenzene		1.2(5)	1.1(5)
130. 1-phenylethanone		1.0(7)	1.1(7)
131. methyl benzoate		0.9(7)	1.0(7)
132. methyl 2-hydroxybenzoate		1.1(5)	0.4(4)
133. ethylbenzene	0.1(2)	1.4(7)	1.1(7)
134. 1,2-dimethylbenzene	0.1(1)	1.7(7)	1.0(7)
135. 1,2-dimethoxybenzene		0.4(4)	0.6(5)
136. 2,4,6-trimethylpyridine		0.9(5)	1.0(5)
137. octan-1-ol		0.8(6)	1.7(7)
138. 1-butoxybutane		0.7(4)	1.0(5)
139. N-butylbutan-1-amine		0.9(7)	0.8(7)
140. isoquinoline	0.0(1)	0.7(4)	1.3(4)
141. quinoline	0.1(2)	1.1(7)	1.2(7)
142. (1-methylethyl)benzene	0.1(2)	1.0(6)	0.7(6)
143. 1,2,4-trimethylbenzene	0.1(1)	1.2(6)	1.0(6)
144. 2,6-dimethylheptan-4-one		1.0(5)	0.9(5)
145. 1-chloronaphthalene		0.5(6)	1.3(7)
146. phenoxybenzene		0.6(4)	1.1(5)

^a Average relative deviation larger than 1 σ is printed in bold, larger than 1.5 σ in bold italic.

volumetric expansion coefficients, and isothermal compressibility from the two force fields are compared to experimental values. Indeed the benchmark is quite revealing, in that systematic deviations can be found and rationalized. The knowledge about such deviations will hopefully be useful for further development of the force fields.

To a first approximation, molecular vibrations can be described as quantum harmonic oscillators.¹⁰⁹ Classical harmonic oscillators do not describe the properties of quantum harmonic oscillators, which makes it necessary to implement corrections in computing for instance heat capacities. The two phase thermodynamics method employed here for estimating c_p and c_v relies on the force constants of the force field used, and on the effective frequencies in the simulations. The density of states obtained

from the velocity autocorrelation is convoluted by a weighting function derived from the partition function for a quantum harmonic oscillator in order to obtain a heat capacity for a corresponding quantum liquid. If a force field would allow one to directly reproduce the “correct” density of states, one could use the much simpler fluctuation formulas, as described by Allen and Tildesley;³⁸ however, heat capacities computed in this manner overestimate the experimental values by about 100% for OPLS/AA and GAFF (Table S10). Going beyond the harmonic approximation should therefore be considered by force field developers. Despite efforts in the context of the MMF94 force field¹¹⁰ and the MM3-MM4 family of force fields,^{111–113} this has not been widely adopted in the biomolecular simulation community, although the polarizable AMOEBA force field¹¹⁴ does feature anharmonic bond and angle potentials as well. In principle, it should be advantageous to use for instance Car–Parrinello molecular dynamics,¹¹⁵ in order to more faithfully represent a liquid than is possible in a classical simulation. This was attempted by Kuo et al. for water.¹¹⁶ They find a large scatter in c_p values due to limited sampling, but also a systematic deviation from the experimental value. Obviously, the computational bottleneck that would be introduced by CPMD or related methods will remain difficult to surmount for the immediate future, and therefore force-field-based methods remain necessary. Nevertheless, it is encouraging that there is a trend to use molecular dynamics simulations based on density functional theory codes to study vibrational properties of biomolecular systems beyond the harmonic approximation.^{117–119}

The dielectric constant seems to be the hardest nut to crack. Nonpolarizable force fields (such as GAFF and OPLS/AA) are known to have difficulties in reproducing the dielectric constant and to some extent also the surface tension. In the case of water, for which a large number of force fields have been developed, there are several studies that describe this (for a review, see, for example, Guillot²⁵). Improving the dielectric function often turns out to be done at the cost of the enthalpy of vaporization and the free energy of solvation—properties that may be more important to reproduce in biomolecular simulations. In addition to systematic problems, like sampling or the lack of polarization in our simulations,¹²⁰ the temperature dependence of the dielectric constant provides both a challenge and an opportunity for future force field development. For most molecules, the temperature dependence is very strong, because molecular motion is the largest factor contributing to $\epsilon(0)$. In his review of water models, Guillot has pointed out that the relation between dielectric constant and other properties is complex, and hence it can be used to test and validate force fields, but not likely as a target for force field optimization.²⁵

The benchmark we present here allows one to pinpoint systematic errors in force fields due to the fact that most chemical moieties are represented more than once. The overall performance of GAFF is surprisingly good, seeing that the parameter development was not aimed at liquids. The results from the OPLS/AA force field are slightly better than GAFF, obviously due to the fact that OPLS/AA was parametrized for liquids. The CHARMM generalized force field seems to be even slightly better, at least for density and enthalpy of vaporization.³⁷ It is reassuring for applications of force field calculations beyond liquids that the parameters in most cases are reasonable; however, the results presented here also show that blind faith in force fields is not warranted in all cases. In Table 2, we list the root-mean-square deviation, as well as the average relative deviation,

of the calculated values from the experimental, for each property we have analyzed. Even if our set of molecules is limited to 146, these numbers give a measurement of how well the properties are reproduced in the two force fields, at least for molecules similar to the set presented here.

Wang and Tingjun have recently reported a similar force field test of 71 organic molecules based on the GAFF and OPLS/AA force fields.³² They report densities and enthalpies of vaporization for these molecules and find small deviations from experimental results that are comparable to our numbers. It is encouraging to note that these authors were able to improve the correspondence to experimental numbers by tuning the Lennard-Jones parameters of some of the atom types. How this affects the other properties that we have studied here, in particular, the dielectric constant and the surface tension, remains to be determined, but it is likely that just tweaking the Lennard-Jones parameters is not sufficient to cure the significant and systematic deviations observed for those properties.

Mobley et al. have performed free energy of solvation (ΔG_{hyd}) benchmarks, reporting a RMS error from experimental numbers of 5.2 kJ/mol for more than 500 molecules.^{121,122} This number is comparable to the RMSD of 6.5 kJ/mol we computed for ΔH_{vap} for OPLS/AA (10.6 kJ/mol for GAFF and 4.7 kJ/mol for CGenFF³⁷). Since both numbers are to a large extent determined by the intermolecular energies, we can conclude that the RMS error in intermolecular energies for (“small”) organic molecules is 5–6 kJ/mol using state of the art simulations and nonpolarizable force fields. It should be noted that this result may be biased by the choice of test set, as has been shown in the context of the SAMPL contest where hydration energies were to be predicted.^{123,124} It was found here that larger molecules with multiple functional groups have similar deviations from the experimental hydration energy—errors up to 10 kJ/mol.¹²³ It seems plausible that part of this error is due to the simple nonpolarizable water model used, however, since the enthalpy of vaporization is approximately additive (which can be seen by plotting ΔH_{vap} for, e.g., alkanes as a function of the number of carbons), the error per functional group should still be relatively low, less than 5 kJ/mol for most groups. In the present work, we studied pure liquids only, providing a simpler test set than what has been used in previous studies. Further tests on pure liquids and liquid mixtures should provide a more detailed understanding of the predictive power of force field calculations. At the same time, systematic methods for force field development^{23,125} could be used for the improvement of classical force fields.

■ ASSOCIATED CONTENT

Supporting Information. Complete molecular topologies and structures for use with the GROMACS software suite as well as equilibrated liquid boxes containing coordinates for all 146 systems are available from our Web site <http://virtualchemistry.org>. Simulation parameter files are available in a zip file. The PDF file contains a derivation of the two phase thermodynamics method, as well as four supporting figures and 13 tables. Figure S1 shows ΔD eq 4; Figure S2, the fits to experimental data as a function of temperature for the dielectric constants; Figure S3, the fits to experimental data as a function of temperature for the heat capacity; and Figure S4, the fits to experimental data as a function of temperature for the isothermal compressibility. Tables S11–S13 give the experimental references corresponding to Figures S2–S4 for each molecule. Table S1 contains a list of all

molecules with formula, molecular weight, CAS number, and ChemSpider ID. Full lists of the calculated values for all properties as well as experimental and CGenFF³⁷ reference data (where applicable) are presented for liquid densities (Table S2), enthalpy of vaporization (Table S3), surface tension (Table S4), dielectric constant (Table S5), volumetric expansion coefficients (Table S6), isothermal compressibility (Table S7), heat capacity c_P (Table S8), heat capacity c_V (Table S9), and heat capacity c_P^{class} (Table S10). The tables are presented using the Hill system. This information is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: spoel@xray.bmc.uu.se.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The Swedish research council is acknowledged for some financial support to D.v.d.S. and for a grant of computer time (SNIC-022-09/10) through the national supercomputer center (NSC) in Linköping and the parallel computing center (PDC) in Stockholm, Sweden. C.C. acknowledges financial support from the Helmholtz Association through the Center for Free-Electron Laser Science. This study was also supported by a Marie Curie Intra-European Fellowship within the seventh European Community Framework Programme to J.S.H. We would like to thank Göran Wallin for stimulating discussions and Marjolein van der Spoel for help with collecting experimental data.

REFERENCES

- Jorgensen, W. L.; Tirado-Rives, J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 6665–6670.
- Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. *J. Comput. Chem.* **2004**, *25*, 1157–1174.
- Wang, J.; Wang, W.; Kollman, P. A.; Case, D. A. *J. Comput. Chem.* **2005**, *25*, 1157–1174.
- Hetyenyi, C.; Paragi, G.; Maran, U.; Timar, Z.; Karelson, M.; Penke, B. *J. Am. Chem. Soc.* **2006**, *128*, 1233–1239.
- Case, D. A.; Cheatham, T. E., III; Darden, T.; Gohlke, H.; Luo, R.; Merz, K. M., Jr.; Onufriev, A.; Simmerling, C.; Wang, B.; Woods, R. J. *J. Comput. Chem.* **2005**, *26*, 1668–1688.
- Fujitani, H.; Tanida, Y.; Matsuura, A. *Phys. Rev. E* **2009**, *79*, 021914.
- Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1984**, *5*, 129–145.
- Besler, B. H.; Merz, K. M., Jr.; Kollman, P. A. *J. Comput. Chem.* **1990**, *11*, 431–439.
- Francl, M. M.; Carey, C.; Chirlian, L. E.; Gange, D. M. *J. Comput. Chem.* **1996**, *17*, 367–383.
- Francl, M. M.; Chirlian, L. E. *Rev. Comput. Chem.* **2000**, *14*, 1–31.
- Bayly, C. I.; Cieplak, P.; Cornell, W. D.; Kollman, P. A. *J. Phys. Chem.* **1993**, *97*, 10269–10280.
- Jakalian, A.; Bush, B. L.; Jack, D. B.; Bayly, C. I. *J. Comput. Chem.* **2000**, *21*, 132–146.
- Jakalian, A.; Jack, D. B.; Bayly, C. I. *J. Comput. Chem.* **2002**, *23*, 1623–1641.
- Mobley, D. L.; Dumont, E.; Chodera, J. D.; Dill, K. A. *J. Phys. Chem. B* **2007**, *111*, 2242–2254.
- Mobley, D. L.; Dumont, E.; Chodera, J. D.; Dill, K. A. *J. Phys. Chem. B* **2011**, *115*, 1329–1332.
- Wallin, G.; Nervall, M.; Carlsson, J.; Åqvist, J. *J. Chem. Theory Comput.* **2009**, *5*, 380–395.
- Storer, J. W.; Giesen, D. J.; Cramer, C. J.; Truhlar, D. G. *J. Comput.-Aided Mol. Des.* **1995**, *9*, 87–110.
- Kaminski, G.; Jorgensen, W. *J. Phys. Chem. B* **1998**, *102*, 1787–1796.
- Chandrasekhar, J.; Shariffskul, S.; Jorgensen, W. *J. Phys. Chem. B* **2002**, *106*, 8078–8085.
- Shirts, M. R.; Pitera, J. W.; Swope, W. C.; Pande, V. S. *J. Chem. Phys.* **2003**, *119*, 5740–5761.
- Wensink, E. J. W.; Hoffmann, A. C.; van Maaren, P. J.; van der Spoel, D. *J. Chem. Phys.* **2003**, *119*, 7308–7317.
- van der Spoel, D.; van Maaren, P. J.; Larsson, P.; Timneanu, N. *J. Phys. Chem. B* **2006**, *110*, 4393–4398.
- van der Spoel, D.; van Maaren, P. J.; Berendsen, H. J. C. *J. Chem. Phys.* **1998**, *108*, 10220–10230.
- Mark, P.; Nilsson, L. *J. Comput. Chem.* **2002**, *23*, 1211–1219.
- Guillot, B. *J. Mol. Liq.* **2002**, *101*, 219–260.
- Hess, B.; van der Vegt, N. F. A. *J. Phys. Chem. B* **2006**, *110*, 17616–17626.
- Caleman, C.; van der Spoel, D. *J. Chem. Phys.* **2006**, *125*, 154508.
- Caleman, C.; van der Spoel, D. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5105–5111.
- Vega, C.; Abascal, J. L. F. *Phys. Chem. Chem. Phys.* **2011**.
- Kaminski, G.; Duffy, E. M.; Matsui, T.; Jorgensen, W. L. *J. Phys. Chem.* **1994**, *98*, 13077–13082.
- Kaminski, G.; Jorgensen, W. L. *J. Phys. Chem.* **1996**, *100*, 18010–18013.
- Wang, J.; Tingjun, H. *J. Chem. Theory Comput.* **2011**, *7*, 2151–2165.
- Berendsen, H. J. C.; van der Spoel, D.; van Drunen, R. *Comput. Phys. Commun.* **1995**, *91*, 43–56.
- Lindahl, E.; Hess, B.; van der Spoel, D. *J. Mol. Model.* **2001**, *7*, 306–317.
- van der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. C. *J. Comput. Chem.* **2005**, *26*, 1701–1718.
- Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. *J. Chem. Theory Comput.* **2008**, *4*, 435–447.
- Vanommeslaeghe, K.; Hatcher, E.; Acharya, C.; Kundu, S.; Zhong, S.; Shim, J.; Darian, E.; Guvench, O.; Lopes, P.; Vorobyov, I.; Mackerell, A. D. *J. Comput. Chem.* **2010**, *31*, 671–690.
- Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford Science Publications: Oxford, 1987.
- Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
- Schuettelkopf, A. W.; van Aalten, D. M. F. *Acta Crystallogr., Sect. D* **2004**, *60*, 1355–1363.
- Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.
- Frisch, M. J.; et al. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- Krishnan, R.; Binkley, J.; Seeger, R.; Pople, J. *J. Chem. Phys.* **1980**, *72*, 650–654.
- McLean, A.; Chandler, G. *J. Chem. Phys.* **1980**, *72*, 5639–5648.
- Glukhovtsev, M.; Pross, A.; McGrath, M.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 1878–1885.
- Curtiss, L.; McGrath, M.; Blaudeau, J.; Davis, N.; Binning, R.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104–6113.
- Blaudeau, J.; McGrath, M.; Curtiss, L.; Radom, L. *J. Chem. Phys.* **1997**, *107*, 5016–5021.
- Feenstra, K. A.; Hess, B.; Berendsen, H. J. C. *J. Comput. Chem.* **1999**, *20*, 786–798.
- Feller, D. *J. Comput. Chem.* **1996**, *17*, 1571–1586.
- Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoothi, V.; Chase, J.; Li, J.; Windus, T. L. *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052.
- Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728.
- Mobley, D. L.; Chodera, J. D.; Dill, K. A. *J. Chem. Phys.* **2006**, *125*, 084902.
- Berendsen, H. J. C.; Postma, J. P. M.; DiNola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684–3690.

- (54) Darden, T.; York, D.; Pedersen, L. *J. Chem. Phys.* **1993**, *98*, 10089–10092.
- (55) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. *J. Chem. Phys.* **1995**, *103*, 8577–8592.
- (56) van der Spoel, D.; van Maaren, P. J. *J. Chem. Theory Comput.* **2006**, *2*, 1–11.
- (57) Lange, O. F.; van der Spoel, D.; de Groot, B. L. *Biophys. J.* **2010**, *99*, 647–655.
- (58) Nosé, S. *Mol. Phys.* **1984**, *52*, 255–268.
- (59) Hoover, W. G. *Phys. Rev. A* **1985**, *31*, 1695–1697.
- (60) Holian, B.; Voter, A.; Ravelo, R. *Phys. Rev. E* **1995**, *52*, 2338–2347.
- (61) Parrinello, M.; Rahman, A. *J. Appl. Phys.* **1981**, *52*, 7182–7190.
- (62) Hess, B.; Bekker, H.; Berendsen, H. J. C.; Fraaije, J. G. E. M. *J. Comput. Chem.* **1997**, *18*, 1463–1472.
- (63) Hess, B. *J. Chem. Theory Comput.* **2008**, *4*, 116–122.
- (64) van Gunsteren, W. F.; Berendsen, H. J. C. *Mol. Sim.* **1988**, *1*, 173–185.
- (65) van Gunsteren, W. F.; Berendsen, H. J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 992–1023.
- (66) Neumann, M. *Mol. Phys.* **1983**, *50*, 841–858.
- (67) Neumann, M.; Steinhäuser, O.; Pawley, G. S. *Mol. Phys.* **1984**, *52*, 97–113.
- (68) Lin, S. T.; Blanco, M.; Goddard, W. A., III. *J. Chem. Phys.* **2003**, *119*, 11792–11805.
- (69) Lin, S.-T.; Maiti, P. K.; Goddard, W. A., III. *J. Phys. Chem. B* **2010**, *114*, 8191–8198.
- (70) Pascal, T. A.; Lin, S.-T.; Goddard, W. A., III. *J. Phys. Chem. Chem. Phys.* **2011**, *13*, 169–181.
- (71) Berens, P. H.; Mackay, D. H. J.; White, G. M.; Wilson, K. R. *J. Chem. Phys.* **1983**, *79*, 2375–2389.
- (72) Hess, B. *J. Chem. Phys.* **2002**, *116*, 209–217.
- (73) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 90th ed.; CRC Press: Cleveland, OH, 2009.
- (74) Frenkel, M.; Hong, X.; Dong, Q.; Yan, X.; Chirico, R. D. *Landolt-Börnstein - Group IV Physical Chemistry, Densities of Halohydrocarbons*; Springer: Berlin, 2000.
- (75) Yaws, C. L. *Thermophysical Properties of Chemicals and Hydrocarbons*; William Andrew Inc.: Beaumont, TX, 2008.
- (76) Caleman, C.; Hub, J. S.; van Maaren, P. J.; van der Spoel, D. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 6838–6842.
- (77) Wohlfahrt, C. *Landolt-Börnstein - Group IV Physical Chemistry*; Springer Verlag: New York, 2008; Chapter Static Dielectric Constants of Pure Liquids and Binary Liquid Mixtures. <http://www.springermaterials.com> (accessed Dec. 2011).
- (78) Whitfield, T. W.; Allison, G. J. M. S.; Bates, S. P.; Vass, H.; Crain, J. J. *J. Phys. Chem. B* **2005**, *110*, 3264–3673.
- (79) Jedlovsky, P.; Turi, L. *J. Phys. Chem. A* **1997**, *101*, 2662–2665.
- (80) MacCallum, J. L.; Tieleman, D. P. *J. Am. Chem. Soc.* **2002**, *124*, 15085–15093.
- (81) van der Spoel, D.; van Buuren, A. R.; Tieleman, D. P.; Berendsen, H. J. C. *J. Biomol. NMR* **1996**, *8*, 229–238.
- (82) Beachy, M.; Chasman, D.; Murphy, R.; Halgren, T.; Friesner, R. *J. Am. Chem. Soc.* **1997**, *119*, 5908–5920.
- (83) Lee, J.; Ripoll, D.; Czaplowski, C.; Pillardy, J.; Wedemeyer, W.; Scheraga, H. *J. Phys. Chem. B* **2001**, *105*, 7291–7298.
- (84) van der Spoel, D.; Lindahl, E. *J. Phys. Chem. B* **2003**, *107*, 11178–11187.
- (85) Lwin, T. Z.; Luo, R. *Protein Sci.* **2006**, *15*, 2642–2655.
- (86) Matthes, D.; de Groot, B. L. *Biophys. J.* **2009**, *97*, 599–608.
- (87) Jiang, J.; Wu, Y.; Wang, Z.-X.; Wu, C. *J. Chem. Theory Comput.* **2010**, *6*, 1199–1209.
- (88) Jha, S.; Coveney, P.; Laughton, C. *J. Comput. Chem.* **2005**, *26*, 1617–1627.
- (89) Jurecka, P.; Sponer, J.; Cerny, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985–1993.
- (90) Fadrna, E.; Spackova, N.; Sarzynska, J.; Koca, J.; Orozco, M.; Cheatham, T. E., III; Kulinski, T.; Sponer, J. *J. Chem. Theory Comput.* **2009**, *5*, 2514–2530.
- (91) Morgado, C. A.; Jurecka, P.; Svozil, D.; Hobza, P.; Sponer, J. *J. Chem. Theory Comput.* **2009**, *5*, 1524–1544.
- (92) Hemmingsen, L.; Madsen, D.; Esbensen, A.; Olsen, L.; Engelsen, S. *Carbohydr. Res.* **2004**, *339*, 937–948.
- (93) Hagler, A.; Lifson, S.; Dauber, P. *J. Am. Chem. Soc.* **1979**, *101*, 5122–5130.
- (94) Shirts, M. R.; Pande, V. S. *J. Chem. Phys.* **2005**, *122*, 134508.
- (95) White, B. R.; Wagner, C. R.; Truhlar, D. G.; Amin, E. A. *J. Chem. Theory Comput.* **2008**, *4*, 1718–1732.
- (96) Valdes, H.; Pluhackova, K.; Pitonak, M.; Rezac, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2747–2757.
- (97) Paton, R. S.; Goodman, J. M. *J. Chem. Inf. Model.* **2009**, *49*, 944–955.
- (98) Åqvist, J. *J. Phys. Chem.* **1990**, *94*, 8021–8024.
- (99) Hess, B.; Holm, C.; van der Vegt, N. *J. Chem. Phys.* **2006**, *124*, 164509.
- (100) Warren, G. L.; Patel, S. *J. Chem. Phys.* **2007**, *127*, 064509.
- (101) Mobley, D. L.; Barber, A. E., II; Fennell, C. J.; Dill, K. A. *J. Phys. Chem. B* **2008**, *112*, 2405–2414.
- (102) Fujitani, H.; Tanida, Y.; Ito, M.; Jayachandran, G.; Snow, C.; Shirts, M.; Sorin, E.; Pande, V. *J. Chem. Phys.* **2005**, *123*, 084108.
- (103) Felts, A.; Gallicchio, E.; Wallqvist, A.; Levy, R. *Proteins: Struct., Funct., Genet.* **2002**, *48*, 404–422.
- (104) Hetényi, C.; van der Spoel, D. *Protein Sci.* **2002**, *11*, 1729–1737.
- (105) Hetényi, C.; van der Spoel, D. *FEBS Lett.* **2006**, *580*, 1447–1450.
- (106) Hetényi, C.; van der Spoel, D. *Protein Sci.* **2011**, *20*, 880–893.
- (107) Industrial Fluid Properties Challenge. <http://www.fluidproperties.org> (accessed Dec. 2011).
- (108) Case, F. H.; Brennan, J.; Chaka, A.; Dobbs, K. D.; Friend, D. G.; Gordon, P. A.; Moore, J. D.; Mountain, R. D.; Olson, J. D.; Ross, R. B.; Schiller, M.; Shen, V. K.; Stahlberg, E. A. *Fluid Phase Equilib.* **2008**, *274*, 2–9.
- (109) McQuarrie, D. A. *Statistical Mechanics*; Harper & Row: New York, 1976.
- (110) Halgren, T. *J. Comput. Chem.* **1996**, *17*, 553–586.
- (111) Nevins, N.; Allinger, N. *J. Comput. Chem.* **1996**, *17*, 730–746.
- (112) Nevins, N.; Chen, K.; Allinger, N. *J. Comput. Chem.* **1996**, *17*, 669–694.
- (113) Nevins, N.; Lü, J.; Allinger, N. *J. Comput. Chem.* **1996**, *17*, 695–729.
- (114) Ponder, J. W.; Wu, C.; Ren, P.; Pande, V. S.; Chodera, J. D.; Schnieders, M. J.; Haque, I.; Mobley, D. L.; Lambrecht, D. S.; DiStasio, R. A., Jr.; Head-Gordon, M.; Clark, G. N. I.; Johnson, M. E.; Head-Gordon, T. *J. Phys. Chem. B* **2010**, *114*, 2549–2564.
- (115) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471–2474.
- (116) Kuo, L.; Mundy, C.; McGrath, M.; Siepmann, J.; VandeVondele, J.; Sprik, M.; Hutter, J.; Chen, B.; Klein, M.; Mohamed, F.; Krack, M.; Parrinello, M. *J. Phys. Chem. B* **2004**, *108*, 12990–12998.
- (117) Gageot, M. P. *J. Phys. Chem. A* **2008**, *112*, 13507–13517.
- (118) Cimas, A.; Vaden, T. D.; de Boer, T. S. J. A.; Snoek, L. C.; Gageot, M. P. *J. Chem. Theory Comput.* **2009**, *5*, 1068–1078.
- (119) Gageot, M.-P. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3336–3359.
- (120) van der Spoel, D.; Hess, B. *Comput. Mol. Sci.* **2011**, *1*, 710–715.
- (121) Mobley, D. L.; Bayly, C. I.; Cooper, M. D.; Dill, K. A. *J. Phys. Chem. B* **2009**, *113*, 4533–4537.
- (122) Mobley, D. L.; Bayly, C. I.; Cooper, M. D.; Shirts, M. R.; Dill, K. A. *J. Chem. Theory Comput.* **2009**, *5*, 350–358.
- (123) Nicholls, A.; Mobley, D. L.; Guthrie, J. P.; Chodera, J. D.; Bayly, C. I.; Cooper, M. D.; Pande, V. S. *J. Med. Chem.* **2008**, *51*, 769–779.
- (124) Geballe, M. T.; Skillman, A. G.; Nicholls, A.; Guthrie, J. P.; Taylor, P. J. *J. Comput.-Aided Mol. Des.* **2010**, *24*, 259–279.
- (125) van Maaren, P. J.; van der Spoel, D. *J. Phys. Chem. B* **2001**, *105*, 2618–2626.
- (126) Hill, E. A. *J. Am. Chem. Soc.* **1900**, *8*, 478–494.

**Force Field Benchmark of Organic Liquids:
Density, Enthalpy of Vaporization, Heat
Capacities, Surface Tension, Compressibility,
Expansion Coefficient and Dielectric Constant**

**Carl Caleman¹ Paul J. van Maaren²
Minyan Hong² Jochen S. Hub²
Luciano T. da Costa³ David van der Spoel^{2*}**

October 18, 2011

¹: Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron
Notkestraße 85, DE-22607 Hamburg, Germany

²: Department of Cell and Molecular Biology, Uppsala University
Husargatan 3, Box 596, SE-75124 Uppsala, Sweden

³: Departamento de Ciências Exatas, Federal University of Alfenas - MG
Rua Gabriel Monteiro da Silva, 700 Alfenas - MG CEP:37130-000, Brazil

*: corresponding author, e-mail: spoel@xray.bmc.uu.se

Contents

1	Derivation of equations of the two-phase thermodynamics method	7
2	Liquidity Test	10
3	Simulation Results per Property	11
4	Polynomial Fits to Experimental Data	80

List of Figures

S1	Liquidity test. The change in MSD , ΔD as defined in the main text. On the x-axis all the simulated molecules are listed in alphabetic order. For all simulations with $ \Delta D \geq 0.5$ the trajectories and MSD for the entire simulation was further investigated to ensure that the system was liquid during the whole simulation.	10
S2	(part 1) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.	80
S2	(part 2) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.	81
S2	(part 3) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.	82
S2	(part 4) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.	83
S2	(part 5) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.	84
S2	(part 6) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.	85
S3	(part 1) Polynomial curves fitted to heat capacity at constant pressure measurements for different molecules. For parameters see Table 5 in the main text.	87
S4	(part 1) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	88
S4	(part 2) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	89

S4	(part 3) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	90
S4	(part 4) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	91
S4	(part 5) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	92
S4	(part 6) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	93
S4	(part 7) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	94
S4	(part 8) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	95
S4	(part 9) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.	96

List of Tables

S1	Name, formula, molecular weight (g/cm ³), CAS number and ChemSpider ID for all molecules in the test set.	12
S1	Name, formula, molecular weight, CAS number, ChemSpider ID - continued.	13
S1	Name, formula, molecular weight, CAS number, ChemSpider ID - continued.	14
S1	Name, formula, molecular weight, CAS number, ChemSpider ID - continued.	15
S1	Name, formula, molecular weight, CAS number, ChemSpider ID - continued.	16
S2	Liquid density ρ (g/l) calculated and experimental. Blue font indicates that the calculated value differs more than 5% from the experimental ones, a red font indicates that it differs by more than 10%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	17
S2	Liquid density - continued	18
S2	Liquid density - continued	19
S2	Liquid density - continued	20
S2	Liquid density - continued	21
S2	Liquid density - continued	22
S2	Liquid density - continued	23
S2	Liquid density - continued	24

S3	Heat of vaporization ΔH_{vap} (kJ/mol) calculated and experimental. Blue font indicates that the calculated value differs more than 10% from the experimental ones, a red font indicates that it differs by more than 25%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	25
S3	Heat of vaporization - continued	26
S3	Heat of vaporization - continued	27
S3	Heat of vaporization - continued	28
S3	Heat of vaporization - continued	29
S3	Heat of vaporization - continued	30
S3	Heat of vaporization - continued	31
S3	Heat of vaporization - continued	32
S4	Surface tension γ (10^{-3}Nm^{-1}) calculated and experimental. Blue font indicates that the calculated value differs more than 10% from the experimental ones, a red font indicates that it differs by more than 25%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	33
S4	Surface tension - continued	34
S4	Surface tension - continued	35
S4	Surface tension - continued	36
S4	Surface tension - continued	37
S4	Surface tension - continued	38
S5	Dielectric constant $\varepsilon(0)$ calculated and experimental. Missing simulated $\varepsilon(0)$ due to simulations not having converged, see main text. Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	39
S5	Dielectric constant - continued	40
S5	Dielectric constant - continued	41
S5	Dielectric constant - continued	42
S5	Dielectric constant - continued	43
S5	Dielectric constant - continued	44
S5	Dielectric constant - continued	45
S6	Thermal expansion coefficient α_P ($10^{-3}/\text{K}$), calculated and experimental. Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	46
S6	Thermal expansion coefficient - continued	47
S6	Thermal expansion coefficient - continued	48
S6	Thermal expansion coefficient - continued	49
S6	Thermal expansion coefficient - continued	50
S6	Thermal expansion coefficient - continued	51

S6	Thermal expansion coefficient - continued	52
S6	Thermal expansion coefficient - continued	53
S7	Isothermal compressibility κ_T (1/GPa), calculated and experimental. Blue font indicates that the calculated value differs more than 10% from the experimental ones, a red font indicates that it differs by more than 25%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	54
S7	Isothermal compressibility - continued	55
S7	Isothermal compressibility - continued	56
S7	Isothermal compressibility - continued	57
S7	Isothermal compressibility - continued	58
S7	Isothermal compressibility - continued	59
S7	Isothermal compressibility - continued	60
S7	Isothermal compressibility - continued	61
S8	Heat capacity at constant pressure c_P (J/mol K) calculated (based on density of states) and experimental. Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	62
S8	Heat capacity at constant pressure c_P based on DoS - continued	63
S8	Heat capacity at constant pressure c_P based on DoS - continued	64
S8	Heat capacity at constant pressure c_P based on DoS - continued	65
S8	Heat capacity at constant pressure c_P based on DoS - continued	66
S9	Heat capacity at constant volume c_V (J/mol K) calculated (based on density of states) compared to the experimental $c_P - \Delta c$ (J/mol K). Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	67
S9	Heat capacity at constant volume c_V based on DoS - continued	68
S9	Heat capacity at constant volume c_V based on DoS - continued	69
S9	Heat capacity at constant volume c_V based on DoS - continued	70
S9	Heat capacity at constant volume c_V based on DoS - continued	71
S10	Classical heat capacity at constant pressure c_P^{class} (J/mol K) calculated and experimental. Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.	72
S10	Classical heat capacity at constant pressure - continued . . .	73
S10	Classical heat capacity at constant pressure - continued . . .	74
S10	Classical heat capacity at constant pressure - continued . . .	75
S10	Classical heat capacity at constant pressure - continued . . .	76
S10	Classical heat capacity at constant pressure - continued . . .	77
S10	Classical heat capacity at constant pressure - continued . . .	78

S10	Classical heat capacity at constant pressure - continued . . .	79
S11	References used for deriving fits of dielectric constants as a function of temperature to experimental data.	86
S12	References used for deriving fits of isothermal compressibilities as a function of temperature to experimental data.	87
S13	References used for deriving fits of isothermal compressibilities as a function of temperature to experimental data.	97
S13	References used for deriving fits of isothermal compressibilities as a function of temperature to experimental data (continued).	98

1 Derivation of equations of the two-phase thermodynamics method

Here we derive the equations needed to implement the two-phase thermodynamic (2PT) model introduced by the Goddard group [1, 2, 3, 4]. This model treats a liquid as something in between a solid and an ideal gas, the rationale for this being that there is existing analytical theory for treating the thermodynamic properties of ideal gases and solids, but no such theory exists for liquids. The reason to summarize the equations here rather than to refer to the original publications, is first and foremost that in the three papers mentioned [1, 2, 3] there is no single complete derivation of the method, and second that the equations below serve as a blueprint for a new GROMACS [5] analysis tool, `g_dos`, that computes properties based on the density of states using the 2PT method. It is important to give credit to one of the first papers in this field by Berens *et al.* [6], that attempted to treat a fluid just like a solid, and which derived most of the equations that the 2PT method is based upon. Another contributing theory is the Carnahan-Starling model of fluids of rigid spheres [7]. Since the equations published by Berens are internally consistent and can be derived from statistical mechanics textbooks (e.g. McQuarrie [8]) we use this as the foundation for deriving the equations below, however, we note as far as possible from which source the equations below were taken. We derive equations in the context of molecular dynamics simulations, i.e. using finite sampling and simulation lengths.

We start from the mass-weighted velocity autocorrelation function:

$$C(t) = \sum_{j=1}^N m_j \sum_{k=1}^3 \langle v_j^k(t) v_j^k(t + \tau) \rangle_{\tau} \quad (\text{S1})$$

where $v_j^k(t)$ is the velocity of atom j in the k direction at time t , N is the number of atoms, m_j are the atomic masses and $\langle \rangle_{\tau}$ indicates averaging over time origins τ ; $C(t)$ has the units of energy. The Fourier transform of $C(t)$ yields the density of states as a function of frequency ν (Equation 7, reference [1]):

$$DoS(\nu) = \frac{2}{k_B T} \lim_{\tau \rightarrow \infty} \int_{-\tau}^{+\tau} C(t) e^{-i2\pi\nu t} dt \approx \frac{4}{k_B T} \sum_{k=0}^{K-1} C(k\Delta t) e^{-i2\pi\nu k\Delta t/K} \quad (\text{S2})$$

where Δt is the time between saving velocities in the MD trajectory (4 fs in our simulations), k_B is Boltzmann's constant and K is the number of data points, and the extra factor two in the summation comes from the lower limit being 0 instead of $-\infty$ in the integral (cf. Equation 22 in reference [1]). Note that the Density of States (DoS) in this definition is a dimensionless quantity. The density of states at zero frequency, $DoS(0)$, is associated with the diffusion constant D through (Equation 3.16, reference [6]):

$$D = \frac{DoS(0)k_B T}{12Mm} \quad (\text{S3})$$

where M is the number of equivalent particles and m is their mass.

The 2PT method approximates

$$DoS_{\text{liquid}}(\nu) = DoS_{\text{gas}}(\nu) + DoS_{\text{solid}}(\nu) \quad (\text{S4})$$

and if we would have an analytical expression for $DoS_{\text{gas}}(\nu)$ – note that Pascal *et al.* [3] use the subscript “diff” rather than “gas” as we do for consistency here – we could subtract this from the $DoS(\nu)$ obtained from the simulation (Eq. S2). Indeed, the gaseous (diffusive) component of the density of states $DoS(\nu)_{\text{gas}}$, described as a gas of hard spheres (Equation 24, reference [1]) can be written as:

$$DoS_{\text{gas}}(\nu) = DoS(0) \left(1 + \left[\frac{DoS(0)\pi\nu}{6fN} \right]^2 \right)^{-1} \quad (\text{S5})$$

where f is the fluidicity, the fraction of the 3N degrees of freedom that corresponds to the diffusional parts of the system, or in other words

$$\int_0^\infty DoS_{\text{gas}}(\nu) d\nu = 3fN, \quad (\text{S6})$$

independent of $DoS(0)$. A derivation of the equation needed to solve for f can be found in reference [1], the final result being (Equation 12, reference [2]):

$$2(f^5/\Delta^3)^{3/2} - 6(f^5/\Delta^3) - (f^7/\Delta^3)^{1/2} + 6(f^5/\Delta^3)^{1/2} + 2f = 2 \quad (\text{S7})$$

where Δ is the dimensionless diffusion constant defined by (Equation 13, reference [2]):

$$\Delta = \frac{2DoS(0)}{9N} \left(\frac{\pi k_B T N}{M} \right)^{1/2} \left(\frac{N}{V} \right)^{1/3} \left(\frac{6}{\pi} \right)^{2/3} \quad (\text{S8})$$

with V is the volume of the system. Eq. S7 is monotonous between 0 and 1 (cf. Figure 2 in reference [1]) and hence a bisection algorithm can be used to solve for f given Δ .

Now we will try to comprehend the solid component of the density of states, $DoS_{\text{solid}}(\nu)$. Here, each mode is considered to be harmonic and we use the partition function for a quantum harmonic oscillator as given by McQuarrie [8]:

$$q_{\text{HO}}^q(\nu) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \quad (\text{S9})$$

where h is Planck’s constant, $\beta = 1/k_B T$. Since the canonical partition function Q of a system is given by the product of the components (Equations 3.18-3.20, reference [6]):

$$Q = \prod_{i=1}^N q_i \quad (\text{S10})$$

and therefore

$$\ln Q = \sum_{i=1}^N \ln q_i \quad (\text{S11})$$

we can write for a system of quantum harmonic oscillators, assuming the frequencies are continuous, that:

$$\ln Q = \int_0^\infty DoS_{\text{solid}}(\nu) \ln q_{\text{HO}}^q(\nu) d\nu. \quad (\text{S12})$$

This equation is used for deriving the thermodynamic properties from the solid. We use the notation of Pascal *et al.* [3], but with corrections based on Berens *et al.* [6]:

$$\begin{aligned} c_V^Q &= 2k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B T \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_{N,V} \\ &= k_B \int_0^\infty DoS_{\text{solid}}(\nu) W_{\text{solid}}^{\text{cv}}(\nu) d\nu \end{aligned} \quad (\text{S13})$$

where the weighting function is defined as:

$$\begin{aligned} W_{\text{solid}}^{\text{cv}}(\nu) &= T \left(\frac{\partial W_{\text{solid}}^S(\nu)}{\partial T} \right) = T \left(2 \frac{\partial \ln q_{\text{HO}}^q(\nu)}{\partial T} + T \frac{\partial^2 \ln q_{\text{HO}}^q(\nu)}{\partial T^2} \right) \\ &= \frac{(\beta h \nu)^2 e^{\beta h \nu}}{(1 - e^{\beta h \nu})^2} \end{aligned} \quad (\text{S14})$$

Now, finally, we can estimate the heat capacity of the liquids using:

$$c_V = k_B \int_0^\infty \left[DoS_{\text{gas}}(\nu) W_{\text{gas}}^{\text{cv}}(\nu) + DoS_{\text{solid}}(\nu) W_{\text{solid}}^{\text{cv}}(\nu) \right] d\nu \quad (\text{S15})$$

where the weighting factor for the diffusive part is:

$$W_{\text{gas}}^{\text{cv}} = \frac{1}{2}. \quad (\text{S16})$$

Similar equations have been presented by the Goddard group for the Helmholtz energy, the entropy and the internal energy [1, 2, 3].

Finally, we can compare the heat capacity at constant volume c_V to the one at constant pressure c_P because they are related according to:

$$c_P = c_V + VT \frac{\alpha_P^2}{\kappa_T} \quad (\text{S17})$$

where α_P is the volumetric thermal expansion coefficient and κ_T the isothermal compressibility (see main text).

2 Liquidity Test

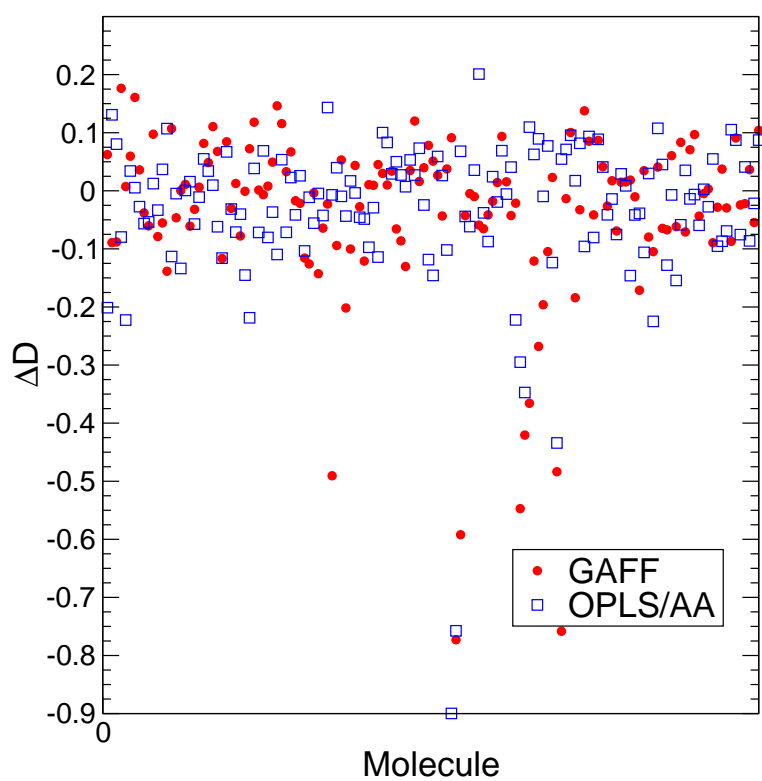


Figure S1: Liquidity test. The change in MSD , ΔD as defined in the main text. On the x-axis all the simulated molecules are listed in alphabetic order. For all simulations with $|\Delta D| \geq 0.5$ the trajectories and MSD for the entire simulation was further investigated to ensure that the system was liquid during the whole simulation.

3 Simulation Results per Property

Table S1: Name, formula, molecular weight (g/cm³), CAS number and ChemSpider ID for all molecules in the test set.

Name	Formula	MW	CAS	CSID
1. chloroform	CHCl ₃	119.378	67-66-3	5977
2. dichloro(fluoro)methane	CHCl ₂ F	102.923	75-43-4	6130
3. dibromomethane	CH ₂ Br ₂	173.835	74-95-3	2916
4. dichloromethane	CH ₂ Cl ₂	84.9325	75-09-2	6104
5. methanal	CH ₂ O	30.0259	50-00-0	692
6. methanoic acid	CH ₂ O ₂	46.0253	64-18-6	278
7. bromomethane	CH ₃ Br	94.9384	74-83-9	6083
8. methanamide	CH ₃ NO	45.0405	75-12-7	693
9. nitromethane	CH ₃ NO ₂	61.0399	75-52-5	6135
10. methanol	CH ₄ O	32.0417	67-56-1	864
11. 1,1,1,2,2-pentachloroethane	C ₂ HCl ₅	202.294	76-01-7	6179
12. 1,1,2,2-tetrachloroethane	C ₂ H ₂ Cl ₄	167.849	79-34-5	6342
13. 1,1-dichloroethene	C ₂ H ₂ Cl ₂	96.9432	75-35-4	13835316
14. 1,1,2-trichloroethane	C ₂ H ₃ Cl ₃	133.404	79-00-5	6326
15. acetonitrile	C ₂ H ₃ N	41.0518	75-05-8	6102
16. 1,2-dibromoethane	C ₂ H ₄ Br ₂	187.861	106-93-4	7551
17. 1,1-dichloroethane	C ₂ H ₄ Cl ₂	98.959	75-34-3	6125
18. 1,2-dichloroethane	C ₂ H ₄ Cl ₂	98.959	107-06-2	13837650
19. methyl formate	C ₂ H ₄ O ₂	60.0518	107-31-3	7577
20. bromoethane	C ₂ H ₅ Br	108.965	74-96-4	6092
21. chloroethane	C ₂ H ₅ Cl	64.5139	75-00-3	6097
22. 2-chloroethanol	C ₂ H ₅ ClO	80.5133	107-07-3	21106015
23. ethanamide	C ₂ H ₅ NO	59.067	60-35-5	173
24. N-methylformamide	C ₂ H ₅ NO	59.067	123-39-7	28994
25. nitroethane	C ₂ H ₅ NO ₂	75.0664	79-24-3	6338
26. methoxymethane	C ₂ H ₆ O	46.0682	115-10-6	7956
27. ethanol	C ₂ H ₆ O	46.0682	64-17-5	682
28. 1,2-ethanedithiol	C ₂ H ₆ S ₂	94.1988	540-63-6	13865015
29. methyldisulfanylmethane	C ₂ H ₆ S ₂	94.1988	624-92-0	11731
30. methylsulfinylmethane	C ₂ H ₆ OS	78.1332	67-68-5	659
31. methylsulfanylmethane	C ₂ H ₆ S	62.1338	75-18-3	1039
32. 2-aminoethanol	C ₂ H ₇ NO	61.0828	141-43-5	13835336
33. ethane-1,2-diamine	C ₂ H ₈ N ₂	60.098	107-15-3	13835550
34. prop-2-enenitrile	C ₃ H ₃ N	53.0625	107-13-1	7567

Table S1: Name, formula, molecular weight, CAS number, ChemSpider ID - continued.

Name	Formula	MW	CAS	CSID
35. 1,3-dioxolan-2-one	C ₃ H ₄ O ₃	88.0619	96-49-1	7030
36. propanenitrile	C ₃ H ₅ N	55.0783	107-12-0	7566
37. 1,2-dibromopropane	C ₃ H ₆ Br ₂	201.888	78-75-1	6305
38. 1,3-dichloropropane	C ₃ H ₆ Cl ₂	112.985	142-28-9	8543
39. (2R)-2-methyloxirane	C ₃ H ₆ O	58.0789	15448-47-2	129014
40. propan-2-one	C ₃ H ₆ O	58.0789	67-64-1	175
41. methyl acetate	C ₃ H ₆ O ₂	74.0783	79-20-9	6335
42. 1,3-dioxolane	C ₃ H ₆ O ₂	74.0783	646-06-0	12066
43. 2-iodopropane	C ₃ H ₇ I	169.992	75-30-9	6122
44. 1-bromopropane	C ₃ H ₇ Br	122.991	106-94-5	7552
45. N,N-dimethylformamide	C ₃ H ₇ NO	73.0935	68-12-2	5993
46. N-methylacetamide	C ₃ H ₇ NO	73.0935	79-16-3	6334
47. 1-nitropropane	C ₃ H ₇ NO ₂	89.0929	108-03-2	7615
48. 2-nitropropane	C ₃ H ₇ NO ₂	89.0929	79-46-9	387
49. dimethoxymethane	C ₃ H ₈ O ₂	76.0941	109-87-5	13837190
50. propane-1,2,3-triol	C ₃ H ₈ O ₃	92.0935	56-81-5	733
51. propan-1-amine	C ₃ H ₉ N	59.1099	107-10-8	7564
52. propan-2-amine	C ₃ H ₉ N	59.1099	75-31-0	6123
53. 2-methylpropane	C ₄ H ₁₀	58.1218	75-28-5	6120
54. ethylsulfanylethane	C ₄ H ₁₀ S	90.1868	352-93-2	9233
55. butane-1-thiol	C ₄ H ₁₀ S	90.1868	109-79-5	7721
56. butan-1-ol	C ₄ H ₁₀ O	74.1212	71-36-3	258
57. 2-methylpropan-2-ol	C ₄ H ₁₀ O	74.1212	75-65-0	6146
58. butane-1,4-diol	C ₄ H ₁₀ O ₂	90.1206	110-63-4	13835209
59. (2-hydroxyethoxy)ethan-2-ol	C ₄ H ₁₀ O ₃	106.12	111-46-6	13835180
60. N-ethylethanamine	C ₄ H ₁₁ N	73.1364	109-89-7	7730
61. butan-1-amine	C ₄ H ₁₁ N	73.1364	109-73-9	7716
62. 2-methylpropan-2-amine	C ₄ H ₁₁ N	73.1364	75-64-9	6145
63. 2-(2-hydroxyethylamino)ethanol	C ₄ H ₁₁ NO ₂	105.135	111-42-2	13835604
64. pyrimidine	C ₄ H ₄ N ₂	80.0878	289-95-2	8903
65. furan	C ₄ H ₄ O	68.0738	110-00-9	7738
66. thiophene	C ₄ H ₄ S	84.1394	110-02-1	7739
67. 1H-pyrrole	C ₄ H ₅ N	67.089	109-97-7	7736
68. ethenyl acetate	C ₄ H ₆ O ₂	86.089	108-05-4	7616

Table S1: Name, formula, molecular weight, CAS number, ChemSpider ID - continued.

Name	Formula	MW	CAS	CSID
69. oxolan-2-one	C ₄ H ₆ O ₂	86.089	96-48-0	7029
70. acetyl acetate	C ₄ H ₆ O ₃	102.088	108-24-7	7630
71. 1,4-dichlorobutane	C ₄ H ₈ Cl ₂	127.012	110-56-5	21106032
72. oxolane	C ₄ H ₈ O	72.1054	109-99-9	7737
73. ethoxyethene	C ₄ H ₈ O	72.1054	109-92-2	7732
74. ethyl acetate	C ₄ H ₈ O ₂	88.1048	141-78-6	8525
75. tetrahydrothiophene 1,1-dioxide	C ₄ H ₈ O ₂ S	120.17	126-33-0	29080
76. thiolane	C ₄ H ₈ S	88.171	110-01-0	1095
77. 1-bromobutane	C ₄ H ₉ Br	137.018	109-65-9	7711
78. 1-chlorobutane	C ₄ H ₉ Cl	92.5669	109-69-3	7714
79. pyrrolidine	C ₄ H ₉ N	71.1206	123-75-1	29008
80. N,N-dimethylacetamide	C ₄ H ₉ NO	87.12	127-19-5	29107
81. morpholine	C ₄ H ₉ NO	87.12	110-91-8	13837537
82. pyridine	C ₅ H ₅ N	79.0997	110-86-1	1020
83. cyclopentanone	C ₅ H ₈ O	84.1161	120-92-3	8141
84. 1-cyclopropylethanone	C ₅ H ₈ O	84.1161	765-43-5	12463
85. pentane-2,4-dione	C ₅ H ₈ O ₂	100.115	123-54-6	29001
86. methyl 2-methylprop-2-enoate	C ₅ H ₈ O ₂	100.115	80-62-6	6406
87. pentanenitrile	C ₅ H ₉ N	83.1313	110-59-8	7770
88. ethyl propanoate	C ₅ H ₁₀ O ₂	102.131	105-37-3	7463
89. diethyl carbonate	C ₅ H ₁₀ O ₃	118.131	105-58-8	7478
90. pentan-1-ol	C ₅ H ₁₂ O	88.1477	71-41-0	6040
91. pentan-3-ol	C ₅ H ₁₂ O	88.1477	584-02-1	10947
92. 2-methylbutan-2-ol	C ₅ H ₁₂ O	88.1477	75-85-4	6165
93. pentane-1,5-diol	C ₅ H ₁₂ O ₂	104.147	111-29-5	13839441
94. pentan-3-amine	C ₅ H ₁₃ N	87.1629	616-24-0	11524
95. 1,2,3,4-tetrafluorobenzene	C ₆ H ₂ F ₄	150.074	551-62-2	21106162
96. 1,2,3,5-tetrafluorobenzene	C ₆ H ₂ F ₄	150.074	2367-82-0	21159625
97. 1,3-difluorobenzene	C ₆ H ₄ F ₂	114.093	372-18-9	9358
98. 1,2-difluorobenzene	C ₆ H ₄ F ₂	114.093	367-11-3	9325
99. fluorobenzene	C ₆ H ₅ F	96.1021	462-06-6	9614
100. nitrobenzene	C ₆ H ₅ NO ₂	123.109	98-95-3	7138
101. 2-chloroaniline	C ₆ H ₆ ClN	127.571	95-51-2	13854248
102. phenol	C ₆ H ₆ O	94.111	108-95-2	971

Table S1: Name, formula, molecular weight, CAS number, ChemSpider ID - continued.

Name	Formula	MW	CAS	CSID
103. benzenethiol	C ₆ H ₆ S	110.177	108-98-5	7681
104. 2-methylpyridine	C ₆ H ₇ N	93.1262	109-06-8	13839199
105. 3-methylpyridine	C ₆ H ₇ N	93.1262	108-99-6	21106520
106. 4-methylpyridine	C ₆ H ₇ N	93.1262	108-89-4	13874733
107. cyclohexanone	C ₆ H ₁₀ O	98.1426	108-94-1	7679
108. (E)-hex-2-ene	C ₆ H ₁₂	84.159	4050-45-7	555073
109. hexan-2-one	C ₆ H ₁₂ O	100.158	591-78-6	11095
110. 2,4,6-trimethyl-1,3,5-trioxane	C ₆ H ₁₂ O ₃	132.157	123-63-7	21106173
111. cyclohexanamine	C ₆ H ₁₃ N	99.1736	108-91-8	7677
112. 2-propan-2-yloxypropane	C ₆ H ₁₄ O	102.174	108-20-3	7626
113. 1-methoxy-2-(2-methoxyethoxy)ethane	C ₆ H ₁₄ O ₃	134.173	111-96-6	13839575
114. triethyl phosphate	C ₆ H ₁₅ O ₄ P	182.154	78-40-0	6287
115. N,N-diethylethanamine	C ₆ H ₁₅ N	101.189	121-44-8	8158
116. N-propan-2-ylpropan-2-amine	C ₆ H ₁₅ N	101.189	108-18-9	7624
117. trifluoromethylbenzene	C ₇ H ₅ F ₃	146.11	98-08-8	7090
118. benzonitrile	C ₇ H ₅ N	103.121	100-47-0	7224
119. benzaldehyde	C ₇ H ₆ O	106.122	100-52-7	235
120. toluene	C ₇ H ₈	92.1381	108-88-3	1108
121. methoxybenzene	C ₇ H ₈ O	108.138	100-66-3	7238
122. phenylmethanol	C ₇ H ₈ O	108.137	100-51-6	13860335
123. 2-methylphenol	C ₇ H ₈ O	108.137	95-48-7	13835772
124. 3-methylphenol	C ₇ H ₈ O	108.137	108-39-4	21105871
125. 4-methylphenol	C ₇ H ₈ O	108.137	106-44-5	13839082
126. diethyl propanedioate	C ₇ H ₁₂ O ₄	160.167	105-53-3	13863636
127. 2,4-dimethylpentan-3-one	C ₇ H ₁₄ O	114.185	565-80-0	10797
128. heptan-2-one	C ₇ H ₁₄ O	114.185	110-43-0	7760
129. ethenylbenzene	C ₈ H ₈	104.149	100-42-5	7220
130. 1-phenylethanone	C ₈ H ₈ O	120.148	98-86-2	7132
131. methyl benzoate	C ₈ H ₈ O ₂	136.148	93-58-3	6883
132. methyl 2-hydroxybenzoate	C ₈ H ₈ O ₃	152.147	119-36-8	13848808
133. ethylbenzene	C ₈ H ₁₀	106.165	100-41-4	7219
134. 1,2-dimethylbenzene	C ₈ H ₁₀	106.165	95-47-6	6967
135. 1,2-dimethoxybenzene	C ₈ H ₁₀ O ₂	138.163	91-16-7	13861009
136. 2,4,6-trimethylpyridine	C ₈ H ₁₁ N	121.179	108-75-8	21106174

Table S1: Name, formula, molecular weight, CAS number, ChemSpider ID - continued.

Name	Formula	MW	CAS	CSID
137. octan-1-ol	C ₈ H ₁₈ O	130.227	111-87-5	932
138. 1-butoxybutane	C ₈ H ₁₈ O	130.227	142-96-1	8569
139. N-butylbutan-1-amine	C ₈ H ₁₉ N	129.242	111-92-2	7856
140. isoquinoline	C ₉ H ₇ N	129.158	119-65-3	8098
141. quinoline	C ₉ H ₇ N	129.158	91-22-5	6780
142. (1-methylethyl)benzene	C ₉ H ₁₂	120.191	98-82-8	7128
143. 1,2,4-trimethylbenzene	C ₉ H ₁₂	120.191	95-63-6	6977
144. 2,6-dimethylheptan-4-one	C ₉ H ₁₈ O	142.238	108-83-8	7670
145. 1-chloronaphthalene	C ₁₀ H ₇ Cl	162.615	90-13-1	6737
146. phenoxybenzene	C ₁₂ H ₁₀ O	170.207	101-84-8	7302

Table S2: Liquid density ρ (g/l) calculated and experimental. Blue font indicates that the calculated value differs more than 5% from the experimental ones, a red font indicates that it differs by more than 10%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ρ	Ref.	ρ	ρ	ρ
1. chloroform	298.15	1479.30	[9]	1375.0 \pm 0.3	1373.2 \pm 0.3	
2. dichloro(fluoro)methane	282.05	1399.17	[10]	1308.0 \pm 1.0	1314.0 \pm 0.8	
3. dibromomethane	293.15	2496.90	[11]	1958.1 \pm 0.6	2490.1 \pm 0.8	
...	298.15	2490.70	[9]	1946.1 \pm 0.3	2475.3 \pm 1.5	
4. dichloromethane	293.15	1326.60	[11]	1268.5 \pm 0.5	1207.1 \pm 0.5	
...	298.15	1394.30	[9]	1258.1 \pm 0.5	1200.4 \pm 1.5	
5. methanal	253.15	815.00	[11]	838.0 \pm 0.2	773.7 \pm 0.1	
...	253.65	810.53	[12]	835.7 \pm 0.3	773.0 \pm 0.1	
6. methanoic acid	293.15	1220.00	[11]	1397.1 \pm 0.4	1142.6 \pm 0.1	
...	298.15	1214.50	[9]	1371.0 \pm 0.2	1136.8 \pm 0.1	
7. bromomethane	276.65	1721.95	[10]	1400.7 \pm 1.2	1803.5 \pm 0.4	
8. methanamide	298.15	1128.80	[9]	1218.5 \pm 0.1	1122.1 \pm 0.1	1187.2
9. nitromethane	293.15	1137.10	[11]	1231.8 \pm 0.1	1110.5 \pm 0.1	
...	298.15	1130.40	[9]	1226.9 \pm 0.1	1103.4 \pm 0.1	
10. methanol	293.15	791.40	[11]	813.0 \pm 0.2	782.9 \pm 0.0	
...	298.15	787.20	[9]	807.5 \pm 0.2	776.8 \pm 0.1	782.5
11. 1,1,1,2,2-pentachloroethane	293.15	1679.60	[11]	1669.2 \pm 0.2	1681.7 \pm 0.2	
12. 1,1,2,2-tetrachloroethane	293.15	1595.30	[11]	1546.2 \pm 0.2	1559.6 \pm 0.3	
...	298.15	1586.50	[9]	1538.1 \pm 0.6	1550.6 \pm 0.3	
13. 1,1-dichloroethene	293.15	1212.90	[10]	1067.8 \pm 0.5	1186.6 \pm 0.2	
...	298.15	1214.90	[10]	1053.8 \pm 0.4	1176.6 \pm 0.3	
14. 1,1,2-trichloroethane	293.15	1439.70	[11]	1417.4 \pm 0.3	1432.8 \pm 0.4	
...	298.15	1431.40	[9]	1408.8 \pm 0.5	1424.9 \pm 0.3	
15. acetonitrile	293.15	785.70	[11]	731.6 \pm 0.2	762.2 \pm 0.3	
...	298.15	776.00	[9]	729.6 \pm 0.1	755.1 \pm 0.2	774.6
16. 1,2-dibromoethane	298.15	2169.30	[9]	1807.5 \pm 0.9	2336.3 \pm 0.5	
17. 1,1-dichloroethane	293.15	1175.70	[11]	1172.8 \pm 0.6	1175.5 \pm 0.2	1182.2
...	298.15	1168.40	[9]	1163.9 \pm 0.3	1166.6 \pm 0.2	
18. 1,2-dichloroethane	298.15	1246.30	[9]	1235.3 \pm 0.2	1236.8 \pm 0.3	
19. methyl formate	293.15	971.30	[11]	1051.7 \pm 0.1	959.1 \pm 0.1	
...	298.15	967.00	[9]	1045.2 \pm 0.1	952.0 \pm 0.1	

Table S2: Liquid density - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ρ	Ref.	ρ	ρ	ρ
20. bromoethane	293.15	1460.40	[11]	1287.9 ± 0.6	1539.7 ± 0.3	1495.4
...	298.15	1449.30	[13]	1277.5 ± 0.4	1528.5 ± 0.5	
21. chloroethane	273.15	923.90	[11]	898.5 ± 0.3	915.3 ± 0.2	915.6
...	285.45	908.44	[13]	878.1 ± 0.2	893.2 ± 0.2	
22. 2-chloroethanol	293.15	1201.90	[11]	1230.1 ± 0.2	1195.7 ± 0.2	
23. ethanamide	358.15	998.60	[11]	1030.8 ± 0.2	1018.7 ± 0.1	
24. N-methylformamide	292.15	1011.00	[11]	1052.0 ± 0.1	985.6 ± 0.1	
...	298.15	999.50	[9]	1046.9 ± 0.2	979.9 ± 0.1	
25. nitroethane	298.15	1044.10	[9]	1096.3 ± 0.0	1032.6 ± 0.1	
26. methoxymethane	240.00	742.08	[13]	773.0 ± 0.2	741.4 ± 0.1	
27. ethanol	293.15	789.30	[11]	802.4 ± 0.1	801.9 ± 0.1	
...	298.15	784.80	[9]	797.3 ± 0.1	796.3 ± 0.0	796.9
28. 1,2-ethanedithiol	293.15	1234.00	[11]	1173.1 ± 0.1	1161.4 ± 0.2	
...	298.15	1118.87	[13]	1166.5 ± 0.2	1156.2 ± 0.1	
29. methyldisulfanylmethane	293.15	1062.50	[11]	1023.3 ± 0.4	1036.9 ± 0.0	
...	298.15	1057.32	[13]	1014.7 ± 0.2	1030.0 ± 0.2	1042.8
30. methylsulfinylmethane	298.15	1095.80	[9]	1136.2 ± 0.1	1101.3 ± 0.1	1118.5
31. methylsulfanylmethane	293.15	848.30	[11]	811.3 ± 0.3	843.7 ± 0.1	
...	298.15	841.90	[9]	801.9 ± 0.2	837.1 ± 0.1	
32. 2-aminoethanol	293.15	1018.00	[11]	1132.7 ± 0.5	1027.4 ± 0.1	
...	320.00	995.57	[13]	1111.2 ± 0.3	998.5 ± 0.3	
33. ethane-1,2-diamine	293.15	897.90	[11]	1040.6 ± 0.2	987.8 ± 0.2	
...	298.15	889.10	[9]	1035.1 ± 0.2	981.0 ± 0.1	
34. prop-2-enenitrile	298.15	801.10	[9]	775.3 ± 0.2	771.2 ± 0.0	
...	350.45	738.79	[13]	707.1 ± 0.2	712.3 ± 0.1	
35. 1,3-dioxolan-2-one	312.15	1321.40	[11]	1360.1 ± 0.1	1320.7 ± 0.2	
36. propanenitrile	293.15	781.80	[11]	750.1 ± 0.1	760.1 ± 0.1	
...	298.15	776.40	[9]	744.8 ± 0.1	753.6 ± 0.1	
37. 1,2-dibromopropane	293.15	1932.40	[11]	1710.5 ± 0.2	2106.6 ± 0.3	
...	298.15	1924.95	[10]	1701.6 ± 0.5	2096.8 ± 0.3	
38. 1,3-dichloropropane	298.15	1178.50	[11]	1164.5 ± 0.1	1169.2 ± 0.2	
39. (2R)-2-methyloxirane	298.15	830.00	[11]	803.1 ± 0.2	774.7 ± 0.1	

Table S2: Liquid density - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ρ	Ref.	ρ	ρ	ρ
40. propan-2-one	298.15	784.90	[9]	785.6 ± 0.1	800.3 ± 0.2	777.8
41. methyl acetate	293.15	934.20	[11]	971.4 ± 0.1	951.6 ± 0.1	
...	298.15	928.30	[9]	967.6 ± 0.1	945.6 ± 0.1	904.5
42. 1,3-dioxolane	293.15	1060.00	[11]	1122.3 ± 0.1	1053.4 ± 0.3	
...	298.15	1064.40	[9]	1116.5 ± 0.2	1046.3 ± 0.3	1025.1
43. 2-iodopropane	293.15	1704.20	[11]	1607.3 ± 0.3	1848.2 ± 0.2	
...	298.15	1737.25	[10]	1599.4 ± 0.4	1836.4 ± 0.4	
44. 1-bromopropane	293.15	1353.70	[11]	1239.3 ± 0.3	1418.4 ± 0.3	
...	298.15	1345.38	[10]	1229.9 ± 0.2	1408.6 ± 0.1	
45. N,N-dimethylformamide	298.15	943.30	[9]	984.2 ± 0.1	922.2 ± 0.1	
46. N-methylacetamide	320.00	920.52	[12]	968.4 ± 0.1	952.0 ± 0.1	
47. 1-nitropropane	298.15	995.40	[9]	1042.2 ± 0.0	989.7 ± 0.0	
48. 2-nitropropane	298.15	983.30	[9]	1034.2 ± 0.1	995.6 ± 0.0	
49. dimethoxymethane	293.15	859.30	[11]	911.5 ± 0.1	881.4 ± 0.1	
...	298.15	853.56	[10]	905.0 ± 0.1	874.6 ± 0.1	
50. propane-1,2,3-triol	293.15	1261.30	[11]	1310.2 ± 0.7	1259.7 ± 0.7	
...	320.00	1243.57	[10]	1289.5 ± 0.1	1232.3 ± 0.5	
51. propan-1-amine	293.15	717.30	[11]	762.9 ± 0.1	733.4 ± 0.3	
...	298.15	711.47	[10]	757.3 ± 0.1	726.3 ± 0.1	
52. propan-2-amine	293.15	689.10	[11]	773.9 ± 0.2	738.7 ± 0.1	
...	298.15	683.08	[10]	768.3 ± 0.1	731.6 ± 0.2	
53. 2-methylpropane	243.65	613.53	[10]	631.3 ± 0.2	643.5 ± 0.1	626.7
54. ethylsulfanylethane	293.15	836.20	[11]	814.4 ± 0.2	842.5 ± 0.1	
...	298.15	831.20	[9]	808.1 ± 0.1	836.9 ± 0.1	
55. butane-1-thiol	293.15	841.60	[11]	856.0 ± 0.2	865.5 ± 0.1	
...	298.15	837.00	[12]	850.4 ± 0.1	860.3 ± 0.2	
56. butan-1-ol	293.15	809.50	[11]	819.1 ± 0.1	810.5 ± 0.1	
...	298.15	805.70	[9]	815.0 ± 0.2	805.3 ± 0.1	
57. 2-methylpropan-2-ol	320.00	757.94	[10]	803.3 ± 0.4	800.7 ± 0.1	
58. butane-1,4-diol	293.15	1017.10	[11]	1048.5 ± 0.2	1023.9 ± 0.1	
...	298.15	1012.60	[9]	1046.7 ± 0.4	1019.0 ± 0.4	
...	320.00	1000.72	[13]	1030.0 ± 0.4	1001.1 ± 0.2	

Table S2: Liquid density - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ρ	Ref.	ρ	ρ	ρ
59. (2-hydroxyethoxy)ethan-2-ol	288.15	1119.70	[11]	1202.3 ± 0.2	1107.7 ± 0.3	
60. N-ethylethanamine	293.15	705.60	[11]	737.7 ± 0.1	723.8 ± 0.1	
...	298.15	701.90	[9]	731.4 ± 0.2	717.0 ± 0.1	
61. butan-1-amine	293.15	741.40	[11]	779.1 ± 0.1	753.4 ± 0.2	
...	298.15	736.60	[9]	773.8 ± 0.1	747.2 ± 0.1	
62. 2-methylpropan-2-amine	293.15	695.80	[11]	781.9 ± 0.1	767.6 ± 0.2	
...	298.15	690.07	[10]	776.6 ± 0.1	761.2 ± 0.2	
63. 2-(2-hydroxyethylamino)ethanol	320.00	1079.23	[12]	1157.0 ± 0.7	1080.4 ± 0.5	
64. pyrimidine	298.15	1016.40	[9]	1116.0 ± 0.2	1094.5 ± 0.1	1030.9
65. furan	293.15	951.40	[11]	971.7 ± 0.3	964.4 ± 0.3	
...	298.15	931.30	[9]	966.0 ± 0.1	958.2 ± 0.6	862.9
66. thiophene	293.15	1064.90	[11]	1057.8 ± 0.3	1093.2 ± 0.2	
...	298.15	1059.01	[12]	1050.0 ± 0.1	1087.6 ± 0.3	1074.7
67. 1H-pyrrole	293.15	969.80	[11]	1020.1 ± 0.2	990.5 ± 0.2	
...	298.15	965.30	[9]	1015.1 ± 0.3	985.6 ± 0.1	952.2
68. ethenyl acetate	298.15	925.60	[11]	979.0 ± 0.0	970.2 ± 0.1	
69. oxolan-2-one	293.15	1129.60	[11]	1142.7 ± 0.0	1105.9 ± 0.2	
70. acetyl acetate	293.15	1082.00	[11]	1131.1 ± 0.1	1122.7 ± 0.1	
71. 1,4-dichlorobutane	298.15	1133.10	[11]	1125.3 ± 0.1	1128.1 ± 0.1	
72. oxolane	298.15	883.70	[9]	893.8 ± 0.2	858.8 ± 0.1	
73. ethoxyethene	293.15	758.90	[11]	766.7 ± 0.2	775.4 ± 0.1	
74. ethyl acetate	293.15	900.30	[11]	936.7 ± 0.1	927.0 ± 0.1	
...	298.15	894.50	[9]	931.8 ± 0.2	921.4 ± 0.1	886.7
75. tetrahydrothiophene 1,1-dioxide	320.00	1248.99	[12]	1299.3 ± 0.2	1260.0 ± 0.2	
76. thiolane	293.15	998.70	[11]	981.3 ± 0.2	986.8 ± 0.1	
...	298.15	994.00	[9]	975.9 ± 0.2	981.4 ± 0.1	
77. 1-bromobutane	293.15	1275.80	[11]	1187.6 ± 0.2	1325.8 ± 0.2	
...	298.15	1268.70	[9]	1180.5 ± 0.3	1317.9 ± 0.2	
78. 1-chlorobutane	293.15	885.70	[11]	876.8 ± 0.1	884.2 ± 0.0	
...	298.15	880.80	[9]	871.1 ± 0.1	877.7 ± 0.2	
79. pyrrolidine	293.15	858.60	[11]	886.5 ± 0.1	860.9 ± 0.1	
...	298.15	853.80	[9]	881.3 ± 0.1	855.0 ± 0.3	874.8

Table S2: Liquid density - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ρ	Ref.	ρ	ρ	ρ
80. N,N-dimethylacetamide	298.15	936.80	[9]	945.8 ± 0.0	927.1 ± 0.1	
81. morpholine	293.15	1000.50	[11]	1088.0 ± 0.2	1045.6 ± 0.3	
82. pyridine	293.15	981.90	[11]	988.1 ± 0.3	980.6 ± 0.2	
...	298.15	977.80	[9]	982.2 ± 0.4	975.3 ± 0.2	987.6
83. cyclopentanone	293.15	948.70	[11]	940.2 ± 0.1	948.1 ± 0.1	
...	298.15	945.20	[9]	936.6 ± 0.2	942.8 ± 0.1	
84. 1-cyclopropylethanone	293.15	898.40	[11]	906.2 ± 0.1	880.3 ± 0.1	
...	298.15	894.48	[14]	901.1 ± 0.1	875.2 ± 0.1	
85. pentane-2,4-dione	298.15	972.00	[9]	985.7 ± 0.1	1015.9 ± 0.1	
86. methyl 2-methylprop-2-enoate	298.15	937.70	[11]	960.7 ± 0.0	984.3 ± 0.1	
87. pentanenitrile	293.15	800.80	[11]	779.8 ± 0.1	788.9 ± 0.1	
...	298.15	794.40	[9]	775.1 ± 0.1	783.3 ± 0.0	
88. ethyl propanoate	298.15	884.20	[9]	908.2 ± 0.1	908.3 ± 0.1	
89. diethyl carbonate	298.15	969.10	[9]	1020.9 ± 0.1	998.6 ± 0.1	
90. pentan-1-ol	293.15	814.40	[11]	823.7 ± 0.1	816.4 ± 0.1	
...	298.15	812.40	[9]	819.6 ± 0.2	811.7 ± 0.1	
...	320.00	794.74	[10]	802.2 ± 0.1	791.1 ± 0.1	
91. pentan-3-ol	293.15	820.30	[11]	821.0 ± 0.1	825.0 ± 0.1	
...	298.15	815.99	[10]	816.4 ± 0.2	819.3 ± 0.1	
92. 2-methylbutan-2-ol	293.15	809.60	[11]	839.2 ± 0.2	835.6 ± 0.1	
...	298.15	805.00	[9]	834.7 ± 0.2	829.4 ± 0.1	
...	320.00	784.30	[10]	814.1 ± 0.2	804.8 ± 0.2	
93. pentane-1,5-diol	293.15	991.40	[11]	1018.8 ± 0.6	993.6 ± 0.3	
...	298.15	986.20	[9]	1016.2 ± 0.5	990.8 ± 0.5	
94. pentan-3-amine	293.15	748.70	[11]	784.5 ± 0.1	772.4 ± 0.1	
...	298.15	743.67	[12]	779.6 ± 0.1	766.7 ± 0.1	
95. 1,2,3,4-tetrafluorobenzene	298.15	1416.10	[15]	1247.8 ± 0.2	1348.3 ± 0.4	
96. 1,2,3,5-tetrafluorobenzene	298.15	1393.00	[16]	1231.9 ± 0.5	1342.8 ± 0.3	
97. 1,3-difluorobenzene	293.15	1157.20	[11]	1068.5 ± 0.2	1115.6 ± 0.2	
...	298.15	1162.02	[12]	1090.6 ± 0.2	1107.1 ± 0.6	1206.7
98. 1,2-difluorobenzene	293.15	1157.07	[12]	1078.2 ± 0.2	1127.6 ± 0.2	
...	298.15	1150.01	[12]	1099.3 ± 0.4	1119.3 ± 0.4	

Table S2: Liquid density - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ρ	Ref.	ρ	ρ	ρ
99. fluorobenzene	293.15	1022.50	[11]	977.3 ± 0.5	1021.4 ± 0.1	
...	298.15	1019.10	[9]	989.6 ± 0.3	1015.0 ± 0.1	1029.6
100. nitrobenzene	293.15	1203.70	[11]	1238.0 ± 0.2	1179.4 ± 0.2	
...	298.15	1198.70	[9]	1233.1 ± 0.2	1174.4 ± 0.2	1155.0
101. 2-chloroaniline	293.15	1210.00	[11]	1239.2 ± 0.2	1228.8 ± 0.1	
102. phenol	318.15	1054.50	[11]	1051.5 ± 0.2	1057.0 ± 0.2	
103. benzenethiol	293.15	1077.50	[11]	1067.7 ± 0.3	1056.8 ± 0.3	
...	298.15	1073.01	[12]	1061.4 ± 0.2	1051.1 ± 0.2	
104. 2-methylpyridine	293.15	944.30	[11]	946.5 ± 0.2	952.9 ± 0.1	
...	298.15	939.80	[9]	941.5 ± 0.2	948.0 ± 0.2	
105. 3-methylpyridine	293.15	956.60	[11]	949.2 ± 0.1	957.0 ± 0.1	
...	298.15	953.30	[9]	944.2 ± 0.2	952.1 ± 0.1	942.9
106. 4-methylpyridine	293.15	954.80	[11]	951.3 ± 0.1	952.9 ± 0.2	
...	298.15	950.30	[9]	950.3 ± 0.2	948.4 ± 0.1	954.6
107. cyclohexanone	293.15	947.80	[11]	941.4 ± 0.1	953.1 ± 0.2	
...	298.15	941.90	[9]	936.8 ± 0.1	947.9 ± 0.2	
108. (E)-hex-2-ene	293.15	678.50	[11]	660.3 ± 0.1	682.0 ± 0.1	668.7
109. hexan-2-one	298.15	807.00	[10]	803.4 ± 0.0	821.5 ± 0.1	
110. 2,4,6-trimethyl-1,3,5-trioxane	293.15	994.30	[11]	1095.7 ± 0.3	1094.8 ± 0.7	
111. cyclohexanamine	298.15	863.00	[12]	921.1 ± 0.5	898.0 ± 0.2	
112. 2-propan-2-yloxypropane	298.15	718.10	[9]	762.7 ± 0.1	748.2 ± 0.1	
113. 1-methoxy-2-(2-methoxyethoxy)ethane	293.15	943.40	[11]	1014.4 ± 0.1	960.3 ± 0.1	
...	298.15	938.30	[9]	1009.1 ± 0.2	954.5 ± 0.1	
114. triethyl phosphate	293.15	1069.50	[11]	1125.2 ± 0.3	1087.1 ± 0.1	
...	298.15	1069.60	[9]	1120.6 ± 0.1	1082.1 ± 0.3	
...	320.00	1057.30	[12]	1099.0 ± 0.2	1058.3 ± 0.1	
115. N,N-diethylethanamine	293.15	727.50	[11]	758.0 ± 0.1	749.5 ± 0.1	
...	298.15	722.80	[9]	753.1 ± 0.1	744.1 ± 0.1	
116. N-propan-2-ylpropan-2-amine	293.15	715.30	[11]	767.2 ± 0.1	756.4 ± 0.1	
...	298.15	712.27	[10]	762.3 ± 0.1	751.0 ± 0.1	
117. trifluoromethylbenzene	293.15	1188.40	[11]	1179.4 ± 0.1	1198.3 ± 0.2	
...	298.15	1177.98	[12]	1171.9 ± 0.3	1191.0 ± 0.1	

Table S2: Liquid density - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ρ	Ref.	ρ	ρ	ρ
118. benzonitrile	288.15	1009.30	[11]	989.3 ± 0.2	1014.1 ± 0.0	
119. benzaldehyde	298.15	1043.60	[9]	1036.9 ± 0.2	1031.4 ± 0.1	1018.6
120. toluene	298.15	861.90	[9]	851.2 ± 0.1	872.0 ± 0.1	845.3
121. methoxybenzene	293.15	994.00	[11]	994.1 ± 0.1	986.0 ± 0.1	
...	298.15	989.40	[9]	991.9 ± 0.1	980.7 ± 0.1	945.1
122. phenylmethanol	297.15	1041.90	[11]	1045.2 ± 0.1	1041.5 ± 0.2	
123. 2-methylphenol	308.15	1032.70	[11]	1040.4 ± 0.1	1039.4 ± 0.2	
124. 3-methylphenol	320.00	1012.38	[10]	1020.4 ± 0.2	1022.2 ± 0.1	
125. 4-methylphenol	313.15	1018.50	[11]	1005.4 ± 0.2	1027.1 ± 0.0	986.6
...	320.00	1012.87	[10]	998.9 ± 0.1	1021.3 ± 0.1	
126. diethyl propanedioate	293.15	1055.10	[11]	1097.8 ± 0.2	1086.4 ± 0.1	
127. 2,4-dimethylpentan-3-one	293.15	810.80	[11]	819.2 ± 0.1	832.8 ± 0.1	
...	298.15	799.93	[10]	816.6 ± 0.0	828.1 ± 0.1	
128. heptan-2-one	293.15	811.10	[11]	813.1 ± 0.1	830.3 ± 0.1	
...	298.15	811.00	[9]	809.4 ± 0.1	825.5 ± 0.1	
129. ethenylbenzene	298.15	901.00	[9]	892.2 ± 0.1	912.1 ± 0.1	
130. 1-phenylethanone	293.15	1028.10	[11]	1026.5 ± 0.1	1030.6 ± 0.1	
...	298.15	1023.40	[9]	1021.5 ± 0.1	1026.0 ± 0.1	
131. methyl benzoate	298.15	1084.00	[9]	1111.3 ± 0.1	1096.8 ± 0.1	
132. methyl 2-hydroxybenzoate	298.15	1181.00	[11]	1222.1 ± 0.4	1200.2 ± 0.2	
...	320.00	1155.59	[12]	1192.7 ± 0.2	1179.5 ± 0.1	
133. ethylbenzene	298.15	862.50	[9]	853.1 ± 0.1	870.0 ± 0.0	847.6
134. 1,2-dimethylbenzene	293.15	879.95	[10]	862.2 ± 0.1	889.0 ± 0.1	860.0
...	298.15	876.00	[9]	857.1 ± 0.1	884.4 ± 0.1	
135. 1,2-dimethoxybenzene	298.15	1082.00	[9]	1075.0 ± 0.0	1057.0 ± 0.1	
136. 2,4,6-trimethylpyridine	295.15	916.60	[11]	908.1 ± 0.1	929.5 ± 0.1	
...	298.15	910.40	[9]	910.2 ± 0.2	926.7 ± 0.1	
137. octan-1-ol	298.15	822.20	[9]	834.2 ± 0.2	888.3 ± 0.1	
...	320.00	806.39	[10]	816.2 ± 0.2	865.3 ± 1.0	
138. 1-butoxybutane	293.15	768.40	[11]	776.5 ± 0.1	773.0 ± 0.1	
...	298.15	764.30	[9]	772.0 ± 0.1	767.8 ± 0.1	
139. N-butylbutan-1-amine	293.15	767.00	[11]	775.3 ± 0.1	774.6 ± 0.1	
...	298.15	757.60	[9]	771.1 ± 0.0	769.6 ± 0.1	

Table S2: Liquid density - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ρ	Ref.	ρ	ρ	ρ
140. isoquinoline	303.15	1091.00	[11]	1105.0 ± 0.2	1124.4 ± 0.2	
...	320.00	1078.37	[12]	1071.8 ± 0.2	1099.9 ± 0.5	
141. quinoline	288.15	1097.70	[11]	1097.2 ± 0.1	1086.4 ± 0.2	
...	298.15	1090.00	[9]	1088.5 ± 0.2	1077.7 ± 0.2	1072.4
142. (1-methylethyl)benzene	298.15	857.30	[9]	856.2 ± 0.1	873.9 ± 0.1	845.7
143. 1,2,4-trimethylbenzene	293.15	875.91	[12]	859.2 ± 0.2	888.8 ± 0.1	864.0
...	298.15	872.00	[12]	854.6 ± 0.1	884.4 ± 0.1	
144. 2,6-dimethylheptan-4-one	293.15	806.20	[11]	823.6 ± 0.1	840.7 ± 0.1	
...	298.15	802.43	[10]	819.3 ± 0.0	836.1 ± 0.1	
145. 1-chloronaphthalene	298.15	1188.00	[11]	1191.0 ± 0.1	1171.7 ± 0.1	
146. phenoxybenzene	303.15	1066.10	[11]	1073.0 ± 0.1	1082.1 ± 0.2	

Table S3: Heat of vaporization ΔH_{vap} (kJ/mol) calculated and experimental. Blue font indicates that the calculated value differs more than 10% from the experimental ones, a red font indicates that it differs by more than 25%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ΔH_{vap}	Ref.	ΔH_{vap}	ΔH_{vap}	ΔH_{vap}
1. chloroform	298.15	31.28	[9]	28.42 \pm 0.01	29.20 \pm 0.01	
2. dichloro(fluoro)methane	282.05	24.95	[13]	23.86 \pm 0.02	21.92 \pm 0.01	
3. dibromomethane	293.15	37.67	[13]	29.05 \pm 0.02	34.41 \pm 0.03	
...	298.15	37.45	[9]	28.55 \pm 0.01	34.17 \pm 0.02	
4. dichloromethane	293.15	29.50	[13]	27.02 \pm 0.03	23.84 \pm 0.02	
...	298.15	28.82	[9]	26.48 \pm 0.01	23.36 \pm 0.03	
5. methanal	253.15	23.10	[13]	24.85 \pm 0.02	24.11 \pm 0.01	
...	253.65	23.08	[13]	24.79 \pm 0.01	24.08 \pm 0.01	
6. methanoic acid	293.15	19.82	[13]	68.74 \pm 0.05	42.79 \pm 0.02	
...	298.15	19.90	[9]	65.46 \pm 0.02	42.48 \pm 0.01	
8. methanamide	298.15	60.57	[9]	62.15 \pm 0.01	59.76 \pm 0.01	
9. nitromethane	293.15	38.39	[13]	55.62 \pm 0.03	43.06 \pm 0.06	
...	298.15	38.62	[9]	55.31 \pm 0.01	38.07 \pm 0.01	
10. methanol	293.15	37.94	[13]	39.92 \pm 0.03	36.89 \pm 0.02	
...	298.15	37.43	[9]	39.62 \pm 0.02	36.44 \pm 0.01	36.86
11. 1,1,1,2,2-pentachloroethane	293.15	46.29	[13]	46.74 \pm 0.02	47.53 \pm 0.02	
12. 1,1,2,2-tetrachloroethane	293.15	44.84	[13]	41.77 \pm 0.05	43.31 \pm 0.06	
...	298.15	45.71	[9]	41.62 \pm 0.05	42.94 \pm 0.04	
13. 1,1-dichloroethene	293.15	26.75	[13]	23.13 \pm 0.03	27.05 \pm 0.03	
...	298.15	26.48	[13]	22.87 \pm 0.02	26.85 \pm 0.01	
14. 1,1,2-trichloroethane	293.15	39.52	[13]	39.61 \pm 0.05	39.81 \pm 0.21	
...	298.15	40.28	[9]	39.22 \pm 0.05	39.64 \pm 0.09	
15. acetonitrile	293.15	33.28	[13]	32.76 \pm 0.03	30.65 \pm 0.03	
...	298.15	33.23	[9]	32.60 \pm 0.01	30.42 \pm 0.02	
16. 1,2-dibromoethane	298.15	41.73	[9]	34.71 \pm 0.04	48.83 \pm 0.08	
17. 1,1-dichloroethane	293.15	31.09	[13]	32.00 \pm 0.02	28.53 \pm 0.03	
...	298.15	30.62	[9]	31.73 \pm 0.03	28.29 \pm 0.01	30.59
18. 1,2-dichloroethane	298.15	35.16	[9]	36.99 \pm 0.02	35.08 \pm 0.05	
19. methyl formate	293.15	28.85	[13]	38.68 \pm 0.02	29.67 \pm 0.03	
...	298.15	30.59	[9]	38.29 \pm 0.01	29.36 \pm 0.02	

Table S3: Heat of vaporization - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ΔH_{vap}	Ref.	ΔH_{vap}	ΔH_{vap}	ΔH_{vap}
20. bromoethane	293.15	27.87	[13]	25.36 ± 0.03	29.85 ± 0.03	
...	298.15	27.62	[13]	25.15 ± 0.02	29.65 ± 0.01	
21. chloroethane	273.15	25.39	[13]	24.86 ± 0.02	24.27 ± 0.01	
...	285.45	24.85	[13]	24.28 ± 0.01	23.67 ± 0.02	
22. 2-chloroethanol	293.15	46.02	[13]	55.03 ± 0.04	48.65 ± 0.11	
23. ethanamide	358.15	62.06	[13]	65.11 ± 0.02	64.67 ± 0.02	
24. N-methylformamide	292.15	57.79	[13]	57.25 ± 0.03	50.52 ± 0.02	
...	298.15	56.25	[9]	56.76 ± 0.02	49.85 ± 0.02	
25. nitroethane	298.15	40.24	[9]	55.23 ± 0.01	41.08 ± 0.01	
26. methoxymethane	240.00	21.72	[13]	24.12 ± 0.02	30.87 ± 0.03	
27. ethanol	293.15	42.85	[13]	46.03 ± 0.04	42.79 ± 0.03	
...	298.15	42.32	[9]	44.62 ± 0.02	42.32 ± 0.02	42.59
28. 1,2-ethanedithiol	293.15	44.37	[13]	41.95 ± 0.02	47.04 ± 0.04	
...	298.15	44.15	[13]	41.66 ± 0.04	46.75 ± 0.01	
29. methylsulfanylmethane	293.15	38.56	[13]	33.08 ± 0.03	37.87 ± 0.04	
...	298.15	38.32	[13]	32.75 ± 0.02	37.52 ± 0.02	35.35
30. methylsulfinylmethane	298.15	52.89	[9]	57.50 ± 0.02	55.62 ± 0.02	
31. methylsulfanylmethane	293.15	28.06	[13]	26.03 ± 0.04	30.59 ± 0.03	
...	298.15	27.65	[9]	23.88 ± 0.02	29.65 ± 0.02	
32. 2-aminoethanol	293.15	64.03	[13]	82.46 ± 0.05	55.17 ± 0.12	
...	320.00	61.71	[13]	79.96 ± 0.05	53.17 ± 0.19	
33. ethane-1,2-diamine	293.15	45.46	[13]	58.51 ± 0.09	50.58 ± 0.40	
...	298.15	46.60	[9]	57.95 ± 0.08	49.79 ± 0.22	
34. prop-2-enenitrile	298.15	33.26	[9]	33.33 ± 0.01	31.47 ± 0.02	
...	350.45	31.71	[13]	30.64 ± 0.01	29.03 ± 0.02	
35. 1,3-dioxolan-2-one	312.15	60.96	[13]	75.55 ± 0.02	64.90 ± 0.02	
36. propanenitrile	293.15	36.31	[13]	36.64 ± 0.04	33.89 ± 0.02	
...	298.15	36.03	[9]	36.29 ± 0.02	33.57 ± 0.03	
37. 1,2-dibromopropane	293.15	48.36	[12]	40.51 ± 0.15	51.03 ± 0.16	
...	298.15	42.20	[17]	40.24 ± 0.04	50.99 ± 0.12	
38. 1,3-dichloropropane	298.15	40.05	[13]	41.97 ± 0.05	40.08 ± 0.06	
39. (2R)-2-methyloxirane	298.15	27.90	[17]	27.87 ± 0.02	26.93 ± 0.01	

Table S3: Heat of vaporization - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ΔH_{vap}	Ref.	ΔH_{vap}	ΔH_{vap}	ΔH_{vap}
40. propan-2-one	298.15	30.99	[9]	34.47 ± 0.02	30.76 ± 0.02	30.63
41. methyl acetate	293.15	32.67	[13]	41.57 ± 0.06	38.05 ± 0.04	
...	298.15	32.29	[9]	41.20 ± 0.02	36.34 ± 0.01	32.38
42. 1,3-dioxolane	293.15	35.80	[17]	43.45 ± 0.01	36.49 ± 0.02	
...	298.15	35.60	[9]	43.18 ± 0.03	36.22 ± 0.04	
43. 2-iodopropane	293.15	34.40	[13]	34.08 ± 0.03	34.26 ± 0.03	
...	298.15	34.20	[13]	33.71 ± 0.02	33.85 ± 0.02	
44. 1-bromopropane	293.15	32.49	[13]	31.98 ± 0.05	35.35 ± 0.04	
...	298.15	32.20	[13]	31.41 ± 0.02	34.83 ± 0.02	
45. N,N-dimethylformamide	298.15	47.57	[9]	52.57 ± 0.02	46.08 ± 0.02	
46. N-methylacetamide	320.00	58.32	[13]	59.68 ± 0.07	55.12 ± 0.08	
47. 1-nitropropane	298.15	43.39	[9]	59.32 ± 0.04	44.97 ± 0.01	
48. 2-nitropropane	298.15	41.34	[9]	56.44 ± 0.02	43.74 ± 0.01	
49. dimethoxymethane	293.15	29.87	[13]	34.92 ± 0.07	32.63 ± 0.07	
...	298.15	29.54	[13]	34.47 ± 0.02	32.23 ± 0.04	
50. propane-1,2,3-triol	293.15	90.21	[13]	99.60 ± 0.06	95.44 ± 0.29	
51. propan-1-amine	293.15	31.29	[13]	39.07 ± 0.05	33.83 ± 0.12	
...	298.15	30.98	[13]	38.36 ± 0.03	33.08 ± 0.04	
52. propan-2-amine	293.15	28.92	[13]	41.27 ± 0.08	34.23 ± 0.06	
...	298.15	28.56	[13]	40.67 ± 0.03	32.70 ± 0.02	
53. 2-methylpropane	243.65	22.35	[13]	25.03 ± 0.02	24.61 ± 0.01	
54. ethylsulfanylethane	293.15	35.89	[13]	35.03 ± 0.07	39.54 ± 0.06	
...	298.15	35.77	[9]	34.55 ± 0.02	39.05 ± 0.03	
55. butane-1-thiol	293.15	37.40	[12]	38.50 ± 0.06	40.94 ± 0.06	
...	298.15	37.14	[12]	38.01 ± 0.04	38.81 ± 0.06	
56. butan-1-ol	293.15	54.04	[13]	60.52 ± 0.11	52.12 ± 0.03	
...	298.15	52.35	[9]	60.08 ± 0.08	51.39 ± 0.05	
57. 2-methylpropan-2-ol	320.00	44.01	[13]	57.28 ± 0.08	47.20 ± 0.07	
58. butane-1,4-diol	293.15	76.71	[13]	90.32 ± 0.22	81.48 ± 0.42	
...	298.15	76.60	[9]	87.23 ± 0.31	81.43 ± 0.24	
...	320.00	75.32	[13]	92.18 ± 1.57	78.62 ± 0.14	
59. (2-hydroxyethoxy)ethan-2-ol	288.15	83.13	[13]	103.66 ± 0.06	78.15 ± 0.19	

Table S3: Heat of vaporization - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ΔH_{vap}	Ref.	ΔH_{vap}	ΔH_{vap}	ΔH_{vap}
60. N-ethylethanamine	293.15	31.54	[13]	37.64 ± 0.12	34.12 ± 0.10	
...	298.15	31.32	[9]	36.96 ± 0.05	33.34 ± 0.07	
61. butan-1-amine	293.15	35.89	[13]	46.59 ± 0.06	39.15 ± 0.08	
...	298.15	35.74	[9]	45.83 ± 0.09	38.53 ± 0.08	
62. 2-methylpropan-2-amine	293.15	29.09	[13]	46.33 ± 0.04	37.24 ± 0.06	
...	298.15	28.80	[13]	45.68 ± 0.03	36.68 ± 0.03	
63. 2-(2-hydroxyethylamino)ethanol	320.00	83.64	[13]	110.71 ± 0.14	88.94 ± 0.30	
64. pyrimidine	298.15	49.81	[9]	50.47 ± 0.02	49.33 ± 0.02	51.09
65. furan	293.15	27.83	[13]	30.65 ± 0.04	30.12 ± 0.04	
...	298.15	27.46	[9]	30.33 ± 0.02	29.81 ± 0.02	23.60
66. thiophene	293.15	34.89	[13]	34.26 ± 0.04	39.51 ± 0.04	
...	298.15	34.65	[13]	32.72 ± 0.01	39.15 ± 0.02	35.40
67. 1H-pyrrole	293.15	45.70	[13]	52.93 ± 0.04	44.54 ± 0.04	
...	298.15	45.15	[9]	52.51 ± 0.03	44.14 ± 0.02	
68. ethenyl acetate	298.15	34.58	[13]	43.40 ± 0.01	44.07 ± 0.02	
69. oxolan-2-one	293.15	52.84	[12]	64.60 ± 0.02	53.12 ± 0.03	
70. acetyl acetate	293.15	47.32	[13]	68.65 ± 0.04	61.27 ± 0.03	
71. 1,4-dichlorobutane	298.15	46.00	[13]	48.84 ± 0.14	46.92 ± 0.04	
72. oxolane	298.15	31.80	[9]	37.14 ± 0.02	32.14 ± 0.02	
73. ethoxyethene	293.15	27.84	[13]	31.93 ± 0.02	31.51 ± 0.03	
74. ethyl acetate	293.15	35.96	[13]	46.32 ± 0.05	42.40 ± 0.06	
...	298.15	35.59	[9]	45.81 ± 0.04	41.91 ± 0.02	35.10
75. tetrahydrothiophene 1,1-dioxide	320.00	66.59	[13]	86.42 ± 0.07	72.33 ± 0.06	
76. thiolane	293.15	39.74	[13]	39.05 ± 0.05	42.93 ± 0.08	
...	298.15	38.62	[9]	38.85 ± 0.02	41.12 ± 0.02	
77. 1-bromobutane	293.15	37.12	[13]	39.92 ± 0.06	40.51 ± 0.05	
...	298.15	36.60	[9]	36.91 ± 0.03	40.05 ± 0.03	
78. 1-chlorobutane	293.15	34.23	[12]	37.73 ± 0.03	37.41 ± 0.05	
...	298.15	33.52	[9]	35.63 ± 0.03	33.77 ± 0.05	
79. pyrrolidine	293.15	37.58	[13]	42.68 ± 0.05	40.94 ± 0.04	
...	298.15	37.57	[9]	42.13 ± 0.02	38.28 ± 0.06	
80. N,N-dimethylacetamide	298.15	50.23	[9]	53.55 ± 0.02	51.82 ± 0.02	

Table S3: Heat of vaporization - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ΔH_{vap}	Ref.	ΔH_{vap}	ΔH_{vap}	ΔH_{vap}
81. morpholine	293.15	45.32	[13]	59.56 ± 0.39	54.13 ± 0.36	
82. pyridine	293.15	40.34	[13]	41.70 ± 0.06	41.72 ± 0.07	
...	298.15	40.15	[9]	41.27 ± 0.03	41.34 ± 0.03	41.97
83. cyclopentanone	293.15	42.38	[13]	48.54 ± 0.07	43.45 ± 0.04	
...	298.15	42.63	[9]	48.17 ± 0.02	42.89 ± 0.02	
84. 1-cyclopropylethanone	293.15			46.09 ± 0.03	44.37 ± 0.04	
...	298.15	39.40	[17]	45.66 ± 0.02	44.04 ± 0.02	
85. pentane-2,4-dione	298.15	41.80	[9]	60.19 ± 0.02	56.39 ± 0.02	
86. methyl 2-methylprop-2-enoate	298.15	39.13	[13]	46.34 ± 0.02	54.73 ± 0.16	
87. pentanenitrile	293.15	44.33	[13]	46.82 ± 0.04	43.13 ± 0.06	
...	298.15	44.08	[9]	46.25 ± 0.03	42.65 ± 0.05	
88. ethyl propanoate	298.15	39.25	[9]	49.58 ± 0.04	46.45 ± 0.03	
89. diethyl carbonate	298.15	41.10	[9]	60.79 ± 0.08	52.66 ± 0.04	
90. pentan-1-ol	293.15	57.64	[13]	65.96 ± 0.12	57.47 ± 0.08	
...	298.15	57.02	[9]	65.43 ± 0.11	56.79 ± 0.08	
...	320.00	54.67	[13]	63.52 ± 0.09	54.33 ± 0.08	
91. pentan-3-ol	293.15	52.82	[13]	58.83 ± 0.14	63.78 ± 0.10	
...	298.15	52.37	[13]	57.79 ± 0.12	53.65 ± 0.16	
92. 2-methylbutan-2-ol	293.15	50.19	[13]	67.55 ± 0.07	51.39 ± 0.27	
...	298.15	50.20	[9]	66.93 ± 0.04	50.64 ± 0.19	
...	320.00	47.17	[13]	64.86 ± 0.08	47.75 ± 0.17	
93. pentane-1,5-diol	293.15	76.36	[13]	101.55 ± 0.22	90.02 ± 0.08	
...	298.15	82.40	[9]	101.08 ± 0.31	89.14 ± 0.14	
94. pentan-3-amine	293.15	39.97	[12]	47.54 ± 0.12	41.05 ± 0.24	
...	298.15	39.64	[12]	46.96 ± 0.10	40.45 ± 0.22	
95. 1,2,3,4-tetrafluorobenzene	298.15	36.61	[18]	35.45 ± 0.02	36.85 ± 0.03	
96. 1,2,3,5-tetrafluorobenzene	298.15	35.40	[18]	33.81 ± 0.02	37.10 ± 0.04	
97. 1,3-difluorobenzene	293.15	36.85	[12]	33.31 ± 0.03	34.84 ± 0.04	
...	298.15	36.58	[12]	33.78 ± 0.02	34.03 ± 0.03	42.76
98. 1,2-difluorobenzene	293.15	36.37	[12]	34.05 ± 0.03	35.27 ± 0.03	
...	298.15	36.11	[12]	35.24 ± 0.03	35.59 ± 0.03	
99. fluorobenzene	293.15	34.79	[13]	33.46 ± 0.08	34.45 ± 0.03	
...	298.15	34.58	[9]	33.87 ± 0.02	34.37 ± 0.01	37.03

Table S3: Heat of vaporization - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ΔH_{vap}	Ref.	ΔH_{vap}	ΔH_{vap}	ΔH_{vap}
100. nitrobenzene	293.15	55.25	[13]	70.34 ± 0.04	55.09 ± 0.06	
...	298.15	55.01	[9]	70.79 ± 0.03	55.40 ± 0.02	54.73
101. 2-chloroaniline	293.15	57.60	[13]	56.13 ± 0.03	57.28 ± 0.02	
102. phenol	318.15	56.32	[13]	53.16 ± 0.03	61.26 ± 0.05	
103. benzenethiol	293.15	48.75	[13]	43.85 ± 0.05	41.43 ± 0.05	
...	298.15	48.47	[13]	43.75 ± 0.02	41.11 ± 0.02	
104. 2-methylpyridine	293.15	42.62	[13]	45.34 ± 0.03	46.07 ± 0.05	
...	298.15	42.92	[9]	44.87 ± 0.02	45.90 ± 0.02	
105. 3-methylpyridine	293.15	44.47	[13]	45.70 ± 0.02	47.37 ± 0.05	
...	298.15	45.23	[9]	45.59 ± 0.03	47.14 ± 0.01	42.80
106. 4-methylpyridine	293.15	44.61	[13]	46.42 ± 0.04	46.70 ± 0.07	
...	298.15	44.81	[9]	46.06 ± 0.02	46.40 ± 0.02	44.60
107. cyclohexanone	293.15	45.42	[13]	52.48 ± 0.10	54.76 ± 0.41	
...	298.15	45.13	[9]	52.10 ± 0.04	47.61 ± 0.03	
108. (E)-hex-2-ene	293.15	32.20	[11]	32.14 ± 0.04	33.62 ± 0.07	31.88
109. hexan-2-one	298.15	42.90	[13]	48.63 ± 0.04	46.44 ± 0.04	
110. 2,4,6-trimethyl-1,3,5-trioxane	293.15	44.96	[13]	76.61 ± 0.04	74.17 ± 0.14	
111. cyclohexanamine	298.15	43.23	[13]	61.77 ± 0.08	50.02 ± 0.03	
112. 2-propan-2-yloxypropane	298.15	32.60	[9]	42.90 ± 0.05	36.69 ± 0.03	
113. 1-methoxy-2-(2-methoxyethoxy)ethane	293.15	52.61	[13]	73.12 ± 0.05	63.02 ± 0.09	
...	298.15	43.15	[9]	72.34 ± 0.11	62.23 ± 0.05	
114. triethyl phosphate	293.15	57.56	[13]	86.80 ± 0.07	78.29 ± 0.08	
...	298.15	57.30	[9]	86.07 ± 0.06	77.69 ± 0.08	
...	320.00	56.27	[13]	83.39 ± 0.08	75.07 ± 0.07	
115. N,N-diethylethanamine	293.15	34.87	[13]	44.09 ± 0.23	38.47 ± 0.33	
...	298.15	34.88	[9]	42.25 ± 0.05	38.16 ± 0.29	
116. N-propan-2-ylpropan-2-amine	293.15	34.98	[13]	45.03 ± 0.06	39.86 ± 0.05	
...	298.15	34.65	[13]	44.51 ± 0.02	39.44 ± 0.06	
117. trifluoromethylbenzene	293.15	38.02	[13]	41.51 ± 0.04	38.61 ± 0.07	
...	298.15	37.73	[13]	41.92 ± 0.02	38.88 ± 0.01	
118. benzonitrile	288.15	52.14	[13]	53.52 ± 0.03	54.09 ± 0.02	
119. benzaldehyde	298.15	39.60	[9]	52.83 ± 0.02	54.47 ± 0.02	47.03

Table S3: Heat of vaporization - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ΔH_{vap}	Ref.	ΔH_{vap}	ΔH_{vap}	ΔH_{vap}
120. toluene	298.15	37.99	[9]	37.39 ± 0.02	40.02 ± 0.02	36.19
121. methoxybenzene	293.15	46.86	[13]	48.86 ± 0.03	47.52 ± 0.04	
...	298.15	45.00	[9]	48.89 ± 0.02	47.53 ± 0.02	41.63
122. phenylmethanol	297.15	65.59	[13]	62.62 ± 0.02	62.16 ± 0.05	
123. 2-methylphenol	308.15	56.90	[13]	63.66 ± 0.04	63.93 ± 0.03	
124. 3-methylphenol	320.00	60.91	[13]	65.20 ± 0.05	66.28 ± 0.07	
125. 4-methylphenol	313.15	63.23	[13]	57.23 ± 0.03	67.37 ± 0.04	
...	320.00	62.67	[13]	56.17 ± 0.04	66.15 ± 0.04	
126. diethyl propanedioate	293.15	57.26	[13]	83.55 ± 0.09	75.40 ± 0.03	
127. 2,4-dimethylpentan-3-one	293.15	40.71	[13]	56.17 ± 0.10	50.04 ± 0.06	
...	298.15	40.50	[13]	56.03 ± 0.07	49.73 ± 0.03	
128. heptan-2-one	293.15	47.37	[13]	55.11 ± 0.09	52.16 ± 0.08	
...	298.15	47.24	[9]	54.72 ± 0.10	51.74 ± 0.05	
129. ethenylbenzene	298.15	43.93	[9]	42.43 ± 0.01	45.02 ± 0.03	
130. 1-phenylethanone	293.15	54.54	[13]	58.76 ± 0.04	61.68 ± 0.08	
...	298.15	53.40	[9]	59.11 ± 0.02	61.62 ± 0.02	
131. methyl benzoate	298.15	55.57	[9]	64.21 ± 0.02	62.22 ± 0.02	
132. methyl 2-hydroxybenzoate	298.15	61.04	[13]	71.92 ± 0.07	71.44 ± 0.27	
133. ethylbenzene	298.15	42.25	[9]	42.36 ± 0.02	44.48 ± 0.02	37.49
134. 1,2-dimethylbenzene	293.15	43.73	[13]	42.40 ± 0.06	46.08 ± 0.06	
...	298.15	43.43	[9]	42.77 ± 0.02	46.45 ± 0.02	41.00
135. 1,2-dimethoxybenzene	298.15	48.38	[9]	64.77 ± 0.01	63.53 ± 0.02	
136. 2,4,6-trimethylpyridine	295.15	49.31	[13]	55.78 ± 0.03	56.74 ± 0.07	
...	298.15	50.34	[9]	54.66 ± 0.03	56.80 ± 0.02	
137. octan-1-ol	298.15	72.00	[9]	85.16 ± 0.11	86.24 ± 0.09	
...	320.00	69.53	[13]	82.02 ± 0.13	82.58 ± 0.25	
138. 1-butoxybutane	293.15	45.48	[13]	53.93 ± 0.08	50.87 ± 0.10	
...	298.15	44.40	[9]	53.39 ± 0.07	50.20 ± 0.04	
139. N-butylbutan-1-amine	293.15	49.81	[13]	58.97 ± 0.12	55.64 ± 0.12	
...	298.15	49.44	[9]	58.56 ± 0.20	55.05 ± 0.12	
140. isoquinoline	303.15	59.43	[13]	62.63 ± 0.03	74.94 ± 0.05	
...	320.00	58.61	[13]	59.23 ± 0.04	70.91 ± 0.10	

Table S3: Heat of vaporization - continued

Name	Experiment			GAFF	OPLS/AA	CGenFF
	T	ΔH_{vap}	Ref.	ΔH_{vap}	ΔH_{vap}	ΔH_{vap}
141. quinoline	288.15	59.51	[13]	61.13 ± 0.06	60.40 ± 0.05	
...	298.15	64.10	[9]	61.37 ± 0.03	61.05 ± 0.03	57.57
142. (1-methylethyl)benzene	298.15	45.14	[9]	46.90 ± 0.02	48.71 ± 0.02	41.80
143. 1,2,4-trimethylbenzene	293.15	47.81	[13]	47.39 ± 0.03	51.84 ± 0.05	
...	298.15	47.57	[13]	47.04 ± 0.03	51.45 ± 0.04	45.19
144. 2,6-dimethylheptan-4-one	293.15	50.83	[13]	58.68 ± 0.15	59.85 ± 0.16	
...	298.15	50.51	[13]	58.14 ± 0.08	59.43 ± 0.12	
145. 1-chloronaphthalene	298.15	64.66	[13]	61.67 ± 0.02	61.67 ± 0.03	
146. phenoxybenzene	303.15	58.42	[13]	69.65 ± 0.03	72.70 ± 0.04	

Table S4: Surface tension γ (10^{-3}Nm^{-1}) calculated and experimental. Blue font indicates that the calculated value differs more than 10% from the experimental ones, a red font indicates that it differs by more than 25%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA
	T	γ	Ref.	γ	γ
1. chloroform	298.15	26.67	[11]	11.7 \pm 0.5	11.8 \pm 0.3
2. dichloro(fluoro)methane	282.05	20.09	[12]	11.8 \pm 0.3	7.9 \pm 0.2
...	300.00	17.60	[14]	9.8 \pm 0.6	7.2 \pm 0.3
3. dibromomethane	298.15	39.05	[11]	13.3 \pm 0.5	25.1 \pm 0.4
4. dichloromethane	298.15	27.20	[11]	15.7 \pm 0.4	10.5 \pm 0.4
5. methanal	253.15	26.01	[12]	23.0 \pm 0.2	22.5 \pm 0.2
...	253.65	25.91	[12]	23.0 \pm 0.2	22.6 \pm 0.4
6. methanoic acid	298.15	37.13	[11]	66.9 \pm 4.4	32.0 \pm 0.4
7. bromomethane	276.65	27.18	[12]	8.7 \pm 0.5	21.1 \pm 0.1
8. methanamide	298.15	57.03	[11]	58.4 \pm 2.3	53.1 \pm 1.1
9. nitromethane	298.15	36.53	[11]	55.2 \pm 0.6	29.2 \pm 0.4
10. methanol	298.15	22.07	[11]	20.6 \pm 0.7	20.1 \pm 0.4
12. 1,1,2,2-tetrachloroethane	298.15	35.58	[11]	22.1 \pm 0.8	24.5 \pm 0.7
13. 1,1-dichloroethene	298.15	21.66	[12]	9.8 \pm 0.4	15.7 \pm 0.5
14. 1,1,2-trichloroethane	298.15	34.02	[11]	23.1 \pm 0.6	25.0 \pm 0.4
15. acetonitrile	298.15	28.66	[11]	21.6 \pm 0.3	16.6 \pm 0.3
16. 1,2-dibromoethane	298.15	39.55	[11]	17.9 \pm 0.3	38.0 \pm 0.7
17. 1,1-dichloroethane	298.15	24.07	[11]	17.1 \pm 0.4	15.1 \pm 0.4
18. 1,2-dichloroethane	298.15	31.86	[11]	24.4 \pm 0.6	23.2 \pm 0.5
19. methyl formate	298.15	24.36	[11]	32.3 \pm 0.5	20.8 \pm 0.3
20. bromoethane	293.15	24.15	[12]	11.7 \pm 0.3	18.9 \pm 0.6
...	298.15	23.62	[11]	11.0 \pm 0.4	18.2 \pm 0.6
21. chloroethane	273.15	21.87	[12]	13.6 \pm 0.4	13.8 \pm 0.3
...	285.45	20.13	[12]	12.0 \pm 0.4	11.9 \pm 0.4
23. ethanamide	358.15	38.96	[14]	34.1 \pm 1.4	36.2 \pm 1.6
24. N-methylformamide	292.15	39.35	[12]	39.7 \pm 0.5	38.6 \pm 0.2
...	298.15	38.52	[12]	38.2 \pm 0.5	36.9 \pm 0.2
25. nitroethane	298.15	32.13	[11]	39.1 \pm 0.6	26.4 \pm 0.4
26. methoxymethane	240.00	20.41	[14]	17.7 \pm 0.3	15.1 \pm 0.2
...	298.08	11.80	[14]	8.3 \pm 0.2	6.0 \pm 0.3

Table S4: Surface tension - continued

Name	Experiment			GAFF	OPLS/AA
	T	γ	Ref.	γ	γ
27. ethanol	298.15	21.97	[11]	18.6 ± 0.2	18.7 ± 0.3
28. 1,2-ethanedithiol	298.15			28.2 ± 0.3	35.9 ± 0.4
29. methylsulfanylmethane	298.15	33.39	[11]	16.9 ± 0.5	20.7 ± 0.5
30. methylsulfinylmethane	298.15	42.92	[11]	41.6 ± 0.9	42.4 ± 0.9
31. methylsulfanylmethane	298.15	24.06	[11]	10.6 ± 0.3	17.6 ± 0.4
32. 2-aminoethanol	293.15	49.17	[12]	56.1 ± 2.4	40.5 ± 1.4
...	298.15	48.32	[11]	57.4 ± 9.7	39.4 ± 0.9
33. ethane-1,2-diamine	298.15	41.12	[12]	45.2 ± 2.2	32.5 ± 0.7
34. prop-2-enenitrile	298.15	26.63	[14]	19.4 ± 0.4	20.4 ± 0.3
...	350.45	20.45	[12]	12.4 ± 0.3	13.3 ± 0.3
35. 1,3-dioxolan-2-one	312.15	63.28	[12]	65.2 ± 2.3	54.7 ± 1.0
...	313.15	50.60	[14]	63.5 ± 2.5	54.4 ± 1.4
36. propanenitrile	298.15	26.75	[11]	21.1 ± 0.4	16.2 ± 0.2
37. 1,2-dibromopropane	298.15	34.50	[12]	20.1 ± 0.6	33.9 ± 0.8
38. 1,3-dichloropropane	298.15	33.93	[12]	25.1 ± 0.6	23.6 ± 0.5
39. (2R)-2-methyloxirane	298.15			14.7 ± 0.4	13.0 ± 0.4
40. propan-2-one	298.15	22.72	[11]	19.2 ± 0.4	17.2 ± 0.2
41. methyl acetate	298.15	24.73	[11]	26.1 ± 0.3	23.2 ± 0.4
42. 1,3-dioxolane	293.15			38.2 ± 0.7	26.6 ± 1.2
...	298.15	32.61	[14]	37.6 ± 0.2	26.0 ± 0.6
43. 2-iodopropane	298.15	26.62	[12]	15.8 ± 0.5	19.1 ± 0.6
44. 1-bromopropane	298.15	25.26	[11]	14.5 ± 0.4	19.4 ± 0.2
45. N,N-dimethylformamide	298.15	35.74	[11]	36.1 ± 0.5	31.5 ± 0.8
46. N-methylacetamide	320.00	31.26	[12]	31.1 ± 0.3	33.0 ± 0.4
47. 1-nitropropane	298.15	29.85	[12]	34.9 ± 0.7	24.0 ± 0.5
48. 2-nitropropane	298.15	29.29	[11]	33.6 ± 0.5	24.9 ± 0.8
49. dimethoxymethane	298.04	20.36	[14]	20.3 ± 0.4	17.1 ± 0.3
...	298.15	18.75	[12]	20.3 ± 0.4	17.1 ± 0.3
50. propane-1,2,3-triol	293.15	77.25	[12]	74.9 ± 17.0	63.1 ± 15.0
...	298.15	63.00	[14]	70.5 ± 17.0	51.8 ± 7.5
51. propan-1-amine	298.15	21.75	[11]	17.2 ± 1.0	12.6 ± 0.6
52. propan-2-amine	298.15	17.36	[12]	17.9 ± 0.2	13.0 ± 0.3

Table S4: Surface tension - continued

Name	Experiment			GAFF	OPLS/AA
	T	γ	Ref.	γ	γ
53. 2-methylpropane	243.65	16.42	[12]	13.0 ± 0.2	12.6 ± 0.3
54. ethylsulfanylethane	298.15	24.57	[11]	14.5 ± 0.2	18.7 ± 0.5
55. butane-1-thiol	298.15	25.22	[12]	17.6 ± 0.3	19.9 ± 0.3
56. butan-1-ol	298.15	24.93	[11]	19.5 ± 1.0	18.6 ± 0.8
57. 2-methylpropan-2-ol	320.00			17.3 ± 1.9	15.8 ± 0.4
58. butane-1,4-diol	298.15	45.47	[14]	48.4 ± 14.0	45.6 ± 3.4
...	320.00	44.23	[12]	35.4 ± 3.4	39.6 ± 3.2
59. (2-hydroxyethoxy)ethan-2-ol	288.15	56.61	[12]	65.6 ± 5.6	41.7 ± 8.2
60. N-ethylethanamine	298.15	19.85	[11]	15.8 ± 0.3	12.6 ± 0.2
61. butan-1-amine	298.15	23.44	[11]	17.6 ± 0.7	14.5 ± 0.1
62. 2-methylpropan-2-amine	298.15	16.87	[11]	17.1 ± 0.8	15.3 ± 0.2
63. 2-(2-hydroxyethylamino)ethanol	320.00	50.60	[12]	49.4 ± 9.1	45.7 ± 7.3
64. pyrimidine	298.15	30.33	[11]	41.1 ± 1.1	41.7 ± 1.2
65. furan	298.15	22.65	[12]	18.7 ± 0.6	19.6 ± 0.4
66. thiophene	298.15	30.68	[11]	19.5 ± 0.6	29.4 ± 0.5
67. 1H-pyrrole	298.15	36.95	[12]	29.9 ± 0.8	28.9 ± 0.9
68. ethenyl acetate	298.15	22.03	[12]	24.0 ± 0.3	27.4 ± 0.6
71. 1,4-dichlorobutane	298.15	35.42	[12]	26.3 ± 0.7	25.4 ± 0.7
72. oxolane	298.15	26.65	[12]	24.4 ± 0.6	17.7 ± 0.5
74. ethyl acetate	298.15	23.39	[11]	24.1 ± 0.5	23.2 ± 0.6
75. tetrahydrothiophene 1,1-dioxide	320.00	53.33	[12]	55.9 ± 5.6	46.2 ± 1.6
76. thiolane	298.15	33.82	[12]	23.7 ± 0.8	26.9 ± 0.6
77. 1-bromobutane	298.15	25.90	[11]	16.5 ± 0.7	20.3 ± 0.6
78. 1-chlorobutane	298.15	23.18	[11]	15.8 ± 0.7	15.1 ± 0.3
79. pyrrolidine	298.15	37.06	[11]	25.7 ± 1.1	19.0 ± 0.8
80. N,N-dimethylacetamide	298.15	33.09	[12]	31.3 ± 0.6	32.1 ± 0.6
81. morpholine	293.15	39.50	[12]	43.7 ± 2.0	33.6 ± 3.2
...	298.15	37.68	[14]	44.4 ± 1.9	32.7 ± 1.2
82. pyridine	298.15	36.56	[11]	27.6 ± 0.5	29.1 ± 0.8
83. cyclopentanone	298.15	32.80	[11]	30.3 ± 0.5	26.2 ± 0.8
84. 1-cyclopropylethanone	298.15			22.9 ± 1.1	24.8 ± 0.7
85. pentane-2,4-dione	298.15	30.90	[14]	33.8 ± 0.6	32.9 ± 0.9

Table S4: Surface tension - continued

Name	Experiment			GAFF	OPLS/AA
	T	γ	Ref.	γ	γ
86. methyl 2-methylprop-2-enoate	298.15	24.24	[12]	23.4 ± 0.5	29.4 ± 0.7
87. pentanenitrile	297.75	27.09	[14]	21.3 ± 0.9	17.8 ± 0.7
...	298.15	26.97	[12]	21.5 ± 1.0	17.5 ± 0.8
88. ethyl propanoate	298.15	23.80	[11]	22.8 ± 0.4	22.3 ± 0.5
89. diethyl carbonate	298.15	25.92	[14]	29.2 ± 1.4	25.0 ± 0.8
90. pentan-1-ol	298.15	25.36	[11]	19.4 ± 1.1	19.0 ± 1.0
91. pentan-3-ol	298.15	23.65	[12]	19.7 ± 1.2	18.8 ± 0.7
92. 2-methylbutan-2-ol	298.15			19.2 ± 2.5	18.4 ± 0.9
93. pentane-1,5-diol	298.15	46.32	[12]	51.4 ± 6.9	46.8 ± 5.3
94. pentan-3-amine	298.15	22.26	[12]	18.1 ± 0.5	15.8 ± 0.3
95. 1,2,3,4-tetrafluorobenzene	298.15			11.2 ± 0.4	14.2 ± 0.4
96. 1,2,3,5-tetrafluorobenzene	298.15			9.4 ± 0.2	13.1 ± 0.8
97. 1,3-difluorobenzene	298.15	25.95	[12]	15.0 ± 0.3	14.1 ± 0.5
98. 1,2-difluorobenzene	298.15	26.07	[12]	16.1 ± 0.3	16.1 ± 0.3
99. fluorobenzene	298.15	26.66	[11]	16.7 ± 0.2	18.3 ± 0.7
100. nitrobenzene	298.15	43.23	[12]	45.3 ± 1.7	33.6 ± 1.0
...	364.15	34.20	[14]	36.0 ± 0.6	25.0 ± 0.7
101. 2-chloroaniline	293.15	40.73	[14]	30.9 ± 0.7	33.1 ± 0.8
102. phenol	318.15	38.72	[12]	27.6 ± 0.6	30.1 ± 2.0
103. benzenethiol	298.15	38.70	[14]	23.9 ± 0.6	21.6 ± 0.3
104. 2-methylpyridine	298.15	33.00	[11]	25.7 ± 0.5	27.6 ± 0.2
105. 3-methylpyridine	293.15	36.63	[14]	26.1 ± 0.5	29.3 ± 0.5
...	298.15	35.04	[12]	26.6 ± 0.5	29.0 ± 0.5
106. 4-methylpyridine	298.15	35.43	[12]	26.8 ± 0.8	27.9 ± 0.3
107. cyclohexanone	298.15	34.57	[11]	30.0 ± 0.9	27.3 ± 1.1
108. (E)-hex-2-ene	293.15			10.8 ± 0.2	12.8 ± 0.3
109. hexan-2-one	298.15	25.45	[11]	20.2 ± 0.7	19.3 ± 0.6
110. 2,4,6-trimethyl-1,3,5-trioxane	293.15	26.16	[14]	36.9 ± 1.9	30.1 ± 2.9
...	373.15	17.66	[11]	24.9 ± 0.5	20.9 ± 0.9
111. cyclohexanamine	298.15	31.22	[11]	29.1 ± 2.6	24.0 ± 1.1
112. 2-propan-2-yloxypropane	298.15	17.27	[11]	16.6 ± 0.2	13.2 ± 0.2
113. 1-methoxy-2-(2-methoxyethoxy)ethane	298.15	29.30	[12]	33.5 ± 1.5	24.9 ± 1.1

Table S4: Surface tension - continued

Name	Experiment			GAFF	OPLS/AA
	T	γ	Ref.	γ	γ
114. triethyl phosphate	298.15	29.61	[12]	31.2 ± 2.7	28.8 ± 1.1
...	311.65	28.30	[14]	29.4 ± 2.3	26.8 ± 1.1
115. N,N-diethylethanamine	298.15	20.22	[11]	16.8 ± 0.3	13.9 ± 0.3
116. N-propan-2-ylpropan-2-amine	298.15	19.14	[11]	18.0 ± 0.7	15.0 ± 0.3
117. trifluoromethylbenzene	298.15	23.21	[12]	16.7 ± 0.7	16.0 ± 0.5
118. benzonitrile	288.15	39.95	[12]	28.6 ± 0.3	35.0 ± 0.6
...	293.15	38.59	[14]	28.0 ± 0.3	33.9 ± 1.1
119. benzaldehyde	298.15	38.00	[11]	31.0 ± 0.4	32.5 ± 0.5
120. toluene	298.15	27.73	[11]	17.0 ± 0.3	20.9 ± 0.5
121. methoxybenzene	298.15	35.10	[11]	25.9 ± 0.5	25.0 ± 0.7
122. phenylmethanol	297.15	36.98	[12]	30.0 ± 1.4	31.9 ± 0.8
...	298.15	35.97	[14]	29.1 ± 0.9	30.9 ± 1.9
123. 2-methylphenol	308.15	36.11	[12]	27.1 ± 0.7	29.7 ± 1.5
125. 4-methylphenol	313.15	34.88	[14]	24.6 ± 0.6	29.0 ± 1.5
127. 2,4-dimethylpentan-3-one	298.15	24.78	[12]	21.4 ± 0.7	20.5 ± 0.5
128. heptan-2-one	298.15	26.12	[11]	21.1 ± 0.5	19.9 ± 0.2
129. ethenylbenzene	298.15	32.00	[12]	18.5 ± 0.5	23.0 ± 0.5
130. 1-phenylethanone	298.15	39.04	[11]	29.1 ± 0.7	33.4 ± 1.2
...	298.25	39.02	[14]	30.0 ± 1.0	33.8 ± 1.1
131. methyl benzoate	298.15	37.17	[11]	34.8 ± 1.3	33.6 ± 0.3
132. methyl 2-hydroxybenzoate	298.15	39.22	[11]	33.9 ± 2.1	36.5 ± 1.4
133. ethylbenzene	298.15	28.75	[11]	18.3 ± 0.8	20.7 ± 0.6
134. 1,2-dimethylbenzene	298.15	29.76	[11]	18.4 ± 0.3	22.8 ± 0.2
135. 1,2-dimethoxybenzene	298.15	32.80	[14]	31.2 ± 0.6	30.4 ± 1.2
136. 2,4,6-trimethylpyridine	295.15	33.64	[12]	23.4 ± 0.6	26.7 ± 0.7
...	298.15	33.30	[12]	24.2 ± 1.1	26.4 ± 0.4
137. octan-1-ol	298.15	27.10	[11]	23.1 ± 1.6	15.6 ± 6.0
138. 1-butoxybutane	298.15	22.44	[14]	18.2 ± 0.2	16.5 ± 0.8
139. N-butylbutan-1-amine	298.15	24.12	[11]	19.1 ± 0.7	16.7 ± 0.6
140. isoquinoline	303.15	45.94	[14]	34.6 ± 1.1	38.3 ± 1.9
141. quinoline	288.15	43.55	[12]	33.6 ± 1.3	35.0 ± 0.7
...	298.15	42.59	[11]	32.1 ± 0.4	33.7 ± 0.9

Table S4: Surface tension - continued

Name	Experiment			GAFF	OPLS/AA
	T	γ	Ref.	γ	γ
142. (1-methylethyl)benzene	298.15	27.69	[11]	19.8 \pm 0.3	21.4 \pm 0.4
143. 1,2,4-trimethylbenzene	293.15	29.72	[12]	19.5 \pm 0.5	24.5 \pm 0.7
...	298.15	29.19	[12]	18.8 \pm 0.6	24.0 \pm 0.4
144. 2,6-dimethylheptan-4-one	298.15	25.80	[12]	20.2 \pm 0.7	20.2 \pm 0.4
145. 1-chloronaphthalene	298.15	39.23	[12]	28.9 \pm 0.8	28.4 \pm 0.7
146. phenoxybenzene	303.15	38.24	[12]	28.8 \pm 0.7	32.6 \pm 1.2

Table S5: Dielectric constant $\epsilon(0)$ calculated and experimental. Missing simulated $\epsilon(0)$ due to simulations not having converged, see main text. Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA
	T	$\epsilon(0)$	Ref.	$\epsilon(0)$	$\epsilon(0)$
1. chloroform	298.15	4.71	[11]		3.3 ± 0.0
2. dichloro(fluoro)methane	282.05			5.6 ± 0.1	2.4 ± 0.0
3. dibromomethane	293.15	7.41	[11]	5.9 ± 0.1	5.2 ± 0.1
...	298.15	7.23	[11]		5.1 ± 0.1
4. dichloromethane	293.15	9.00	[11]	10.1 ± 0.1	4.4 ± 0.0
...	298.15	8.82	[11]	9.8 ± 0.1	4.2 ± 0.1
5. methanal	253.15			37.9 ± 0.2	37.1 ± 0.3
...	253.65			37.2 ± 0.4	37.2 ± 0.6
6. methanoic acid	293.15	53.33	[11]		8.1 ± 0.2
...	298.15	51.10	[11]		7.8 ± 0.1
7. bromomethane	276.65			7.2 ± 0.1	14.3 ± 0.1
8. methanamide	298.15	108.94	[11]	41.1 ± 1.6	
9. nitromethane	293.15	37.27	[11]	32.7 ± 0.5	26.5 ± 0.4
...	298.15	36.56	[11]	30.8 ± 1.1	25.8 ± 0.2
10. methanol	293.15	33.00	[11]	25.5 ± 0.9	26.5 ± 0.7
...	298.15	31.92		25.5 ± 1.0	24.7 ± 0.7
11. 1,1,1,2,2-pentachloroethane	293.15	3.79		2.5 ± 0.0	2.1 ± 0.0
12. 1,1,2,2-tetrachloroethane	293.15	8.50	[11]	3.1 ± 0.1	3.8 ± 0.1
...	298.15	7.91		2.9 ± 0.1	3.6 ± 0.1
13. 1,1-dichloroethene	293.15	4.60	[11]	4.2 ± 0.0	
...	298.15			4.1 ± 0.0	3.7 ± 0.0
14. 1,1,2-trichloroethane	293.15	7.36	[11]	6.5 ± 0.1	
...	298.15	7.19	[11]	6.4 ± 0.2	6.1 ± 0.1
15. acetonitrile	293.15	36.64	[11]	24.3 ± 0.3	20.6 ± 0.3
...	298.15	35.69	[11]	23.7 ± 0.3	20.4 ± 0.3
16. 1,2-dibromoethane	298.15	4.93	[11]	5.7 ± 0.1	20.8 ± 0.6
17. 1,1-dichloroethane	293.15	10.36	[11]		3.3 ± 0.0
...	298.15	10.10	[11]	10.0 ± 0.3	3.2 ± 0.0
18. 1,2-dichloroethane	298.15	10.13	[11]	19.8 ± 0.4	13.4 ± 0.2
19. methyl formate	293.15	9.02	[11]	6.6 ± 0.2	5.6 ± 0.1
...	298.15	8.84	[11]		5.4 ± 0.1

Table S5: Dielectric constant - continued

Name	Experiment			GAFF	OPLS/AA
	T	$\epsilon(0)$	Ref.	$\epsilon(0)$	$\epsilon(0)$
20. bromoethane	293.15	9.25	[11]	8.3 ± 0.1	9.4 ± 0.2
...	298.15	9.01	[11]	8.0 ± 0.1	9.4 ± 0.1
21. chloroethane	273.15	10.41	[11]	10.8 ± 0.1	8.1 ± 0.1
...	285.45	9.80	[11]	10.1 ± 0.2	7.4 ± 0.1
22. 2-chloroethanol	293.15	25.80	[11]	23.2 ± 1.4	18.7 ± 0.9
23. ethanamide	358.15	67.87			32.8 ± 1.6
24. N-methylformamide	292.15			13.6 ± 0.6	18.8 ± 0.6
...	298.15	189.00	[13]	13.3 ± 0.3	19.2 ± 0.7
25. nitroethane	298.15	28.29	[11]	20.8 ± 0.7	18.9 ± 0.3
26. methoxymethane	240.00	6.88	[11]	7.8 ± 0.1	8.8 ± 0.1
27. ethanol	293.15	25.30	[11]	16.0 ± 0.9	21.7 ± 1.3
...	298.15	24.85	[11]	14.2 ± 0.6	
28. 1,2-ethanedithiol	293.15	7.26	[11]	11.1 ± 0.1	7.4 ± 0.1
...	298.15	7.20	[11]	10.8 ± 0.2	6.9 ± 0.0
29. methyldisulfanylmethane	293.15	9.81		9.1 ± 0.1	
...	298.15	9.60	[11]	8.6 ± 0.1	18.3 ± 0.3
30. methylsulfinylmethane	298.15	46.83	[11]	59.6 ± 2.5	43.6 ± 2.1
31. methylsulfanylmethane	293.15	6.58		7.0 ± 0.0	10.3 ± 0.1
...	298.15	6.45		6.8 ± 0.1	9.8 ± 0.1
32. 2-aminoethanol	293.15	32.10			48.9 ± 3.3
...	320.00			22.3 ± 1.9	37.5 ± 1.9
33. ethane-1,2-diamine	293.15	13.82	[11]	14.8 ± 0.6	22.1 ± 1.0
...	298.15	13.52	[11]	14.2 ± 0.4	22.8 ± 0.5
34. prop-2-enenitrile	298.15	32.36	[11]	22.3 ± 0.5	11.1 ± 0.2
...	350.45	24.94	[11]	17.8 ± 0.2	8.8 ± 0.1
35. 1,3-dioxolan-2-one	312.15	89.91		85.8 ± 6.6	
36. propanenitrile	293.15	29.70	[11]	18.3 ± 0.4	15.4 ± 0.1
...	298.15	29.32	[11]	17.7 ± 0.5	15.0 ± 0.2
37. 1,2-dibromopropane	293.15	4.57	[11]	5.4 ± 0.1	15.0 ± 0.5
...	298.15	4.55	[11]	5.2 ± 0.1	
38. 1,3-dichloropropane	298.15	10.18		8.3 ± 0.1	6.7 ± 0.1
39. (2R)-2-methyloxirane	298.15				14.7 ± 0.2

Table S5: Dielectric constant - continued

Name	Experiment			GAFF	OPLS/AA
	T	$\epsilon(0)$	Ref.	$\epsilon(0)$	$\epsilon(0)$
40. propan-2-one	298.15	20.49	[11]	12.0 ± 0.2	15.4 ± 0.2
41. methyl acetate	293.15	6.97	[11]	5.0 ± 0.1	
...	298.15	6.86	[11]	5.0 ± 0.1	4.6 ± 0.0
42. 1,3-dioxolane	293.15	7.11		3.4 ± 0.0	3.1 ± 0.0
...	298.15	6.98		3.3 ± 0.0	3.0 ± 0.0
43. 2-iodopropane	293.15			8.4 ± 0.3	
...	298.15	8.19	[11]	8.3 ± 0.2	2.7 ± 0.0
44. 1-bromopropane	293.15	8.09	[11]	7.3 ± 0.1	8.0 ± 0.2
...	298.15	8.05	[11]	7.2 ± 0.1	7.8 ± 0.1
45. N,N-dimethylformamide	298.15			24.5 ± 0.8	14.9 ± 0.5
46. N-methylacetamide	320.00			10.4 ± 0.4	14.2 ± 0.4
47. 1-nitropropane	298.15	23.73	[11]	14.5 ± 0.7	12.2 ± 0.2
48. 2-nitropropane	298.15	25.65	[11]	15.6 ± 0.3	15.0 ± 0.4
49. dimethoxymethane	293.15	2.64	[11]		4.5 ± 0.0
...	298.15	2.65		3.9 ± 0.0	4.4 ± 0.0
50. propane-1,2,3-triol	320.00	41.69	[11]	24.5 ± 1.1	25.6 ± 0.9
51. propan-1-amine	293.15	5.12	[11]		6.1 ± 0.1
...	298.15	5.11	[19]	5.9 ± 0.2	5.7 ± 0.1
52. propan-2-amine	293.15	5.63	[11]	5.7 ± 0.1	5.4 ± 0.1
...	298.15	5.47	[19]	5.5 ± 0.1	
53. 2-methylpropane	243.65	1.85	[11]	1.1 ± 0.0	1.0 ± 0.0
54. ethylsulfanylethane	293.15	5.83		5.6 ± 0.1	7.7 ± 0.2
...	298.15	5.72	[11]	5.5 ± 0.1	7.7 ± 0.2
55. butane-1-thiol	293.15	5.11	[11]	6.1 ± 0.2	4.4 ± 0.1
...	298.15	5.01	[11]	6.0 ± 0.1	4.2 ± 0.1
56. butan-1-ol	293.15	17.84	[11]	8.4 ± 0.2	14.1 ± 0.9
...	298.15	17.33	[11]	9.8 ± 0.2	12.8 ± 0.7
58. butane-1,4-diol	293.15	32.86	[11]		18.0 ± 0.9
...	320.00	27.87	[11]	19.0 ± 0.3	20.5 ± 2.0
59. (2-hydroxyethoxy)ethan-2-ol	288.15	32.81	[11]		16.3 ± 0.7
60. N-ethylethanamine	293.15	3.68	[11]	4.4 ± 0.1	
...	298.15	3.58	[11]	4.5 ± 0.1	4.6 ± 0.1

Table S5: Dielectric constant - continued

Name	Experiment			GAFF	OPLS/AA
	T	$\epsilon(0)$	Ref.	$\epsilon(0)$	$\epsilon(0)$
61. butan-1-amine	293.15	4.71	[11]	5.4 ± 0.2	4.9 ± 0.1
...	298.15	4.62	[11]	5.2 ± 0.2	4.7 ± 0.0
62. 2-methylpropan-2-amine	293.15	4.40		3.5 ± 0.1	
...	298.15	4.01		3.4 ± 0.1	3.8 ± 0.1
64. pyrimidine	298.15			8.6 ± 0.3	8.8 ± 0.3
65. furan	293.15	2.97		1.5 ± 0.0	1.6 ± 0.0
...	298.15	2.94		1.5 ± 0.0	1.5 ± 0.0
66. thiophene	293.15	2.74	[11]	1.4 ± 0.0	2.7 ± 0.0
...	298.15	2.73			2.6 ± 0.0
67. 1H-pyrrole	293.15	8.01	[11]	4.0 ± 0.1	4.0 ± 0.1
...	298.15	7.92	[11]	4.2 ± 0.1	4.0 ± 0.1
68. ethenyl acetate	298.15			3.3 ± 0.1	4.1 ± 0.1
69. oxolan-2-one	293.15	39.00	[11]		30.2 ± 0.9
70. acetyl acetate	293.15	22.45	[11]	12.5 ± 0.5	8.9 ± 0.2
71. 1,4-dichlorobutane	298.15	9.51	[19]	8.6 ± 0.2	8.4 ± 0.2
72. oxolane	298.15	8.04	[19]		5.7 ± 0.1
73. ethoxyethene	293.15				4.4 ± 0.0
74. ethyl acetate	293.15	6.08	[11]	3.9 ± 0.1	4.2 ± 0.1
...	298.15	5.99	[11]	3.9 ± 0.1	4.0 ± 0.1
75. tetrahydrothiophene 1,1-dioxide	320.00	41.24		25.1 ± 2.5	15.5 ± 0.5
76. thiolane	293.15			6.3 ± 0.1	7.2 ± 0.2
...	298.15			6.1 ± 0.1	7.1 ± 0.1
77. 1-bromobutane	293.15	7.02	[11]	5.4 ± 0.1	6.5 ± 0.1
...	298.15	6.89	[11]	5.6 ± 0.1	6.3 ± 0.1
78. 1-chlorobutane	298.15	7.09	[11]	6.2 ± 0.1	4.9 ± 0.1
79. pyrrolidine	293.15	8.28	[11]		5.5 ± 0.2
...	298.15	8.04	[11]	4.8 ± 0.1	5.2 ± 0.1
80. N,N-dimethylacetamide	298.15	38.90	[13]	19.4 ± 0.5	14.3 ± 0.2
81. morpholine	293.15	7.46	[19]	5.8 ± 0.2	4.2 ± 0.3
82. pyridine	293.15	13.26	[11]	6.8 ± 0.1	6.9 ± 0.2
...	298.15	12.98	[11]		6.7 ± 0.1
83. cyclopentanone	293.15	13.76	[11]	8.3 ± 0.2	9.6 ± 0.2
...	298.15	13.58	[11]	8.3 ± 0.2	9.5 ± 0.2

Table S5: Dielectric constant - continued

Name	Experiment			GAFF	OPLS/AA
	T	$\epsilon(0)$	Ref.	$\epsilon(0)$	$\epsilon(0)$
84. 1-cyclopropylethanone	293.15			14.8 ± 0.6	14.6 ± 0.4
...	298.15			13.8 ± 0.5	13.9 ± 0.3
85. pentane-2,4-dione	298.15	26.28		28.9 ± 1.0	5.1 ± 0.1
86. methyl 2-methylprop-2-enoate	298.15	6.53	[19]	4.0 ± 0.1	25.0 ± 1.0
87. pentanenitrile	293.15	20.04	[11]	12.9 ± 0.5	10.9 ± 0.3
...	298.15	19.89	[11]		10.7 ± 0.3
88. ethyl propanoate	298.15	5.76	[13]	3.0 ± 0.1	3.7 ± 0.0
89. diethyl carbonate	298.15	2.84	[19]	1.3 ± 0.0	
90. pentan-1-ol	293.15	15.26	[11]	9.1 ± 0.4	10.2 ± 0.6
...	298.15	15.13	[11]	9.5 ± 0.1	10.6 ± 0.6
...	320.00	12.38	[11]	10.9 ± 0.4	7.2 ± 0.3
91. pentan-3-ol	293.15	14.07	[11]	7.7 ± 0.4	7.6 ± 0.5
...	298.15	13.35	[11]	8.4 ± 0.2	8.5 ± 0.6
92. 2-methylbutan-2-ol	293.15	5.97	[11]		5.3 ± 0.2
...	320.00			2.0 ± 0.1	
94. pentan-3-amine	293.15			3.5 ± 0.1	
94. pentan-3-amine	298.15				3.4 ± 0.1
95. 1,2,3,4-tetrafluorobenzene	298.15			7.2 ± 0.1	5.3 ± 0.1
97. 1,3-difluorobenzene	293.15	5.14	[11]	3.1 ± 0.0	3.9 ± 0.1
...	298.15	5.06	[11]		3.8 ± 0.1
98. 1,2-difluorobenzene	293.15	13.94	[11]	8.8 ± 0.2	
...	298.15	13.59	[11]		11.3 ± 0.2
99. fluorobenzene	293.15	5.46	[11]	3.3 ± 0.0	4.4 ± 0.1
...	298.15	5.34	[19]	3.3 ± 0.0	
100. nitrobenzene	293.15	35.65	[11]	25.6 ± 1.7	8.4 ± 0.3
...	298.15	34.81	[11]	25.2 ± 1.6	8.0 ± 0.3
101. 2-chloroaniline	293.15	13.40	[11]	4.7 ± 0.1	8.0 ± 0.3
102. phenol	318.15	11.15	[11]		5.8 ± 0.3
103. benzenethiol	293.15	4.29		3.0 ± 0.0	2.5 ± 0.0
...	298.15	4.27		2.9 ± 0.0	2.4 ± 0.0
104. 2-methylpyridine	293.15	10.18	[11]	5.4 ± 0.1	5.4 ± 0.1
...	298.15	9.95	[11]		5.2 ± 0.1

Table S5: Dielectric constant - continued

Name	Experiment			GAFF	OPLS/AA
	T	$\epsilon(0)$	Ref.	$\epsilon(0)$	$\epsilon(0)$
105. 3-methylpyridine	293.15	11.97		5.9 ± 0.1	6.9 ± 0.1
...	298.15	11.64		5.6 ± 0.1	7.1 ± 0.2
106. 4-methylpyridine	293.15	12.18	[11]	6.1 ± 0.2	7.3 ± 0.2
...	298.15	11.96	[11]	6.6 ± 0.2	
107. cyclohexanone	293.15	15.92	[11]	9.1 ± 0.3	7.6 ± 0.1
...	298.15	15.62	[11]	8.5 ± 0.3	7.6 ± 0.2
108. (E)-hex-2-ene	293.15			1.0 ± 0.0	1.0 ± 0.0
109. hexan-2-one	298.15	14.60	[13]		10.1 ± 0.2
111. cyclohexanamine	298.15	4.55	[13]	4.0 ± 0.2	4.3 ± 0.1
112. 2-propan-2-yloxypropane	298.15	3.97	[19]	13.9 ± 0.6	2.6 ± 0.0
113. 1-methoxy-2-(2-methoxyethoxy)ethane	293.15			8.4 ± 0.5	6.1 ± 0.1
...	298.15	7.23	[11]	7.8 ± 0.3	6.0 ± 0.2
114. triethyl phosphate	293.15				20.0 ± 1.1
...	298.15	13.20	[11]	3.4 ± 0.1	28.2 ± 0.3
...	320.00	12.01	[11]	3.9 ± 0.1	24.7 ± 0.7
115. N,N-diethylethanamine	293.15	2.42	[11]	1.4 ± 0.0	2.8 ± 0.0
...	298.15	2.38	[11]	1.4 ± 0.0	2.7 ± 0.1
116. N-propan-2-ylpropan-2-amine	293.15			5.9 ± 0.1	2.6 ± 0.0
116. N-propan-2-ylpropan-2-amine	298.15				2.5 ± 0.0
117. trifluoromethylbenzene	293.15			6.6 ± 0.2	6.5 ± 0.2
...	298.15	9.22	[11]	6.5 ± 0.2	
118. benzonitrile	288.15	26.41	[11]	16.9 ± 0.8	6.6 ± 0.3
119. benzaldehyde	298.15	17.40	[19]	10.9 ± 0.6	
120. toluene	298.15	2.37	[11]	1.1 ± 0.0	1.2 ± 0.0
121. methoxybenzene	293.15	4.41	[19]	2.6 ± 0.0	2.4 ± 0.0
...	298.15	4.22	[11]	2.6 ± 0.0	2.4 ± 0.0
122. phenylmethanol	297.15	13.09		5.8 ± 0.1	7.9 ± 0.5
123. 2-methylphenol	308.15	6.44	[11]	4.2 ± 0.3	4.2 ± 0.2
124. 3-methylphenol	320.00	10.43	[11]	5.2 ± 0.3	6.9 ± 0.4
125. 4-methylphenol	313.15	11.21	[11]	3.9 ± 0.1	7.1 ± 0.5
...	320.00	10.62	[11]	3.5 ± 0.1	7.8 ± 0.3
126. diethyl propanedioate	293.15	8.10		4.1 ± 0.2	4.6 ± 0.2

Table S5: Dielectric constant - continued

Name	Experiment			GAFF	OPLS/AA
	T	$\epsilon(0)$	Ref.	$\epsilon(0)$	$\epsilon(0)$
127. 2,4-dimethylpentan-3-one	293.15			38.7 ± 2.1	13.4 ± 0.7
...	298.15			60.8 ± 2.7	12.9 ± 0.6
128. heptan-2-one	293.15	11.95	[11]	6.6 ± 0.2	9.5 ± 0.3
...	298.15	11.66	[11]	6.7 ± 0.1	9.1 ± 0.3
129. ethenylbenzene	298.15	2.46	[11]	1.1 ± 0.0	1.0 ± 0.0
130. 1-phenylethanone	293.15	17.73	[19]		7.5 ± 0.2
...	298.15	17.44	[11]	11.0 ± 0.7	6.9 ± 0.3
131. methyl benzoate	298.15	6.64	[13]	3.9 ± 0.2	3.4 ± 0.1
132. methyl 2-hydroxybenzoate	298.15	9.47	[11]	6.0 ± 0.2	
...	320.00	8.71	[11]	6.8 ± 0.4	7.1 ± 0.2
133. ethylbenzene	298.15	2.43	[11]	1.1 ± 0.0	1.2 ± 0.0
134. 1,2-dimethylbenzene	293.15	2.56	[11]	1.2 ± 0.0	1.5 ± 0.0
...	298.15	2.55	[11]	1.2 ± 0.0	1.5 ± 0.0
135. 1,2-dimethoxybenzene	298.15	4.41	[11]		4.0 ± 0.1
136. 2,4,6-trimethylpyridine	295.15	7.92		4.4 ± 0.1	4.8 ± 0.1
...	298.15	7.81	[11]	4.0 ± 0.2	4.4 ± 0.2
137. octan-1-ol	298.15	9.86	[11]		5.6 ± 0.3
...	320.00	8.29	[11]		5.8 ± 0.3
138. 1-butoxybutane	293.15	3.08	[11]	2.2 ± 0.0	2.3 ± 0.0
...	298.15	3.05	[11]		2.2 ± 0.0
139. N-butylbutan-1-amine	293.15	2.77	[11]	2.3 ± 0.1	3.1 ± 0.1
...	298.15	2.74	[11]	2.2 ± 0.1	3.1 ± 0.1
140. isoquinoline	303.15	10.60	[11]	4.5 ± 0.3	2.2 ± 0.0
...	320.00	9.56	[11]	4.5 ± 0.1	2.0 ± 0.1
141. quinoline	288.15	9.31	[11]	4.3 ± 0.1	4.2 ± 0.1
...	298.15	9.00	[11]	4.0 ± 0.1	4.0 ± 0.1
143. 1,2,4-trimethylbenzene	293.15	2.38	[11]	1.1 ± 0.0	1.2 ± 0.0
...	298.15	2.37	[11]	1.1 ± 0.0	1.2 ± 0.0
144. 2,6-dimethylheptan-4-one	293.15	9.91	[11]	4.2 ± 0.1	9.3 ± 0.4
...	298.15	9.70	[11]	4.0 ± 0.1	8.8 ± 0.4
145. 1-chloronaphthalene	298.15	5.04	[11]		3.3 ± 0.1
146. phenoxybenzene	303.15	3.65	[19]		1.7 ± 0.0

Table S6: Thermal expansion coefficient α_P (10^{-3} /K), calculated and experimental. Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA
	T	α_P	Ref.	α_P	α_P
1. chloroform	298.15	1.29	[9]	1.91 ± 0.05	2.28 ± 0.11
2. dichloro(fluoro)methane	282.05	1.66	[20]	2.48 ± 0.11	2.56 ± 0.09
3. dibromomethane	293.15	1.01	[20]	1.64 ± 0.05	1.43 ± 0.07
...	298.15	1.02	[9]	1.48 ± 0.06	1.44 ± 0.05
4. dichloromethane	293.15	1.42	[20]	1.52 ± 0.10	1.89 ± 0.09
...	298.15	1.35	[9]	1.73 ± 0.06	2.31 ± 0.09
5. methanal	253.15	2.10	[20]	2.01 ± 0.07	1.82 ± 0.05
...	253.65	2.11	[20]	1.96 ± 0.07	1.88 ± 0.07
6. methanoic acid	293.15	0.99	[20]	0.88 ± 0.05	1.00 ± 0.07
...	298.15	1.02	[9]	0.58 ± 0.13	1.05 ± 0.05
7. bromomethane	276.65	1.53	[20]	2.39 ± 0.13	1.75 ± 0.07
8. methanamide	298.15	0.75	[9]	0.75 ± 0.07	0.80 ± 0.05
9. nitromethane	293.15	1.15	[20]	0.80 ± 0.09	1.25 ± 0.05
...	298.15	1.22	[9]	0.92 ± 0.10	1.31 ± 0.06
10. methanol	293.15	1.14	[20]	1.33 ± 0.09	1.47 ± 0.11
...	298.15	1.19	[9]	1.41 ± 0.12	1.53 ± 0.06
11. 1,1,1,2,2-pentachloroethane	293.15	0.86	[20]	1.01 ± 0.07	1.14 ± 0.02
12. 1,1,2,2-tetrachloroethane	293.15	0.95	[20]	1.08 ± 0.07	1.15 ± 0.08
...	298.15	0.97	[9]	1.05 ± 0.08	1.19 ± 0.07
13. 1,1-dichloroethene	293.15	1.43	[20]	2.75 ± 0.10	1.81 ± 0.11
...	298.15	1.50	[20]	2.90 ± 0.15	2.23 ± 0.10
14. 1,1,2-trichloroethane	293.15	1.12	[20]	1.16 ± 0.06	1.17 ± 0.06
...	298.15	1.00	[9]	1.35 ± 0.08	1.17 ± 0.08
15. acetonitrile	293.15	1.33	[20]	1.57 ± 0.11	1.89 ± 0.04
...	298.15	1.38	[9]	1.59 ± 0.07	1.92 ± 0.09
16. 1,2-dibromoethane	298.15	0.94	[9]	1.42 ± 0.05	1.06 ± 0.08
17. 1,1-dichloroethane	293.15	1.31	[20]	1.36 ± 0.08	1.52 ± 0.10
...	298.15	1.33	[9]	1.46 ± 0.07	1.60 ± 0.07
18. 1,2-dichloroethane	298.15	1.15	[9]	1.25 ± 0.07	1.43 ± 0.06
19. methyl formate	293.15	1.50	[20]	0.98 ± 0.13	1.44 ± 0.08
...	298.15	1.61	[9]	1.16 ± 0.10	1.32 ± 0.06

Table S6: Thermal expansion coefficient - continued

Name	Experiment			GAFF	OPLS/AA
	T	α_P	Ref.	α_P	α_P
20. bromoethane	293.15	1.41	[20]	1.75 ± 0.17	1.53 ± 0.07
...	298.15	1.40	[20]	2.14 ± 0.13	1.47 ± 0.07
21. chloroethane	273.15	1.30	[20]	1.79 ± 0.18	2.07 ± 0.11
...	285.45	1.37	[20]	1.83 ± 0.18	2.09 ± 0.08
22. 2-chloroethanol	293.15	0.86	[20]	0.91 ± 0.11	1.00 ± 0.09
23. ethanamide	358.15	0.90	[20]	0.87 ± 0.14	0.79 ± 0.05
...	494.30	1.21	[20]	1.20 ± 0.14	1.11 ± 0.05
24. N-methylformamide	292.15	0.83	[20]	0.80 ± 0.09	1.16 ± 0.11
...	298.15	0.88	[9]	0.85 ± 0.10	0.99 ± 0.06
25. nitroethane	298.15	1.14	[9]	1.08 ± 0.20	1.16 ± 0.06
26. methoxymethane	240.00	1.81	[20]	1.73 ± 0.18	2.36 ± 0.11
27. ethanol	293.15	1.16	[20]	1.14 ± 0.16	1.33 ± 0.08
...	298.15	1.09	[9]	1.26 ± 0.14	1.44 ± 0.12
28. 1,2-ethanedithiol	293.15			0.96 ± 0.09	0.96 ± 0.07
...	298.15			1.14 ± 0.10	1.06 ± 0.07
29. methylsulfanylmethane	293.15	1.04	[20]	1.47 ± 0.10	1.28 ± 0.06
...	298.15	1.10	[20]	1.60 ± 0.07	1.40 ± 0.08
30. methylsulfinylmethane	298.15	0.91	[9]	0.74 ± 0.06	1.03 ± 0.05
31. methylsulfanylmethane	293.15	1.40	[20]	1.71 ± 0.13	1.65 ± 0.06
...	298.15	1.30	[9]	2.03 ± 0.19	1.69 ± 0.07
32. 2-aminoethanol	293.15	0.77	[20]	0.59 ± 0.15	0.96 ± 0.14
...	320.00	0.82	[20]	0.61 ± 0.11	1.17 ± 0.07
33. ethane-1,2-diamine	293.15	0.92	[20]	1.02 ± 0.13	1.28 ± 0.10
...	298.15	0.79	[9]	0.86 ± 0.13	1.25 ± 0.13
34. prop-2-enenitrile	298.15	1.42	[9]	1.70 ± 0.06	1.30 ± 0.12
...	350.45	1.70	[20]	2.04 ± 0.11	1.78 ± 0.07
35. 1,3-dioxolan-2-one	312.15	0.75	[20]	0.84 ± 0.08	0.72 ± 0.08
36. propanenitrile	293.15	1.22	[20]	1.55 ± 0.11	1.61 ± 0.11
...	298.15	1.33	[9]	1.71 ± 0.16	1.77 ± 0.10
37. 1,2-dibromopropane	293.15	0.78	[20]	1.13 ± 0.11	0.99 ± 0.06
...	298.15	0.80	[20]	1.11 ± 0.08	1.04 ± 0.08
38. 1,3-dichloropropane	298.15	1.00	[20]	1.12 ± 0.08	1.09 ± 0.08

Table S6: Thermal expansion coefficient - continued

Name	Experiment			GAFF	OPLS/AA
	T	α_P	Ref.	α_P	α_P
39. (2R)-2-methyloxirane	298.15			1.93 ± 0.08	2.00 ± 0.47
40. propan-2-one	298.15	1.45	[9]	1.56 ± 0.19	1.57 ± 0.06
41. methyl acetate	293.15	1.37	[20]	1.28 ± 0.04	1.18 ± 0.08
...	298.15	1.42	[9]	1.16 ± 0.11	1.34 ± 0.08
42. 1,3-dioxolane	293.15			0.97 ± 0.12	1.22 ± 0.07
...	298.15	1.18	[9]	0.95 ± 0.07	1.45 ± 0.10
43. 2-iodopropane	293.15	1.13	[20]	1.23 ± 0.16	1.27 ± 0.06
...	298.15	1.10	[20]	0.91 ± 0.13	1.13 ± 0.08
44. 1-bromopropane	293.15	1.25	[20]	1.35 ± 0.13	1.29 ± 0.09
...	298.15	1.30	[20]	1.56 ± 0.14	1.28 ± 0.07
45. N,N-dimethylformamide	298.15	1.00	[9]	0.71 ± 0.10	1.21 ± 0.13
46. N-methylacetamide	320.00	0.85	[20]	1.07 ± 0.14	0.90 ± 0.07
47. 1-nitropropane	298.15	1.01	[9]	0.93 ± 0.12	1.34 ± 0.09
48. 2-nitropropane	298.15	1.04	[9]	0.91 ± 0.11	1.07 ± 0.09
49. dimethoxymethane	293.15	1.49	[20]	1.41 ± 0.10	1.56 ± 0.08
...	298.15	1.50	[20]	1.50 ± 0.16	1.57 ± 0.11
50. propane-1,2,3-triol	293.15	0.46	[20]	0.20 ± 0.10	0.59 ± 0.10
...	320.00	0.49	[20]	1.64 ± 0.08	0.63 ± 0.10
51. propan-1-amine	293.15	1.39	[20]	1.68 ± 0.17	1.99 ± 0.08
...	298.15	1.40	[20]	1.50 ± 0.19	2.03 ± 0.07
52. propan-2-amine	293.15	1.57	[20]	1.46 ± 0.19	1.89 ± 0.15
...	298.15	1.60	[20]	1.40 ± 0.14	1.82 ± 0.11
53. 2-methylpropane	243.65	1.68	[20]	1.80 ± 0.20	2.12 ± 0.15
54. ethylsulfanylethane	293.15	1.13	[20]	1.43 ± 0.15	1.36 ± 0.13
...	298.15	1.45	[9]	1.60 ± 0.17	1.39 ± 0.12
55. butane-1-thiol	293.15	1.14	[20]	1.37 ± 0.16	1.17 ± 0.11
...	298.15	1.20	[20]	1.61 ± 0.22	1.07 ± 0.10
56. butan-1-ol	293.15	1.00	[20]	1.07 ± 0.13	1.35 ± 0.12
...	298.15	0.93	[9]	0.91 ± 0.10	1.18 ± 0.12
57. 2-methylpropan-2-ol	320.00			1.24 ± 0.17	1.52 ± 0.12
58. butane-1,4-diol	293.15	0.89	[20]	0.49 ± 0.17	0.60 ± 0.12
...	298.15	0.65	[9]	0.82 ± 0.13	0.60 ± 0.14
...	320.00	0.94	[20]	0.76 ± 0.10	0.58 ± 0.17

Table S6: Thermal expansion coefficient - continued

Name	Experiment			GAFF	OPLS/AA
	T	α_P	Ref.	α_P	α_P
59. (2-hydroxyethoxy)ethan-2-ol	288.15	0.63	[20]	0.19 ± 0.10	0.80 ± 0.13
60. N-ethylethanamine	293.15	1.44	[20]	1.76 ± 0.17	1.86 ± 0.09
...	298.15	1.56	[9]	1.78 ± 0.18	2.05 ± 0.09
61. butan-1-amine	293.15	1.18	[20]	1.14 ± 0.14	1.68 ± 0.15
...	298.15	1.35	[9]	1.25 ± 0.15	1.69 ± 0.08
62. 2-methylpropan-2-amine	293.15	1.36	[20]	1.26 ± 0.21	1.57 ± 0.09
...	298.15	1.40	[20]	1.56 ± 0.38	1.73 ± 0.07
63. 2-(2-hydroxyethylamino)ethanol	320.00	0.61	[20]	0.63 ± 0.11	0.76 ± 0.09
64. pyrimidine	298.15	0.89	[9]	1.14 ± 0.17	1.04 ± 0.08
65. furan	293.15	1.46	[20]	1.64 ± 0.13	1.43 ± 0.12
...	298.15	0.73	[9]	1.51 ± 0.15	1.56 ± 0.09
66. thiophene	293.15	1.10	[20]	1.42 ± 0.10	1.15 ± 0.05
...	298.15	1.10	[20]	1.40 ± 0.09	1.01 ± 0.10
67. 1H-pyrrole	293.15	0.86	[20]	0.99 ± 0.05	0.93 ± 0.11
...	298.15	0.87	[9]	0.81 ± 0.07	1.05 ± 0.09
68. ethenyl acetate	298.15	1.30	[20]	1.41 ± 0.14	1.04 ± 0.09
69. oxolan-2-one	293.15	0.74	[20]	0.80 ± 0.09	0.69 ± 0.09
70. acetyl acetate	293.15	1.15	[20]	0.83 ± 0.16	0.85 ± 0.05
71. 1,4-dichlorobutane	298.15	1.00	[20]	0.92 ± 0.10	1.10 ± 0.11
72. oxolane	298.15	1.29	[9]	1.32 ± 0.15	1.83 ± 0.15
73. ethoxyethene	293.15	1.57	[20]	1.82 ± 0.24	1.65 ± 0.08
74. ethyl acetate	293.15	1.30	[20]	0.99 ± 0.12	1.35 ± 0.11
...	298.15	1.38	[9]	1.44 ± 0.16	1.16 ± 0.04
75. tetrahydrothiophene 1,1-dioxide	320.00			0.88 ± 0.11	0.88 ± 0.08
76. thiolane	293.15	0.76	[20]	1.48 ± 0.14	1.17 ± 0.07
...	298.15	0.95	[9]	1.07 ± 0.11	1.07 ± 0.13
77. 1-bromobutane	293.15	1.11	[20]	1.47 ± 0.13	1.19 ± 0.12
...	298.15	1.14	[9]	1.30 ± 0.10	1.21 ± 0.12
78. 1-chlorobutane	293.15	1.28	[20]	1.53 ± 0.15	1.34 ± 0.10
...	298.15	0.80	[9]	1.34 ± 0.13	1.56 ± 0.08
79. pyrrolidine	293.15	1.06	[20]	1.16 ± 0.16	1.51 ± 0.16
...	298.15	1.13	[9]	1.25 ± 0.10	1.38 ± 0.13

Table S6: Thermal expansion coefficient - continued

Name	Experiment			GAFF	OPLS/AA
	T	α_P	Ref.	α_P	α_P
80. N,N-dimethylacetamide	298.15	0.98	[9]	1.21 ± 0.15	1.03 ± 0.11
81. morpholine	293.15	0.91	[20]	0.81 ± 0.11	1.01 ± 0.13
82. pyridine	293.15	1.08	[20]	1.06 ± 0.08	1.02 ± 0.08
...	298.15	1.02	[9]	1.14 ± 0.15	1.07 ± 0.11
83. cyclopentanone	293.15	1.01	[20]	1.04 ± 0.10	1.09 ± 0.08
...	298.15	1.02	[9]	0.86 ± 0.13	0.92 ± 0.08
84. 1-cyclopropylethanone	293.15			1.04 ± 0.23	1.24 ± 0.05
...	298.15			1.13 ± 0.16	1.29 ± 0.09
85. pentane-2,4-dione	298.15	1.09	[9]	0.85 ± 0.17	1.02 ± 0.07
86. methyl 2-methylprop-2-enoate	298.15	1.20	[20]	1.05 ± 0.10	1.03 ± 0.11
87. pentanenitrile	293.15	1.04	[20]	1.09 ± 0.17	1.27 ± 0.11
...	298.15	1.06	[9]	1.19 ± 0.12	1.43 ± 0.14
88. ethyl propanoate	298.15	1.25	[9]	1.39 ± 0.17	1.24 ± 0.10
89. diethyl carbonate	298.15	1.10	[9]	0.72 ± 0.16	1.10 ± 0.08
90. pentan-1-ol	293.15	0.95	[20]	0.98 ± 0.09	1.00 ± 0.15
...	298.15	0.89	[9]	0.86 ± 0.11	1.11 ± 0.11
...	320.00	1.02	[20]	1.01 ± 0.17	1.35 ± 0.14
91. pentan-3-ol	293.15	1.20	[20]	0.98 ± 0.16	1.04 ± 0.11
...	298.15	1.20	[20]	1.25 ± 0.22	1.51 ± 0.13
92. 2-methylbutan-2-ol	293.15			0.89 ± 0.18	1.51 ± 0.07
...	298.15	1.14	[9]	0.92 ± 0.11	1.23 ± 0.14
...	320.00			1.03 ± 0.12	1.65 ± 0.12
93. pentane-1,5-diol	293.15	0.88	[20]	0.64 ± 0.10	0.48 ± 0.14
...	298.15	0.61	[9]	0.56 ± 0.15	0.86 ± 0.12
94. pentan-3-amine	293.15	1.31	[20]	1.37 ± 0.19	1.36 ± 0.13
...	298.15	1.30	[20]	1.41 ± 0.13	1.62 ± 0.17
95. 1,2,3,4-tetrafluorobenzene	298.15			1.77 ± 0.05	1.52 ± 0.08
96. 1,2,3,5-tetrafluorobenzene	298.15			1.80 ± 0.14	1.77 ± 0.07
97. 1,3-difluorobenzene	293.15	1.18	[20]	1.71 ± 0.14	1.59 ± 0.05
...	298.15	1.20	[20]	1.36 ± 0.12	1.75 ± 0.09
98. 1,2-difluorobenzene	293.15	1.17	[20]	1.58 ± 0.10	1.38 ± 0.08
...	298.15	1.20	[20]	1.53 ± 0.11	1.67 ± 0.10

Table S6: Thermal expansion coefficient - continued

Name	Experiment			GAFF	OPLS/AA
	T	α_P	Ref.	α_P	α_P
99. fluorobenzene	293.15	1.12	[20]	1.53 ± 0.09	1.25 ± 0.09
...	298.15	1.18	[9]	1.60 ± 0.10	1.20 ± 0.05
100. nitrobenzene	293.15	0.81	[20]	0.65 ± 0.07	0.66 ± 0.06
...	298.15	0.85	[9]	0.77 ± 0.08	0.82 ± 0.09
101. 2-chloroaniline	293.15			0.86 ± 0.10	0.90 ± 0.07
102. phenol	318.15	0.80	[20]	1.15 ± 0.08	0.92 ± 0.11
103. benzenethiol	293.15	0.88	[20]	1.28 ± 0.09	1.18 ± 0.05
...	298.15	0.90	[20]	1.38 ± 0.05	1.11 ± 0.10
104. 2-methylpyridine	293.15	0.98	[20]	1.01 ± 0.17	1.10 ± 0.10
...	298.15	0.99	[9]	0.96 ± 0.13	1.14 ± 0.05
105. 3-methylpyridine	293.15	0.96	[20]	1.15 ± 0.07	1.11 ± 0.08
...	298.15	0.97	[9]	0.97 ± 0.10	0.96 ± 0.10
106. 4-methylpyridine	293.15	0.94	[20]	1.20 ± 0.11	0.99 ± 0.13
...	298.15	0.96	[9]	1.29 ± 0.16	0.95 ± 0.11
107. cyclohexanone	293.15	0.89	[20]	1.12 ± 0.14	1.02 ± 0.12
...	298.15	0.95	[9]	1.05 ± 0.13	0.99 ± 0.07
108. (E)-hex-2-ene	293.15			1.70 ± 0.10	1.53 ± 0.16
109. hexan-2-one	298.15	1.10	[20]	1.45 ± 0.18	1.28 ± 0.15
110. 2,4,6-trimethyl-1,3,5-trioxane	293.15	1.10	[20]	0.63 ± 0.22	1.18 ± 0.09
111. cyclohexanamine	298.15	1.00	[20]	0.83 ± 0.18	1.20 ± 0.16
112. 2-propan-2-yloxypropane	298.15	1.48	[9]	1.46 ± 0.21	1.59 ± 0.12
113. 1-methoxy-2-(2-methoxyethoxy)ethane	293.15	1.05	[20]	0.84 ± 0.21	0.91 ± 0.21
...	298.15	1.07	[9]	1.10 ± 0.13	1.03 ± 0.14
114. triethyl phosphate	293.15	0.91	[20]	1.21 ± 0.19	1.01 ± 0.13
...	298.15	0.96	[9]	0.24 ± 0.20	1.03 ± 0.13
...	320.00	0.95	[20]	1.03 ± 0.17	0.94 ± 0.12
115. N,N-diethylethanamine	293.15	1.22	[20]	1.33 ± 0.08	1.46 ± 0.12
...	298.15	1.30	[9]	1.47 ± 0.20	1.79 ± 0.17
116. N-propan-2-ylpropan-2-amine	293.15	1.28	[20]	1.22 ± 0.24	1.49 ± 0.13
...	298.15	1.30	[20]	1.19 ± 0.16	1.35 ± 0.14
117. trifluoromethylbenzene	293.15	1.14	[20]	1.28 ± 0.06	1.23 ± 0.13
...	298.15	1.20	[20]	1.36 ± 0.08	1.35 ± 0.09

Table S6: Thermal expansion coefficient - continued

Name	Experiment			GAFF	OPLS/AA
	T	α_P	Ref.	α_P	α_P
118. benzonitrile	288.15	0.83	[20]	1.05 ± 0.13	0.89 ± 0.05
119. benzaldehyde	298.15	0.25	[9]	1.06 ± 0.06	0.77 ± 0.06
120. toluene	298.15	1.07	[9]	1.62 ± 0.15	1.49 ± 0.04
121. methoxybenzene	293.15	0.91	[20]	1.05 ± 0.12	1.22 ± 0.10
...	298.15	0.95	[9]	1.18 ± 0.13	1.08 ± 0.09
122. phenylmethanol	297.15	0.69	[20]	0.81 ± 0.07	0.80 ± 0.17
123. 2-methylphenol	308.15	0.79	[20]	0.96 ± 0.13	0.93 ± 0.08
124. 3-methylphenol	320.00	0.75	[20]	1.00 ± 0.12	0.98 ± 0.14
125. 4-methylphenol	313.15	0.85	[20]	0.96 ± 0.07	0.81 ± 0.07
...	320.00	0.86	[20]	0.81 ± 0.12	0.86 ± 0.14
126. diethyl propanedioate	293.15	0.99	[20]	0.93 ± 0.16	0.97 ± 0.09
127. 2,4-dimethylpentan-3-one	293.15	1.12	[20]	0.95 ± 0.14	1.15 ± 0.09
...	298.15	1.10	[20]	1.08 ± 0.17	1.10 ± 0.14
128. heptan-2-one	293.15	1.05	[20]	1.46 ± 0.17	1.17 ± 0.12
...	298.15	1.06	[9]	0.91 ± 0.17	1.01 ± 0.12
129. ethenylbenzene	298.15	0.97	[9]	1.14 ± 0.11	1.18 ± 0.11
130. 1-phenylethanone	293.15			1.01 ± 0.10	0.92 ± 0.09
...	298.15	0.84	[9]	1.00 ± 0.08	0.89 ± 0.08
131. methyl benzoate	298.15	0.88	[9]	0.72 ± 0.10	0.71 ± 0.12
132. methyl 2-hydroxybenzoate	298.15	0.70	[20]	0.99 ± 0.11	0.80 ± 0.08
...	320.00	0.78	[20]	0.94 ± 0.11	0.89 ± 0.07
133. ethylbenzene	298.15	1.02	[9]	1.35 ± 0.16	1.19 ± 0.10
134. 1,2-dimethylbenzene	293.15	0.92	[20]	1.17 ± 0.17	1.20 ± 0.13
...	298.15	0.95	[9]	1.40 ± 0.12	1.05 ± 0.09
135. 1,2-dimethoxybenzene	298.15	0.93	[9]	0.97 ± 0.10	1.00 ± 0.08
136. 2,4,6-trimethylpyridine	295.15	0.92	[20]	0.92 ± 0.39	0.89 ± 0.09
...	298.15	0.83	[9]	0.86 ± 0.54	0.99 ± 0.09
137. octan-1-ol	298.15	0.84	[9]	0.64 ± 0.18	0.70 ± 0.14
...	320.00	0.94	[20]	0.89 ± 0.15	2.09 ± 0.16
138. 1-butoxybutane	293.15	1.09	[20]	1.42 ± 0.25	1.51 ± 0.11
...	298.15	1.13	[9]	0.77 ± 0.18	1.52 ± 0.14
139. N-butylbutan-1-amine	293.15	1.01	[20]	1.25 ± 0.24	1.18 ± 0.08
...	298.15	1.12	[9]	1.27 ± 0.15	1.41 ± 0.16

Table S6: Thermal expansion coefficient - continued

Name	Experiment			GAFF	OPLS/AA
	T	α_P	Ref.	α_P	α_P
140. isoquinoline	303.15	0.68	[20]	0.84 ± 0.11	0.45 ± 0.14
...	320.00	0.70	[20]	0.81 ± 0.11	0.91 ± 0.12
141. quinoline	288.15	0.66	[20]	0.94 ± 0.11	0.81 ± 0.07
...	298.15	0.73	[9]	0.78 ± 0.08	0.90 ± 0.04
142. (1-methylethyl)benzene	298.15	0.98	[9]	1.43 ± 0.17	0.99 ± 0.10
143. 1,2,4-trimethylbenzene	293.15	0.89	[20]	1.15 ± 0.18	1.23 ± 0.09
...	298.15	0.90	[20]	1.05 ± 0.12	0.99 ± 0.12
144. 2,6-dimethylheptan-4-one	293.15	0.95	[20]	1.42 ± 0.21	1.07 ± 0.16
...	298.15	1.00	[20]	0.93 ± 0.27	1.33 ± 0.16
145. 1-chloronaphthalene	298.15	0.70	[20]	0.75 ± 0.11	0.99 ± 0.11
146. phenoxybenzene	303.15	0.65	[20]	0.74 ± 0.14	0.76 ± 0.11

Table S7: Isothermal compressibility κ_T (1/GPa), calculated and experimental Blue font indicates that the calculated value differs more than 10% from the experimental ones, a red font indicates that it differs by more than 25%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA
	T	κ_T	Ref.	κ_T	κ_T
1. chloroform	298.15	1.03	[9]	1.79 ± 0.06	2.16 ± 0.09
2. dichloro(fluoro)methane	282.05			2.56 ± 0.10	2.82 ± 0.12
3. dibromomethane	293.15			1.65 ± 0.05	0.86 ± 0.02
...	298.15	0.70	[9]	1.45 ± 0.05	0.91 ± 0.01
4. dichloromethane	293.15	0.99		1.30 ± 0.03	1.74 ± 0.07
...	298.15	1.03	[9]	1.47 ± 0.04	2.22 ± 0.09
5. methanal	253.15			1.18 ± 0.03	1.12 ± 0.03
...	253.65			1.15 ± 0.02	1.15 ± 0.04
6. methanoic acid	293.15			0.22 ± 0.00	0.54 ± 0.01
...	298.15	0.65	[9]	0.24 ± 0.01	0.54 ± 0.01
7. bromomethane	276.65			2.84 ± 0.11	1.14 ± 0.03
8. methanamide	298.15	0.40	[9]	0.29 ± 0.01	0.36 ± 0.01
9. nitromethane	293.15			0.30 ± 0.01	0.72 ± 0.01
...	298.15	0.72	[9]	0.31 ± 0.01	0.77 ± 0.01
10. methanol	293.15	1.22		1.01 ± 0.02	1.08 ± 0.03
...	298.15	1.25	[9]	1.02 ± 0.02	1.08 ± 0.02
11. 1,1,1,2,2-pentachloroethane	293.15			0.71 ± 0.01	0.77 ± 0.01
12. 1,1,2,2-tetrachloroethane	293.15	0.65		0.79 ± 0.02	0.80 ± 0.03
...	298.15	0.62	[9]	0.83 ± 0.03	0.84 ± 0.02
13. 1,1-dichloroethene	293.15			3.48 ± 0.14	1.84 ± 0.05
...	298.15			3.88 ± 0.17	2.13 ± 0.05
14. 1,1,2-trichloroethane	293.15	0.73		0.82 ± 0.02	0.80 ± 0.02
...	298.15	0.75		0.91 ± 0.02	0.80 ± 0.03
15. acetonitrile	293.15			1.15 ± 0.03	1.60 ± 0.03
...	298.15	1.07	[9]	1.18 ± 0.04	1.62 ± 0.05
16. 1,2-dibromoethane	298.15	0.64	[9]	1.17 ± 0.04	0.54 ± 0.02
17. 1,1-dichloroethane	293.15			1.22 ± 0.03	1.39 ± 0.03
...	298.15	1.15	[9]	1.26 ± 0.04	1.33 ± 0.04
18. 1,2-dichloroethane	298.15	0.82	[9]	0.86 ± 0.02	0.95 ± 0.03
19. methyl formate	293.15			0.57 ± 0.01	0.99 ± 0.04
...	298.15			0.62 ± 0.01	1.00 ± 0.02

Table S7: Isothermal compressibility - continued

Name	Experiment			GAFF	OPLS/AA
	T	κ_T	Ref.	κ_T	κ_T
20. bromoethane	293.15	1.19		1.92 ± 0.07	1.14 ± 0.03
...	298.15	1.25		2.10 ± 0.08	1.17 ± 0.03
21. chloroethane	273.15	1.02	[21]	1.63 ± 0.06	1.68 ± 0.05
...	285.45			1.91 ± 0.10	1.88 ± 0.05
22. 2-chloroethanol	293.15			0.49 ± 0.01	0.56 ± 0.02
23. ethanamide	358.15			0.48 ± 0.01	0.46 ± 0.01
...	494.30			1.20 ± 0.02	1.05 ± 0.03
24. N-methylformamide	292.15	0.58		0.41 ± 0.01	0.47 ± 0.01
...	298.15	0.56	[9]	0.41 ± 0.01	0.46 ± 0.01
25. nitroethane	298.15	0.79	[9]	0.41 ± 0.01	0.71 ± 0.02
26. methoxymethane	240.00			1.23 ± 0.04	1.51 ± 0.04
27. ethanol	293.15	1.10		0.91 ± 0.02	0.93 ± 0.03
...	298.15	1.15	[9]	0.98 ± 0.03	0.95 ± 0.01
28. 1,2-ethanedithiol	293.15			0.67 ± 0.02	0.51 ± 0.01
...	298.15			0.74 ± 0.01	0.50 ± 0.01
29. methylsulfanylmethane	293.15			1.17 ± 0.04	0.99 ± 0.01
...	298.15			1.28 ± 0.02	1.01 ± 0.03
30. methylsulfinylmethane	298.15	0.52	[9]	0.41 ± 0.01	0.41 ± 0.01
31. methylsulfanylmethane	293.15			2.07 ± 0.07	1.23 ± 0.04
...	298.15			2.22 ± 0.08	1.28 ± 0.04
32. 2-aminoethanol	293.15	0.38		0.22 ± 0.01	0.45 ± 0.01
...	320.00	0.44		0.25 ± 0.01	0.55 ± 0.01
33. ethane-1,2-diamine	293.15			0.34 ± 0.01	0.53 ± 0.01
...	298.15	0.51	[9]	0.33 ± 0.01	0.53 ± 0.02
34. prop-2-enenitrile	298.15			1.33 ± 0.03	1.00 ± 0.02
...	350.45			2.36 ± 0.09	1.74 ± 0.05
35. 1,3-dioxolan-2-one	312.15			0.26 ± 0.01	0.32 ± 0.01
36. propanenitrile	293.15			1.05 ± 0.03	1.41 ± 0.04
...	298.15	1.11	[9]	1.14 ± 0.03	1.50 ± 0.05
37. 1,2-dibromopropane	293.15			0.89 ± 0.02	0.49 ± 0.01
...	298.15			0.96 ± 0.03	0.52 ± 0.01
38. 1,3-dichloropropane	298.15	0.76		0.83 ± 0.02	0.85 ± 0.01

Table S7: Isothermal compressibility - continued

Name	Experiment			GAFF	OPLS/AA
	T	κ_T	Ref.	κ_T	κ_T
39. (2R)-2-methyloxirane	298.15			1.47 ± 0.04	1.70 ± 0.04
40. propan-2-one	298.15	1.32	[9]	1.14 ± 0.02	1.31 ± 0.02
41. methyl acetate	293.15	1.10		0.64 ± 0.01	0.76 ± 0.02
...	298.15	1.14	[9]	0.69 ± 0.02	0.83 ± 0.01
42. 1,3-dioxolane	293.15	0.72		0.44 ± 0.01	0.69 ± 0.01
...	298.15	0.76		0.47 ± 0.01	0.77 ± 0.02
43. 2-iodopropane	293.15			1.20 ± 0.03	0.93 ± 0.02
...	298.15			1.26 ± 0.03	1.01 ± 0.03
44. 1-bromopropane	293.15	1.09		1.31 ± 0.03	0.96 ± 0.03
...	298.15	1.13		1.47 ± 0.05	0.99 ± 0.02
45. N,N-dimethylformamide	298.15	0.64	[9]	0.48 ± 0.01	0.58 ± 0.01
46. N-methylacetamide	320.00			0.55 ± 0.02	0.50 ± 0.01
47. 1-nitropropane	298.15	0.80	[9]	0.44 ± 0.01	0.74 ± 0.01
48. 2-nitropropane	298.15	0.89	[9]	0.47 ± 0.01	0.73 ± 0.02
49. dimethoxymethane	293.15			0.88 ± 0.03	1.15 ± 0.02
...	298.15			1.02 ± 0.03	1.18 ± 0.01
50. propane-1,2,3-triol	293.15	0.24		0.15 ± 0.00	0.22 ± 0.01
...	320.00	0.26		0.31 ± 0.01	0.33 ± 0.02
51. propan-1-amine	293.15	1.16		0.97 ± 0.02	1.49 ± 0.04
...	298.15	1.21		1.00 ± 0.03	1.55 ± 0.03
52. propan-2-amine	293.15			0.90 ± 0.02	1.40 ± 0.05
...	298.15			0.95 ± 0.02	1.50 ± 0.05
53. 2-methylpropane	243.65			1.45 ± 0.03	1.66 ± 0.04
54. ethylsulfanyethane	293.15			1.27 ± 0.04	0.98 ± 0.02
...	298.15			1.34 ± 0.05	1.06 ± 0.03
55. butane-1-thiol	293.15			1.06 ± 0.02	0.89 ± 0.02
...	298.15			1.10 ± 0.03	0.95 ± 0.02
56. butan-1-ol	293.15	0.91		0.73 ± 0.02	0.86 ± 0.02
...	298.15	0.94	[9]	0.77 ± 0.03	0.88 ± 0.02
57. 2-methylpropan-2-ol	320.00			1.03 ± 0.03	1.08 ± 0.02
58. butane-1,4-diol	293.15			0.30 ± 0.02	0.32 ± 0.01
...	298.15	0.44	[9]	0.32 ± 0.02	0.34 ± 0.01
...	320.00			0.33 ± 0.01	0.38 ± 0.01

Table S7: Isothermal compressibility - continued

Name	Experiment			GAFF	OPLS/AA
	T	κ_T	Ref.	κ_T	κ_T
59. (2-hydroxyethoxy)ethan-2-ol	288.15			0.16 ± 0.00	0.35 ± 0.02
60. N-ethylethanamine	293.15			1.15 ± 0.04	1.54 ± 0.03
...	298.15	1.51	[9]	1.18 ± 0.02	1.62 ± 0.04
61. butan-1-amine	293.15			0.85 ± 0.02	1.20 ± 0.03
...	298.15	1.14	[9]	0.90 ± 0.02	1.28 ± 0.03
62. 2-methylpropan-2-amine	293.15			0.86 ± 0.03	1.15 ± 0.02
...	298.15			0.93 ± 0.02	1.25 ± 0.03
63. 2-(2-hydroxyethylamino)ethanol	320.00			0.23 ± 0.01	0.37 ± 0.02
64. pyrimidine	298.15			0.41 ± 0.01	0.44 ± 0.02
65. furan	293.15			1.00 ± 0.03	0.99 ± 0.06
...	298.15			1.01 ± 0.04	1.04 ± 0.03
66. thiophene	293.15			0.97 ± 0.02	0.63 ± 0.03
...	298.15			0.96 ± 0.03	0.62 ± 0.03
67. 1H-pyrrole	293.15			0.52 ± 0.01	0.57 ± 0.01
...	298.15	0.65	[9]	0.51 ± 0.01	0.60 ± 0.01
68. ethenyl acetate	298.15			0.78 ± 0.02	0.67 ± 0.02
69. oxolan-2-one	293.15			0.34 ± 0.01	0.42 ± 0.01
70. acetyl acetate	293.15			0.39 ± 0.01	0.36 ± 0.01
71. 1,4-dichlorobutane	298.15	0.69		0.71 ± 0.02	0.80 ± 0.01
72. oxolane	298.15	0.95	[9]	0.76 ± 0.02	1.10 ± 0.02
73. ethoxyethene	293.15			1.50 ± 0.03	1.40 ± 0.04
74. ethyl acetate	293.15			0.71 ± 0.02	0.76 ± 0.02
...	298.15	1.21	[9]	0.74 ± 0.02	0.80 ± 0.02
75. tetrahydrothiophene 1,1-dioxide	320.00			0.26 ± 0.01	0.36 ± 0.01
76. thiolane	293.15			0.73 ± 0.02	0.65 ± 0.02
...	298.15			0.77 ± 0.02	0.67 ± 0.04
77. 1-bromobutane	293.15			1.15 ± 0.03	0.88 ± 0.03
...	298.15	1.03	[9]	1.20 ± 0.02	0.93 ± 0.03
78. 1-chlorobutane	293.15	1.07		1.24 ± 0.04	1.26 ± 0.02
...	298.15	1.21		1.23 ± 0.02	1.34 ± 0.01
79. pyrrolidine	293.15			0.64 ± 0.01	0.96 ± 0.03
...	298.15	0.81	[9]	0.66 ± 0.02	0.92 ± 0.02

Table S7: Isothermal compressibility - continued

Name	Experiment			GAFF	OPLS/AA
	T	κ_T	Ref.	κ_T	κ_T
80. N,N-dimethylacetamide	298.15	0.63	[9]	0.56 ± 0.02	0.53 ± 0.00
81. morpholine	293.15			0.32 ± 0.01	0.51 ± 0.02
82. pyridine	293.15	0.67		0.59 ± 0.02	0.60 ± 0.02
...	298.15	0.71	[9]	0.64 ± 0.02	0.64 ± 0.03
83. cyclopentanone	293.15			0.57 ± 0.01	0.66 ± 0.01
...	298.15			0.56 ± 0.02	0.69 ± 0.01
84. 1-cyclopropylethanone	293.15			0.76 ± 0.01	0.72 ± 0.02
...	298.15			0.75 ± 0.02	0.76 ± 0.03
85. pentane-2,4-dione	298.15			0.51 ± 0.01	0.50 ± 0.01
86. methyl 2-methylprop-2-enoate	298.15			0.73 ± 0.03	0.61 ± 0.01
87. pentanenitrile	293.15	0.91		0.84 ± 0.01	1.09 ± 0.03
...	298.15	0.95		0.88 ± 0.02	1.15 ± 0.03
88. ethyl propanoate	298.15	1.30	[9]	0.77 ± 0.01	0.77 ± 0.01
89. diethyl carbonate	298.15	1.00	[9]	0.53 ± 0.01	0.68 ± 0.02
90. pentan-1-ol	293.15	0.85		0.69 ± 0.03	0.80 ± 0.02
...	298.15	0.88	[9]	0.74 ± 0.02	0.82 ± 0.01
...	320.00	1.01		0.81 ± 0.02	1.02 ± 0.01
91. pentan-3-ol	293.15	0.89		0.74 ± 0.03	0.77 ± 0.01
...	298.15	0.93		0.76 ± 0.02	0.88 ± 0.02
92. 2-methylbutan-2-ol	293.15	1.03		0.70 ± 0.02	0.82 ± 0.02
...	298.15	1.11	[9]	0.69 ± 0.02	0.87 ± 0.02
...	320.00			0.91 ± 0.02	1.07 ± 0.02
93. pentane-1,5-diol	293.15	0.40		0.29 ± 0.02	0.29 ± 0.01
...	298.15	0.46	[9]	0.30 ± 0.01	0.41 ± 0.01
94. pentan-3-amine	293.15			0.84 ± 0.03	1.08 ± 0.03
...	298.15			0.91 ± 0.01	1.15 ± 0.03
95. 1,2,3,4-tetrafluorobenzene	298.15			1.84 ± 0.06	1.39 ± 0.03
96. 1,2,3,5-tetrafluorobenzene	298.15			1.96 ± 0.09	1.51 ± 0.04
97. 1,3-difluorobenzene	293.15			1.45 ± 0.05	1.28 ± 0.05
...	298.15			1.25 ± 0.05	1.44 ± 0.06
98. 1,2-difluorobenzene	293.15			1.43 ± 0.03	1.20 ± 0.05
...	298.15			1.26 ± 0.02	1.40 ± 0.05

Table S7: Isothermal compressibility - continued

Name	Experiment			GAFF	OPLS/AA
	T	κ_T	Ref.	κ_T	κ_T
99. fluorobenzene	293.15			1.31 ± 0.04	0.94 ± 0.01
...	298.15	0.94	[9]	1.26 ± 0.05	1.01 ± 0.02
100. nitrobenzene	293.15			0.33 ± 0.01	0.47 ± 0.01
...	298.15	0.51	[9]	0.34 ± 0.00	0.48 ± 0.01
101. 2-chloroaniline	293.15			0.51 ± 0.01	0.47 ± 0.01
102. phenol	318.15			0.61 ± 0.02	0.54 ± 0.02
103. benzenethiol	293.15			0.85 ± 0.02	0.86 ± 0.02
...	298.15			0.85 ± 0.02	0.83 ± 0.03
104. 2-methylpyridine	293.15			0.69 ± 0.02	0.62 ± 0.02
...	298.15			0.72 ± 0.01	0.63 ± 0.02
105. 3-methylpyridine	293.15			0.67 ± 0.02	0.58 ± 0.02
...	298.15			0.66 ± 0.01	0.59 ± 0.01
106. 4-methylpyridine	293.15			0.64 ± 0.02	0.60 ± 0.01
...	298.15	0.70	[9]	0.67 ± 0.02	0.60 ± 0.02
107. cyclohexanone	293.15			0.52 ± 0.01	0.60 ± 0.02
...	298.15	0.66	[9]	0.56 ± 0.02	0.65 ± 0.02
108. (E)-hex-2-ene	293.15			1.86 ± 0.08	1.55 ± 0.04
109. hexan-2-one	298.15	1.01		0.87 ± 0.02	0.93 ± 0.03
110. 2,4,6-trimethyl-1,3,5-trioxane	293.15			0.31 ± 0.01	0.55 ± 0.01
111. cyclohexanamine	298.15			0.50 ± 0.01	0.68 ± 0.01
112. 2-propan-2-yloxypropane	298.15	1.61	[9]	1.08 ± 0.02	1.48 ± 0.05
113. 1-methoxy-2-(2-methoxyethoxy)ethane	293.15			0.46 ± 0.01	0.64 ± 0.02
...	298.15	0.64		0.46 ± 0.01	0.68 ± 0.01
114. triethyl phosphate	293.15			0.46 ± 0.01	0.54 ± 0.01
...	298.15	1.49	[9]	0.37 ± 0.01	0.58 ± 0.02
...	320.00			0.47 ± 0.01	0.66 ± 0.02
115. N,N-diethylethanamine	293.15			0.96 ± 0.02	1.28 ± 0.03
...	298.15	1.38	[9]	1.03 ± 0.02	1.34 ± 0.04
116. N-propan-2-ylpropan-2-amine	293.15			0.93 ± 0.01	1.19 ± 0.02
...	298.15	1.45		0.99 ± 0.04	1.26 ± 0.02
117. trifluoromethylbenzene	293.15			1.05 ± 0.02	1.11 ± 0.04
...	298.15			1.16 ± 0.03	1.15 ± 0.02

Table S7: Isothermal compressibility - continued

Name	Experiment			GAFF	OPLS/AA
	T	κ_T	Ref.	κ_T	κ_T
118. benzonitrile	288.15			0.68 ± 0.02	0.48 ± 0.01
119. benzaldehyde	298.15	0.23	[9]	0.58 ± 0.01	0.48 ± 0.01
120. toluene	298.15	0.92	[9]	1.06 ± 0.03	0.88 ± 0.03
121. methoxybenzene	293.15			0.66 ± 0.02	0.62 ± 0.01
...	298.15	0.69	[9]	0.65 ± 0.01	0.65 ± 0.02
122. phenylmethanol	297.15			0.51 ± 0.01	0.46 ± 0.02
123. 2-methylphenol	308.15			0.52 ± 0.02	0.50 ± 0.01
124. 3-methylphenol	320.00	0.61		0.56 ± 0.01	0.53 ± 0.01
125. 4-methylphenol	313.15			0.60 ± 0.01	0.49 ± 0.02
...	320.00			0.63 ± 0.03	0.48 ± 0.02
126. diethyl propanedioate	293.15			0.42 ± 0.01	0.49 ± 0.01
127. 2,4-dimethylpentan-3-one	293.15			0.80 ± 0.02	0.82 ± 0.02
...	298.15			0.77 ± 0.02	0.84 ± 0.02
128. heptan-2-one	293.15	0.93		0.79 ± 0.02	0.83 ± 0.02
...	298.15	0.96		0.79 ± 0.01	0.87 ± 0.02
129. ethenylbenzene	298.15			0.88 ± 0.02	0.74 ± 0.02
130. 1-phenylethanone	293.15			0.54 ± 0.01	0.44 ± 0.01
...	298.15	0.56	[9]	0.54 ± 0.01	0.48 ± 0.01
131. methyl benzoate	298.15	0.45	[9]	0.47 ± 0.01	0.47 ± 0.01
132. methyl 2-hydroxybenzoate	298.15			0.37 ± 0.01	0.39 ± 0.01
...	320.00			0.47 ± 0.02	0.47 ± 0.01
133. ethylbenzene	298.15	0.86	[9]	0.96 ± 0.02	0.83 ± 0.01
134. 1,2-dimethylbenzene	293.15	0.78		0.93 ± 0.02	0.70 ± 0.03
...	298.15	0.81	[9]	0.98 ± 0.02	0.74 ± 0.02
135. 1,2-dimethoxybenzene	298.15			0.50 ± 0.01	0.53 ± 0.01
136. 2,4,6-trimethylpyridine	295.15			0.68 ± 0.02	0.59 ± 0.02
...	298.15			0.65 ± 0.01	0.58 ± 0.01
137. octan-1-ol	298.15	0.76	[9]	0.60 ± 0.02	0.49 ± 0.02
...	320.00	0.89		0.66 ± 0.02	0.91 ± 0.02
138. 1-butoxybutane	293.15			0.91 ± 0.02	1.09 ± 0.02
...	298.15			0.96 ± 0.03	1.13 ± 0.03
139. N-butylbutan-1-amine	293.15			0.83 ± 0.03	1.02 ± 0.03
...	298.15	1.06	[9]	0.86 ± 0.03	1.06 ± 0.04

Table S7: Isothermal compressibility - continued

Name	Experiment			GAFF	OPLS/AA
	T	κ_T	Ref.	κ_T	κ_T
140. isoquinoline	303.15			0.43 ± 0.01	0.27 ± 0.01
...	320.00			0.56 ± 0.02	0.42 ± 0.02
141. quinoline	288.15			0.50 ± 0.02	0.45 ± 0.01
...	298.15	0.44	[9]	0.49 ± 0.03	0.48 ± 0.02
142. (1-methylethyl)benzene	298.15	0.98	[9]	0.90 ± 0.01	0.79 ± 0.02
143. 1,2,4-trimethylbenzene	293.15	0.79		0.85 ± 0.02	0.68 ± 0.01
...	298.15	0.84		0.90 ± 0.02	0.70 ± 0.01
144. 2,6-dimethylheptan-4-one	293.15			0.73 ± 0.02	0.76 ± 0.02
...	298.15			0.77 ± 0.02	0.77 ± 0.02
145. 1-chloronaphthalene	298.15	0.49		0.53 ± 0.01	0.55 ± 0.01
146. phenoxybenzene	303.15			0.56 ± 0.03	0.46 ± 0.01

Table S8: Heat capacity at constant pressure c_P (J/mol K) calculated (based on density of states) and experimental. Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA
	T	c_P	Ref.	c_P	c_P
1. chloroform	298.15	117.00	[9]	94.2 ± 4.4	94.4 ± 7.7
2. dichloro(fluoro)methane	282.05	107.07	[13]	80.7 ± 5.8	78.9 ± 5.0
3. dibromomethane	298.15	104.90	[9]	83.1 ± 5.7	81.2 ± 4.4
4. dichloromethane	298.15	100.88	[13]	76.9 ± 4.0	70.4 ± 4.9
5. methanal	253.65	79.78	[22]	50.9 ± 2.5	57.1 ± 3.3
6. methanoic acid	298.15	99.00	[9]	74.8 ± 24.2	79.5 ± 5.9
7. bromomethane	276.65	78.75	[13]		59.2 ± 3.5
8. methanamide	298.15	107.60	[9]	83.0 ± 11.7	87.1 ± 7.9
9. nitromethane	298.15	105.80	[9]	101.9 ± 15.8	96.6 ± 6.8
10. methanol	298.15	81.47	[9]	73.4 ± 9.3	75.8 ± 4.8
11. 1,1,1,2,2-pentachloroethane	293.15	173.96	[22]	154.6 ± 14.8	154.8 ± 5.2
12. 1,1,2,2-tetrachloroethane	298.15	165.70	[9]	139.7 ± 16.5	135.4 ± 12.3
13. 1,1-dichloroethene	298.15	111.33	[13]	81.8 ± 6.9	86.7 ± 5.9
14. 1,1,2-trichloroethane	298.15	148.50	[9]	122.6 ± 10.3	119.7 ± 12.8
15. acetonitrile	298.15	91.40	[9]	74.7 ± 5.2	58.2 ± 4.4
16. 1,2-dibromoethane	298.15	136.00	[9]	105.1 ± 6.8	112.6 ± 12.2
17. 1,1-dichloroethane	298.15	126.20	[9]	106.9 ± 7.7	103.8 ± 7.0
18. 1,2-dichloroethane	298.15	128.90	[9]	104.4 ± 9.0	106.6 ± 7.2
19. methyl formate	298.15	119.70	[9]	100.2 ± 11.9	102.6 ± 6.7
20. bromoethane	298.15	99.73	[13]	84.4 ± 7.7	90.6 ± 6.4
21. chloroethane	273.15	101.18	[13]	82.9 ± 12.4	83.2 ± 6.5
...	285.45	102.80	[13]	83.1 ± 12.4	82.8 ± 5.0
22. 2-chloroethanol	293.15	109.03	[13]	117.6 ± 19.6	120.0 ± 16.5
23. ethanamide	358.15	148.39	[13]	133.0 ± 29.7	137.2 ± 13.8
24. N-methylformamide	298.15	123.80	[9]	115.0 ± 19.7	119.4 ± 10.8
25. nitroethane	298.15	138.50	[9]	131.7 ± 34.1	127.5 ± 9.9
27. ethanol	298.15	112.30	[9]	106.2 ± 16.5	109.0 ± 12.5
28. 1,2-ethanedithiol	298.15			133.5 ± 15.9	144.4 ± 14.5
29. methyldisulfanylmethane	298.15	145.96	[13]	126.9 ± 7.9	133.7 ± 12.3
30. methylsulfinylmethane	298.15	153.10	[9]	132.4 ± 16.7	132.0 ± 9.1

Table S8: Heat capacity at constant pressure c_p based on DoS - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_p	Ref.	c_p	c_p
31. methylsulfanylmethane	298.15	118.10	[9]	96.3 ± 13.1	105.7 ± 6.8
32. 2-aminoethanol	293.15			128.0 ± 47.4	133.5 ± 28.2
33. ethane-1,2-diamine	298.15	172.50	[9]	139.6 ± 29.5	143.4 ± 20.8
34. prop-2-enenitrile	298.15	108.60	[9]	83.4 ± 4.7	81.2 ± 10.8
...	350.45	114.98	[13]	89.3 ± 7.7	82.3 ± 5.2
35. 1,3-dioxolan-2-one	312.15	133.84	[13]	135.8 ± 18.5	142.4 ± 22.0
36. propanenitrile	298.15	119.70	[9]	105.0 ± 13.9	89.3 ± 7.5
37. 1,2-dibromopropane	298.15	172.80	[22]	136.9 ± 14.3	147.0 ± 16.7
38. 1,3-dichloropropane	298.15	159.45	[13]	136.2 ± 14.1	137.1 ± 14.0
39. (2R)-2-methyloxirane	298.15			103.0 ± 6.8	111.7 ± 36.9
40. propan-2-one	298.15	124.90	[9]	111.7 ± 18.9	117.3 ± 6.6
41. methyl acetate	298.15	143.90	[9]	133.4 ± 18.4	135.9 ± 11.8
42. 1,3-dioxolane	293.15	120.32	[23]	123.7 ± 21.8	124.3 ± 10.6
43. 2-iodopropane	298.15	139.72	[13]	123.6 ± 24.7	125.7 ± 12.5
44. 1-bromopropane	298.15	133.47	[13]	116.5 ± 15.8	122.8 ± 9.5
45. N,N-dimethylformamide	298.15	148.30	[9]	142.9 ± 28.4	148.9 ± 22.2
47. 1-nitropropane	298.15	175.30	[9]	161.7 ± 31.0	159.7 ± 16.0
48. 2-nitropropane	298.15	170.20	[9]	163.6 ± 28.9	163.6 ± 20.3
49. dimethoxymethane	298.15	161.50	[13]	144.1 ± 21.8	145.7 ± 14.6
50. propane-1,2,3-triol	293.15	216.70	[22]	171.3 ± 121.9	174.1 ± 43.9
51. propan-1-amine	298.15	162.79	[13]	138.5 ± 25.8	139.0 ± 7.2
52. propan-2-amine	298.15	163.81	[13]	142.5 ± 20.7	141.9 ± 13.4
54. ethylsulfanylethane	298.15	171.40	[9]	156.3 ± 24.1	167.8 ± 21.2
55. butane-1-thiol	298.15	171.20	[11]	161.2 ± 32.0	170.5 ± 21.9
56. butan-1-ol	298.15	177.00	[9]	168.1 ± 26.7	174.0 ± 25.6
58. butane-1,4-diol	298.15	202.20	[9]	185.1 ± 44.0	195.5 ± 63.8
59. (2-hydroxyethoxy)ethan-2-ol	288.15	256.39	[22]	197.6 ± 147.8	210.7 ± 51.8
60. N-ethylethanamine	298.15	176.70	[9]	161.7 ± 22.8	164.2 ± 10.6
61. butan-1-amine	298.15	188.00	[9]	170.5 ± 29.0	172.8 ± 12.8
62. 2-methylpropan-2-amine	298.15	192.10	[13]	180.1 ± 62.5	182.0 ± 12.0
64. pyrimidine	298.15	133.70	[9]	120.9 ± 25.9	124.6 ± 14.7
65. furan	298.15	114.80	[9]	97.3 ± 13.9	99.3 ± 9.0

Table S8: Heat capacity at constant pressure c_p based on DoS - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_p	Ref.	c_p	c_p
66. thiophene	298.15	123.98	[13]	104.4 ± 10.4	110.3 ± 16.9
67. 1H-pyrrole	298.15	128.20	[9]	113.9 ± 14.1	116.2 ± 14.7
68. ethenyl acetate	298.15	171.47	[13]	144.3 ± 20.3	150.9 ± 19.0
69. oxolan-2-one	293.15	139.96	[22]	140.5 ± 23.4	147.3 ± 27.2
70. acetyl acetate	293.15	189.13	[13]	172.0 ± 46.3	179.8 ± 15.1
71. 1,4-dichlorobutane	298.15	189.23	[13]	167.3 ± 25.6	169.3 ± 24.1
72. oxolane	298.15	123.90	[9]	131.6 ± 22.0	134.8 ± 16.0
73. ethoxyethene	293.15	153.58	[13]	130.4 ± 24.6	135.2 ± 10.0
74. ethyl acetate	298.15	167.70	[9]	164.6 ± 25.6	169.6 ± 10.0
76. thiolane	298.15	139.80	[9]	139.6 ± 20.7	147.2 ± 26.4
77. 1-bromobutane	298.15	168.10	[9]	147.0 ± 15.7	155.4 ± 22.9
78. 1-chlorobutane	298.15	174.60	[9]	146.2 ± 21.0	151.1 ± 10.9
79. pyrrolidine	298.15	156.50	[9]	141.3 ± 16.3	146.5 ± 19.4
80. N,N-dimethylacetamide	298.15	176.00	[9]	174.6 ± 31.7	182.3 ± 27.5
81. morpholine	293.15	173.88	[13]	160.6 ± 30.4	167.8 ± 30.0
82. pyridine	298.15	135.60	[9]	120.8 ± 23.3	125.9 ± 19.5
83. cyclopentanone	298.15	154.50	[9]	152.8 ± 32.9	159.1 ± 18.8
84. 1-cyclopropylethanone	298.15			158.4 ± 31.1	167.4 ± 18.2
85. pentane-2,4-dione	298.15	208.20	[9]	184.0 ± 53.4	197.2 ± 19.9
86. methyl 2-methylprop-2-enoate	298.15	189.82	[13]	178.1 ± 25.9	187.4 ± 29.4
87. pentanenitrile	298.15	189.70	[9]	167.8 ± 25.3	156.6 ± 22.0
88. ethyl propanoate	298.15	196.10	[9]	195.6 ± 34.6	203.0 ± 24.6
89. diethyl carbonate	298.15	212.40	[9]	219.5 ± 68.2	223.6 ± 24.1
90. pentan-1-ol	298.15	208.90	[9]	197.3 ± 35.2	207.3 ± 28.3
91. pentan-3-ol	298.15	247.72	[13]	200.7 ± 50.9	208.7 ± 25.9
92. 2-methylbutan-2-ol	298.15	244.30	[9]	204.2 ± 36.4	212.8 ± 33.9
93. pentane-1,5-diol	298.15	225.50	[9]	214.9 ± 82.7	228.2 ± 44.8
94. pentan-3-amine	298.15	205.13	[22]		206.7 ± 31.0
95. 1,2,3,4-tetrafluorobenzene	298.15	190.06	[23]	170.7 ± 8.8	173.4 ± 13.9
96. 1,2,3,5-tetrafluorobenzene	298.15	190.19	[23]	169.7 ± 19.5	176.0 ± 10.6
97. 1,3-difluorobenzene	298.15	159.10	[11]	140.5 ± 18.6	145.2 ± 12.3
98. 1,2-difluorobenzene	298.15	159.00	[11]	140.7 ± 14.0	146.4 ± 13.4

Table S8: Heat capacity at constant pressure c_p based on DoS - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_p	Ref.	c_p	c_p
99. fluorobenzene	298.15	146.30	[9]	126.9 ± 12.4	155.6 ± 9.9
100. nitrobenzene	298.15	177.20	[9]	177.9 ± 26.7	174.9 ± 27.9
101. 2-chloroaniline	293.15	196.88	[13]	174.5 ± 29.7	175.2 ± 20.7
102. phenol	318.15	202.77	[13]	160.4 ± 17.0	167.4 ± 29.7
103. benzenethiol	298.15	173.55	[13]	153.1 ± 8.6	153.4 ± 19.9
104. 2-methylpyridine	298.15	159.20	[9]	154.7 ± 30.6	161.4 ± 10.6
105. 3-methylpyridine	298.15	159.00	[9]	153.7 ± 21.8	161.6 ± 23.6
106. 4-methylpyridine	298.15	159.00	[9]	154.3 ± 28.1	160.6 ± 25.7
107. cyclohexanone	298.15	179.30	[9]	182.4 ± 33.3	193.2 ± 20.3
109. hexan-2-one	298.15	213.17	[13]	203.8 ± 36.5	213.9 ± 36.8
110. 2,4,6-trimethyl-1,3,5-trioxane	293.15	255.56	[13]	246.4 ± 124.1	249.4 ± 28.7
111. cyclohexanamine	298.15	200.84	[22]	207.9 ± 63.1	216.7 ± 40.7
112. 2-propan-2-yloxypropane	298.15	216.10	[9]	221.6 ± 44.7	225.5 ± 25.4
113. 1-methoxy-2-(2-methoxyethoxy)ethane	298.15	226.00	[9]	267.9 ± 46.0	273.6 ± 53.0
114. triethyl phosphate	298.15			325.4 ± 390.7	333.3 ± 60.5
115. N,N-diethylethanamine	298.15	224.40	[9]	221.5 ± 42.9	228.9 ± 30.9
116. N-propan-2-ylpropan-2-amine	298.15	226.35	[13]	230.0 ± 44.9	235.7 ± 33.7
117. trifluoromethylbenzene	298.15	188.80	[13]	185.2 ± 16.4	184.3 ± 18.1
118. benzonitrile	288.15	163.00	[13]	150.4 ± 26.0	165.2 ± 13.2
119. benzaldehyde	298.15	172.00	[9]	161.1 ± 14.0	169.5 ± 19.6
120. toluene	298.15	157.20	[9]	153.5 ± 21.1	161.7 ± 8.4
121. methoxybenzene	298.15	208.60	[9]	177.3 ± 28.1	179.6 ± 22.2
122. phenylmethanol	297.15	216.44	[13]	182.8 ± 23.5	188.8 ± 55.4
123. 2-methylphenol	308.15	234.03	[13]	194.2 ± 36.4	201.1 ± 24.4
125. 4-methylphenol	313.15	229.41	[13]	195.6 ± 20.1	203.5 ± 24.5
126. diethyl propanedioate	293.15	284.24	[13]	281.3 ± 68.0	293.6 ± 38.6
127. 2,4-dimethylpentan-3-one	298.15	235.51	[13]	244.2 ± 54.5	251.1 ± 44.3
128. heptan-2-one	298.15	243.60	[9]	235.3 ± 63.3	247.5 ± 42.5
129. ethenylbenzene	298.15	182.50	[9]	164.0 ± 22.5	171.2 ± 22.3
130. 1-phenylethanone	298.15	204.60	[9]	195.8 ± 21.9	202.7 ± 25.5
131. methyl benzoate	298.15	221.30	[9]	214.4 ± 43.8	221.7 ± 51.5
132. methyl 2-hydroxybenzoate	298.15	247.51	[13]	237.3 ± 37.0	250.1 ± 37.8

Table S8: Heat capacity at constant pressure c_p based on DoS - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_p	Ref.	c_p	c_p
133. ethylbenzene	298.15	185.50	[9]	182.8 ± 31.1	191.8 ± 22.6
134. 1,2-dimethylbenzene	298.15	188.00	[9]	189.6 ± 23.1	200.6 ± 25.7
135. 1,2-dimethoxybenzene	298.15			235.3 ± 35.0	238.2 ± 27.2
136. 2,4,6-trimethylpyridine	298.15	214.00	[9]	226.0 ± 199.7	235.2 ± 29.9
137. octan-1-ol	298.15	305.50	[9]	289.9 ± 113.2	304.8 ± 86.9
138. 1-butoxybutane	298.15	251.90	[9]	280.2 ± 95.7	289.4 ± 38.3
139. N-butylbutan-1-amine	298.15	292.80	[9]	288.2 ± 48.1	301.3 ± 51.0
141. quinoline	298.15	200.00	[9]	190.6 ± 28.6	194.1 ± 15.1
142. (1-methylethyl)benzene	298.15	198.90	[9]	217.9 ± 37.3	226.4 ± 32.2
144. 2,6-dimethylheptan-4-one	298.15	297.30	[11]	300.0 ± 124.7	317.0 ± 55.5
145. 1-chloronaphthalene	298.15	222.14	[13]	208.2 ± 41.6	211.9 ± 35.1
146. phenoxybenzene	303.15	269.87	[13]	262.9 ± 71.8	270.2 ± 56.0

Table S9: Heat capacity at constant volume c_V (J/mol K) calculated (based on density of states) compared to the experimental $c_P - \Delta c$ (J/mol K). Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA
	T	c_V	Ref.	c_V	c_V
1. chloroform	298.15	116.98	[9]	94.2 ± 0.6	94.3 ± 0.1
2. dichloro(fluoro)methane	282.05			80.7 ± 0.1	78.9 ± 0.3
3. dibromomethane	298.15	104.88	[9]	83.1 ± 0.3	81.2 ± 0.5
4. dichloromethane	298.15	100.86	[9]	76.9 ± 0.1	70.3 ± 0.3
5. methanal	253.65			50.9 ± 0.1	57.1 ± 0.2
6. methanoic acid	298.15	98.99	[9]	74.8 ± 0.2	79.5 ± 0.2
7. bromomethane	276.65				59.2 ± 0.1
8. methanamide	298.15	107.59	[9]	83.0 ± 0.2	87.1 ± 0.1
9. nitromethane	298.15	105.78	[9]	101.9 ± 0.2	96.6 ± 0.1
10. methanol	298.15	81.46	[9]	73.4 ± 0.1	75.8 ± 0.4
11. 1,1,1,2,2-pentachloroethane	293.15			154.6 ± 0.3	154.8 ± 0.5
12. 1,1,2,2-tetrachloroethane	298.15	165.67	[9]	139.7 ± 0.2	135.3 ± 0.2
13. 1,1-dichloroethene	298.15			81.8 ± 0.2	86.6 ± 0.2
14. 1,1,2-trichloroethane	298.15	148.48	[9]	122.6 ± 0.3	119.7 ± 0.3
15. acetonitrile	298.15	91.38	[9]	74.7 ± 0.2	58.1 ± 0.3
16. 1,2-dibromoethane	298.15	135.98	[9]	105.0 ± 0.3	112.6 ± 0.3
17. 1,1-dichloroethane	298.15	126.18	[9]	106.9 ± 0.4	103.7 ± 0.4
18. 1,2-dichloroethane	298.15	128.88	[9]	104.4 ± 0.3	106.5 ± 0.2
19. methyl formate	298.15			100.1 ± 0.2	102.6 ± 0.3
20. bromoethane	298.15	99.71	[20]	84.4 ± 0.2	90.6 ± 0.4
21. chloroethane	273.15	101.16	[20]	82.9 ± 0.3	83.2 ± 0.5
...	285.45			83.1 ± 0.4	82.8 ± 0.5
22. 2-chloroethanol	293.15			117.6 ± 0.3	120.0 ± 0.2
23. ethanamide	358.15			133.0 ± 0.2	137.2 ± 0.2
24. N-methylformamide	298.15	123.78	[9]	115.0 ± 0.2	119.4 ± 0.2
25. nitroethane	298.15	138.48	[9]	131.7 ± 0.4	127.5 ± 0.2
27. ethanol	298.15	112.29	[9]	106.1 ± 0.2	109.0 ± 0.1
28. 1,2-ethanedithiol	298.15			133.5 ± 0.3	144.4 ± 0.3
29. methylsulfanylmethane	298.15			126.8 ± 0.4	133.7 ± 0.3
30. methylsulfinylmethane	298.15	153.08	[9]	132.4 ± 0.1	131.9 ± 0.3

Table S9: Heat capacity at constant volume c_V based on DoS - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_V	Ref.	c_V	c_V
31. methylsulfanylmethane	298.15			96.3 ± 0.2	105.6 ± 0.3
32. 2-aminoethanol	293.15			128.0 ± 0.1	133.5 ± 0.1
33. ethane-1,2-diamine	298.15	172.49	[9]	139.6 ± 0.2	143.4 ± 0.2
34. prop-2-enenitrile	298.15			83.4 ± 0.2	81.2 ± 0.3
...	350.45			89.3 ± 0.2	82.3 ± 0.2
35. 1,3-dioxolan-2-one	312.15			135.8 ± 0.3	142.4 ± 0.2
36. propanenitrile	298.15	119.68	[9]	105.0 ± 0.3	89.3 ± 0.2
37. 1,2-dibromopropane	298.15			136.9 ± 0.2	147.0 ± 0.2
38. 1,3-dichloropropane	298.15	159.43	[20]	136.2 ± 0.2	137.0 ± 0.2
39. (2R)-2-methyloxirane	298.15			103.0 ± 0.4	111.6 ± 0.4
40. propan-2-one	298.15	124.88	[9]	111.7 ± 0.4	117.3 ± 0.1
41. methyl acetate	298.15	143.88	[9]	133.3 ± 0.1	135.9 ± 0.3
42. 1,3-dioxolane	293.15			123.7 ± 0.2	124.2 ± 0.3
43. 2-iodopropane	298.15			123.5 ± 0.2	125.7 ± 0.3
44. 1-bromopropane	298.15	133.44	[20]	116.5 ± 0.5	122.8 ± 0.3
45. N,N-dimethylformamide	298.15	148.28	[9]	142.9 ± 0.2	148.8 ± 0.4
47. 1-nitropropane	298.15	175.28	[9]	161.7 ± 0.2	159.7 ± 0.2
48. 2-nitropropane	298.15	170.18	[9]	163.6 ± 0.3	163.6 ± 0.4
49. dimethoxymethane	298.15			144.1 ± 0.3	145.6 ± 0.4
50. propane-1,2,3-triol	293.15	216.69	[20]	171.2 ± 0.3	174.1 ± 0.2
51. propan-1-amine	298.15	162.77	[20]	138.4 ± 0.3	138.9 ± 0.4
52. propan-2-amine	298.15			142.5 ± 0.2	141.8 ± 0.2
54. ethylsulfanylethane	298.15			156.3 ± 0.8	167.8 ± 0.2
55. butane-1-thiol	298.15			161.2 ± 0.2	170.4 ± 0.3
56. butan-1-ol	298.15	176.99	[9]	168.1 ± 0.2	174.0 ± 0.4
58. butane-1,4-diol	298.15	202.19	[9]	185.1 ± 0.2	195.4 ± 0.4
59. (2-hydroxyethoxy)ethan-2-ol	288.15			197.6 ± 0.2	210.7 ± 0.1
60. N-ethylethanamine	298.15	176.67	[9]	161.7 ± 0.4	164.1 ± 0.2
61. butan-1-amine	298.15	187.97	[9]	170.5 ± 0.6	172.8 ± 0.5
62. 2-methylpropan-2-amine	298.15			180.0 ± 0.2	181.9 ± 0.1
64. pyrimidine	298.15			120.8 ± 0.3	124.6 ± 0.1
65. furan	298.15			97.3 ± 0.2	99.3 ± 0.4

Table S9: Heat capacity at constant volume c_V based on DoS - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_V	Ref.	c_V	c_V
66. thiophene	298.15			104.4 ± 0.2	110.3 ± 0.0
67. 1H-pyrrole	298.15	128.19	[9]	113.8 ± 0.3	116.2 ± 0.2
68. ethenyl acetate	298.15			144.2 ± 0.5	150.8 ± 0.5
69. oxolan-2-one	293.15			140.5 ± 0.2	147.3 ± 0.3
70. acetyl acetate	293.15			172.0 ± 0.2	179.8 ± 0.2
71. 1,4-dichlorobutane	298.15	189.20	[20]	167.2 ± 0.3	169.3 ± 0.4
72. oxolane	298.15	123.87	[9]	131.6 ± 0.5	134.8 ± 0.4
73. ethoxyethene	293.15			130.3 ± 0.2	135.2 ± 0.4
74. ethyl acetate	298.15	167.67	[9]	164.5 ± 0.2	169.5 ± 0.4
76. thiolane	298.15			139.5 ± 0.2	147.2 ± 0.4
77. 1-bromobutane	298.15	168.07	[9]	147.0 ± 0.4	155.4 ± 0.2
78. 1-chlorobutane	298.15	174.59	[9]	146.2 ± 0.4	151.0 ± 0.3
79. pyrrolidine	298.15	156.48	[9]	141.3 ± 0.4	146.5 ± 0.4
80. N,N-dimethylacetamide	298.15	175.97	[9]	174.5 ± 0.2	182.2 ± 0.2
81. morpholine	293.15			160.5 ± 0.2	167.8 ± 0.2
82. pyridine	298.15	135.58	[9]	120.8 ± 0.3	125.9 ± 0.2
83. cyclopentanone	298.15			152.8 ± 0.2	159.1 ± 0.5
84. 1-cyclopropylethanone	298.15			158.4 ± 0.3	167.4 ± 0.6
85. pentane-2,4-dione	298.15			183.9 ± 0.3	197.2 ± 0.2
86. methyl 2-methylprop-2-enoate	298.15			178.1 ± 0.3	187.4 ± 0.3
87. pentanenitrile	298.15	189.68	[9]	167.8 ± 0.3	156.6 ± 0.4
88. ethyl propanoate	298.15	196.07	[9]	195.5 ± 0.8	202.9 ± 0.6
89. diethyl carbonate	298.15	212.37	[9]	219.5 ± 0.4	223.6 ± 0.4
90. pentan-1-ol	298.15	208.88	[9]	197.3 ± 0.3	207.2 ± 0.4
91. pentan-3-ol	298.15	247.69	[20]	200.6 ± 0.3	208.7 ± 0.2
92. 2-methylbutan-2-ol	298.15	244.28	[9]	204.2 ± 0.3	212.8 ± 0.3
93. pentane-1,5-diol	298.15	225.49	[9]	214.8 ± 0.1	228.2 ± 0.3
94. pentan-3-amine	298.15				206.6 ± 0.3
95. 1,2,3,4-tetrafluorobenzene	298.15			170.6 ± 0.3	173.3 ± 0.4
96. 1,2,3,5-tetrafluorobenzene	298.15			169.7 ± 0.4	175.9 ± 0.3
97. 1,3-difluorobenzene	298.15			140.5 ± 0.3	145.2 ± 0.2
98. 1,2-difluorobenzene	298.15			140.7 ± 0.5	146.3 ± 0.4

Table S9: Heat capacity at constant volume c_V based on DoS - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_V	Ref.	c_V	c_V
99. fluorobenzene	298.15	146.28	[9]	126.9 ± 0.4	155.5 ± 0.1
100. nitrobenzene	298.15	177.17	[9]	177.9 ± 0.3	174.9 ± 0.3
101. 2-chloroaniline	293.15			174.4 ± 0.4	175.1 ± 0.3
102. phenol	318.15			160.4 ± 0.3	167.4 ± 0.2
103. benzenethiol	298.15			153.1 ± 0.4	153.4 ± 0.1
104. 2-methylpyridine	298.15			154.6 ± 0.6	161.4 ± 0.5
105. 3-methylpyridine	298.15			153.7 ± 0.2	161.6 ± 0.3
106. 4-methylpyridine	298.15	158.98	[9]	154.2 ± 0.5	160.6 ± 0.4
107. cyclohexanone	298.15	179.27	[9]	182.3 ± 0.5	193.2 ± 0.3
109. hexan-2-one	298.15	213.14	[20]	203.7 ± 0.2	213.9 ± 0.4
110. 2,4,6-trimethyl-1,3,5-trioxane	293.15			246.4 ± 0.2	249.4 ± 0.4
111. cyclohexanamine	298.15			207.9 ± 0.1	216.7 ± 0.3
112. 2-propan-2-yloxypropane	298.15	216.06	[9]	221.6 ± 0.7	225.5 ± 0.5
113. 1-methoxy-2-(2-methoxyethoxy)ethane	298.15	225.95	[9]	267.8 ± 0.3	273.6 ± 0.5
114. triethyl phosphate	298.15			325.4 ± 0.2	333.2 ± 0.3
115. N,N-diethylethanamine	298.15	224.37	[9]	221.5 ± 0.5	228.8 ± 0.5
116. N-propan-2-ylpropan-2-amine	298.15	226.32	[20]	229.9 ± 0.5	235.6 ± 0.5
117. trifluoromethylbenzene	298.15			185.1 ± 0.5	184.2 ± 0.4
118. benzonitrile	288.15			150.3 ± 0.3	165.2 ± 0.2
119. benzaldehyde	298.15	172.00	[9]	161.1 ± 0.1	169.5 ± 0.5
120. toluene	298.15	157.18	[9]	153.5 ± 0.3	161.7 ± 0.4
121. methoxybenzene	298.15	208.57	[9]	177.3 ± 0.4	179.5 ± 0.3
122. phenylmethanol	297.15			182.7 ± 0.4	188.8 ± 0.3
123. 2-methylphenol	308.15			194.2 ± 0.2	201.0 ± 0.2
125. 4-methylphenol	313.15			195.6 ± 0.2	203.5 ± 0.4
126. diethyl propanedioate	293.15			281.2 ± 0.3	293.5 ± 0.4
127. 2,4-dimethylpentan-3-one	298.15			244.1 ± 0.4	251.1 ± 0.6
128. heptan-2-one	298.15	243.57	[9]	235.3 ± 0.8	247.4 ± 0.3
129. ethenylbenzene	298.15			163.9 ± 0.5	171.2 ± 0.3
130. 1-phenylethanone	298.15	204.57	[9]	195.8 ± 0.3	202.6 ± 0.3
131. methyl benzoate	298.15	221.26	[9]	214.4 ± 0.3	221.7 ± 0.4
132. methyl 2-hydroxybenzoate	298.15			237.2 ± 0.2	250.1 ± 0.4

Table S9: Heat capacity at constant volume c_V based on DoS - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_V	Ref.	c_V	c_V
133. ethylbenzene	298.15	185.47	[9]	182.7 ± 0.2	191.7 ± 0.3
134. 1,2-dimethylbenzene	298.15	187.98	[9]	189.6 ± 0.5	200.5 ± 0.3
135. 1,2-dimethoxybenzene	298.15			235.2 ± 0.4	238.1 ± 0.3
136. 2,4,6-trimethylpyridine	298.15			225.9 ± 0.7	235.2 ± 0.2
137. octan-1-ol	298.15	305.47	[9]	289.9 ± 0.5	304.7 ± 0.5
138. 1-butoxybutane	298.15			280.2 ± 0.7	289.3 ± 0.3
139. N-butylbutan-1-amine	298.15	292.76	[9]	288.2 ± 0.3	301.2 ± 0.5
141. quinoline	298.15	199.97	[9]	190.6 ± 0.3	194.0 ± 0.2
142. (1-methylethyl)benzene	298.15	198.88	[9]	217.9 ± 0.3	226.4 ± 0.3
144. 2,6-dimethylheptan-4-one	298.15			299.9 ± 0.5	316.9 ± 0.3
145. 1-chloronaphthalene	298.15	222.12	[20]	208.2 ± 0.4	211.9 ± 0.5
146. phenoxybenzene	303.15			262.9 ± 0.3	270.1 ± 0.6

Table S10: Classical heat capacity at constant pressure c_P^{class} (J/mol K) calculated and experimental. Blue font indicates that the calculated value differs more than 25% from the experimental ones, a red font indicates that it differs by more than 50%. The temperature in the calculations is noted in case it deviates from the one used in experiments.

Name	Experiment			GAFF	OPLS/AA
	T	c_P	Ref.	c_P^{class}	c_P^{class}
1. chloroform	298.15	117.00	[9]	140 ± 2	154 ± 4
2. dichloro(fluoro)methane	282.05	107.07	[13]	140 ± 2	137 ± 2
3. dibromomethane	293.15	104.62	[13]	126 ± 2	135 ± 1
...	298.15	104.90	[9]	121 ± 2	134 ± 2
4. dichloromethane	293.15	100.51	[13]	121 ± 1	123 ± 2
...	298.15	100.88	[13]	120 ± 2	133 ± 2
5. methanal	253.15	79.68	[22]	226 ± 4	94 ± 1
...	253.65	79.78	[22]	230 ± 3	94 ± 1
6. methanoic acid	293.15	99.03	[13]	150 ± 2	130 ± 2
...	298.15	99.00	[9]	140 ± 3	125 ± 2
7. bromomethane	276.65	78.75	[13]	123 ± 1	119 ± 1
8. methanamide	298.15	107.60	[9]	153 ± 2	202 ± 3
9. nitromethane	293.15	106.26	[13]	163 ± 2	155 ± 3
...	298.15	105.80	[9]	154 ± 2	157 ± 1
10. methanol	293.15	80.22	[13]	142 ± 3	150 ± 2
...	298.15	81.47	[9]	142 ± 2	148 ± 2
11. 1,1,1,2,2-pentachloroethane	293.15	173.96	[22]	190 ± 2	213 ± 2
12. 1,1,2,2-tetrachloroethane	293.15			193 ± 2	200 ± 3
...	298.15	165.70	[9]	193 ± 2	205 ± 4
13. 1,1-dichloroethene	293.15	110.53	[13]	206 ± 3	152 ± 2
...	298.15	111.33	[13]	210 ± 3	160 ± 2
14. 1,1,2-trichloroethane	293.15	150.05	[13]	190 ± 2	193 ± 3
...	298.15	148.50	[9]	197 ± 2	192 ± 3
15. acetonitrile	293.15	91.05	[13]	134 ± 2	125 ± 1
...	298.15	91.40	[9]	136 ± 2	123 ± 2
16. 1,2-dibromoethane	298.15	136.00	[9]	182 ± 3	203 ± 3
17. 1,1-dichloroethane	293.15	126.10	[13]	180 ± 2	183 ± 3
...	298.15	126.20	[9]	183 ± 3	172 ± 3
18. 1,2-dichloroethane	298.15	128.90	[9]	187 ± 2	189 ± 3
19. methyl formate	293.15	118.10	[13]	187 ± 2	170 ± 3
...	298.15	119.70	[9]	191 ± 3	176 ± 3

Table S10: Classical heat capacity at constant pressure - continued

Name	Experiment			GAFF c_P^{class}	OPLS/AA c_P^{class}
	T	c_P	Ref.		
20. bromoethane	293.15	99.04	[13]	178 ± 2	177 ± 4
...	298.15	99.73	[13]	174 ± 4	177 ± 2
21. chloroethane	273.15	101.18	[13]	177 ± 3	172 ± 3
...	285.45	102.80	[13]	175 ± 1	179 ± 2
22. 2-chloroethanol	293.15	109.03	[13]	232 ± 3	234 ± 3
23. ethanamide	358.15	148.39	[13]	220 ± 4	246 ± 4
...	494.30	165.92	[13]	214 ± 2	201 ± 3
24. N-methylformamide	292.15			210 ± 5	208 ± 4
...	298.15	123.80	[9]	212 ± 4	205 ± 2
25. nitroethane	298.15	138.50	[9]	220 ± 2	216 ± 5
26. methoxymethane	240.00	102.17	[13]	192 ± 4	202 ± 3
27. ethanol	293.15	110.46	[13]	206 ± 5	211 ± 5
...	298.15	112.30	[9]	209 ± 3	220 ± 4
28. 1,2-ethanedithiol	293.15			228 ± 3	227 ± 3
...	298.15			230 ± 4	224 ± 4
29. methylsulfanylmethane	293.15	145.55	[13]	225 ± 4	219 ± 4
...	298.15	145.96	[13]	225 ± 3	221 ± 4
30. methylsulfinylmethane	298.15	153.10	[9]	235 ± 4	235 ± 2
31. methylsulfanylmethane	293.15	117.60	[13]	207 ± 3	199 ± 3
...	298.15	118.10	[9]	203 ± 3	202 ± 5
32. 2-aminoethanol	293.15			284 ± 7	293 ± 4
...	320.00	164.75	[13]	285 ± 8	286 ± 3
33. ethane-1,2-diamine	293.15	172.24	[13]	337 ± 9	333 ± 8
...	298.15	172.50	[9]	329 ± 9	333 ± 5
34. prop-2-enenitrile	298.15	108.60	[9]	205 ± 3	130 ± 2
...	350.45	114.98	[13]	198 ± 3	135 ± 1
35. 1,3-dioxolan-2-one	312.15	133.84	[13]	224 ± 4	208 ± 4
36. propanenitrile	293.15	118.88	[13]	201 ± 3	181 ± 3
...	298.15	119.70	[9]	201 ± 4	186 ± 3
37. 1,2-dibromopropane	293.15	172.20	[22]	238 ± 4	253 ± 6
...	298.15	172.80	[22]	235 ± 4	250 ± 5
38. 1,3-dichloropropane	298.15	159.45	[13]	240 ± 3	243 ± 3

Table S10: Classical heat capacity at constant pressure - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_P	Ref.	c_P^{class}	c_P^{class}
39. (2R)-2-methyloxirane	298.15			213 ± 4	203 ± 4
40. propan-2-one	298.15	124.90	[9]	207 ± 3	195 ± 3
41. methyl acetate	293.15	140.67	[13]	240 ± 4	232 ± 4
...	298.15	143.90	[9]	244 ± 4	229 ± 4
42. 1,3-dioxolane	293.15	120.32	[23]	225 ± 3	225 ± 3
...	298.15	118.00	[11]	230 ± 4	235 ± 4
43. 2-iodopropane	293.15	138.41	[13]	230 ± 5	233 ± 3
...	298.15	139.72	[13]	221 ± 3	242 ± 5
44. 1-bromopropane	293.15	132.65	[13]	232 ± 4	238 ± 5
...	298.15	133.47	[13]	236 ± 3	231 ± 4
45. N,N-dimethylformamide	298.15	148.30	[9]	251 ± 6	247 ± 3
46. N-methylacetamide	320.00			269 ± 5	274 ± 6
47. 1-nitropropane	298.15	175.30	[9]	287 ± 6	277 ± 4
48. 2-nitropropane	298.15	170.20	[9]	284 ± 6	269 ± 4
49. dimethoxymethane	293.15	160.40	[13]	278 ± 4	287 ± 5
...	298.15	161.50	[13]	291 ± 6	277 ± 4
50. propane-1,2,3-triol	293.15	216.70	[22]	290 ± 6	285 ± 5
...	320.00	229.32	[22]	556 ± 6	353 ± 13
51. propan-1-amine	293.15	162.40	[13]	318 ± 9	319 ± 7
...	298.15	162.79	[13]	319 ± 7	325 ± 3
52. propan-2-amine	293.15	163.27	[13]	320 ± 4	321 ± 7
...	298.15	163.81	[13]	305 ± 5	324 ± 6
53. 2-methylpropane	243.65	125.50	[13]	283 ± 4	300 ± 9
54. ethylsulfanylethane	293.15	170.32	[13]	315 ± 10	312 ± 4
...	298.15	171.40	[9]	321 ± 10	320 ± 7
55. butane-1-thiol	293.15			322 ± 5	314 ± 7
...	298.15	171.20	[11]	325 ± 7	312 ± 7
56. butan-1-ol	293.15	174.72	[13]	319 ± 7	350 ± 4
...	298.15	177.00	[9]	323 ± 5	341 ± 8
57. 2-methylpropan-2-ol	320.00	238.62	[13]	395 ± 8	366 ± 7
58. butane-1,4-diol	293.15	172.42	[13]	408 ± 18	394 ± 9
...	298.15	202.20	[9]	371 ± 11	366 ± 7
...	320.00	200.66	[13]	364 ± 11	375 ± 12

Table S10: Classical heat capacity at constant pressure - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_P	Ref.	c_P^{class}	c_P^{class}
59. (2-hydroxyethoxy)ethan-2-ol	288.15	256.39	[22]	338 ± 9	405 ± 13
60. N-ethylethanamine	293.15	172.62	[13]	367 ± 7	386 ± 6
...	298.15	176.70	[9]	366 ± 6	380 ± 4
61. butan-1-amine	293.15	192.12	[13]	400 ± 7	386 ± 6
...	298.15	188.00	[9]	406 ± 11	399 ± 10
62. 2-methylpropan-2-amine	293.15	191.36	[13]	383 ± 10	392 ± 8
...	298.15	192.10	[13]	359 ± 9	380 ± 7
63. 2-(2-hydroxyethylamino)ethanol	320.00	275.72	[13]	387 ± 7	439 ± 11
64. pyrimidine	298.15	133.70	[9]	222 ± 4	222 ± 3
65. furan	293.15	113.61	[13]	195 ± 4	188 ± 2
...	298.15	114.80	[9]	193 ± 4	190 ± 4
66. thiophene	293.15	123.13	[13]	196 ± 3	192 ± 4
...	298.15	123.98	[13]	196 ± 3	190 ± 2
67. 1H-pyrrole	293.15	126.58	[13]	315 ± 5	223 ± 5
...	298.15	128.20	[9]	322 ± 5	215 ± 4
68. ethenyl acetate	298.15	171.47	[13]	354 ± 6	252 ± 5
69. oxolan-2-one	293.15	139.96	[22]	253 ± 4	240 ± 4
70. acetyl acetate	293.15	189.13	[13]	293 ± 5	284 ± 3
71. 1,4-dichlorobutane	298.15	189.23	[13]	304 ± 5	309 ± 5
72. oxolane	298.15	123.90	[9]	261 ± 5	266 ± 5
73. ethoxyethene	293.15	153.58	[13]	355 ± 5	286 ± 4
74. ethyl acetate	293.15	169.57	[13]	314 ± 8	299 ± 6
...	298.15	167.70	[9]	311 ± 8	293 ± 7
75. tetrahydrothiophene 1,1-dioxide	320.00	185.91	[13]	331 ± 8	312 ± 4
76. thiolane	293.15	138.69	[13]	267 ± 4	262 ± 5
...	298.15	139.80	[9]	256 ± 4	268 ± 4
77. 1-bromobutane	293.15	161.24	[13]	304 ± 9	300 ± 6
...	298.15	168.10	[9]	305 ± 10	306 ± 5
78. 1-chlorobutane	293.15			293 ± 4	293 ± 4
...	298.15	174.60	[9]	301 ± 6	311 ± 5
79. pyrrolidine	293.15	156.19	[13]	324 ± 7	334 ± 5
...	298.15	156.50	[9]	303 ± 6	319 ± 5

Table S10: Classical heat capacity at constant pressure - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_P	Ref.	c_P^{class}	c_P^{class}
80. N,N-dimethylacetamide	298.15	176.00	[9]	329 ± 6	309 ± 8
81. morpholine	293.15	173.88	[13]	334 ± 12	336 ± 9
82. pyridine	293.15	131.65	[13]	232 ± 5	226 ± 4
...	298.15	135.60	[9]	234 ± 6	232 ± 2
83. cyclopentanone	293.15	148.02	[13]	286 ± 4	274 ± 5
...	298.15	154.50	[9]	286 ± 6	288 ± 9
84. 1-cyclopropylethanone	293.15			300 ± 5	358 ± 7
...	298.15			299 ± 5	385 ± 11
85. pentane-2,4-dione	298.15	208.20	[9]	318 ± 5	326 ± 6
86. methyl 2-methylprop-2-enoate	298.15	189.82	[13]	354 ± 5	317 ± 6
87. pentanenitrile	293.15	188.51	[13]	316 ± 7	306 ± 5
...	298.15	189.70	[9]	306 ± 4	307 ± 5
88. ethyl propanoate	298.15	196.10	[9]	383 ± 7	363 ± 5
89. diethyl carbonate	298.15	212.40	[9]	386 ± 4	386 ± 7
90. pentan-1-ol	293.15	205.78	[13]	378 ± 8	419 ± 10
...	298.15	208.90	[9]	382 ± 11	407 ± 6
...	320.00	225.74	[13]	409 ± 6	420 ± 5
91. pentan-3-ol	293.15	242.82	[13]	435 ± 16	442 ± 7
...	298.15	247.72	[13]	446 ± 14	481 ± 10
92. 2-methylbutan-2-ol	293.15	243.36	[13]	383 ± 8	436 ± 5
...	298.15	244.30	[9]	378 ± 10	433 ± 8
...	320.00	269.99	[13]	394 ± 8	451 ± 8
93. pentane-1,5-diol	293.15	224.40	[13]	419 ± 8	417 ± 10
...	298.15	225.50	[9]	407 ± 11	484 ± 11
94. pentan-3-amine	293.15	203.80	[22]	437 ± 11	429 ± 6
...	298.15	205.13	[22]	448 ± 13	435 ± 8
95. 1,2,3,4-tetrafluorobenzene	298.15	190.06	[23]	265 ± 4	270 ± 3
96. 1,2,3,5-tetrafluorobenzene	298.15	190.19	[23]	276 ± 6	289 ± 4
97. 1,3-difluorobenzene	293.15			263 ± 6	265 ± 3
...	298.15	159.10	[11]	249 ± 3	260 ± 3
98. 1,2-difluorobenzene	293.15			267 ± 5	269 ± 6
...	298.15	159.00	[11]	249 ± 3	272 ± 7

Table S10: Classical heat capacity at constant pressure - continued

Name	Experiment			GAFF c_P^{class}	OPLS/AA c_P^{class}
	T	c_P	Ref.		
99. fluorobenzene	293.15	146.29	[13]	265 ± 4	231 ± 5
...	298.15	146.30	[9]	247 ± 5	230 ± 3
100. nitrobenzene	293.15	180.71	[13]	312 ± 6	294 ± 4
...	298.15	177.20	[9]	304 ± 4	296 ± 6
101. 2-chloroaniline	293.15	196.88	[13]	321 ± 9	331 ± 6
102. phenol	318.15	202.77	[13]	299 ± 4	305 ± 7
103. benzenethiol	293.15	172.65	[13]	292 ± 3	277 ± 7
...	298.15	173.55	[13]	287 ± 6	277 ± 6
104. 2-methylpyridine	293.15	157.42	[13]	296 ± 6	289 ± 8
...	298.15	159.20	[9]	275 ± 6	281 ± 5
105. 3-methylpyridine	293.15	157.68	[13]	279 ± 3	281 ± 5
...	298.15	159.00	[9]	282 ± 5	291 ± 6
106. 4-methylpyridine	293.15	157.83	[13]	291 ± 5	288 ± 5
...	298.15	159.00	[9]	281 ± 5	283 ± 7
107. cyclohexanone	293.15	182.28	[13]	346 ± 10	338 ± 7
...	298.15	179.30	[9]	362 ± 9	363 ± 9
108. (E)-hex-2-ene	293.15			359 ± 6	358 ± 6
109. hexan-2-one	298.15	213.17	[13]	402 ± 6	398 ± 6
110. 2,4,6-trimethyl-1,3,5-trioxane	293.15	255.56	[13]	374 ± 8	418 ± 11
111. cyclohexanamine	298.15	200.84	[22]	475 ± 9	453 ± 13
112. 2-propan-2-yloxypropane	298.15	216.10	[9]	444 ± 13	432 ± 11
113. 1-methoxy-2-(2-methoxyethoxy)ethane	293.15	273.08	[13]	552 ± 10	529 ± 16
...	298.15	226.00	[9]	544 ± 10	541 ± 13
114. triethyl phosphate	293.15			625 ± 19	539 ± 12
...	298.15			522 ± 14	557 ± 18
...	320.00			544 ± 11	544 ± 11
115. N,N-diethylethanamine	293.15	219.40	[13]	450 ± 8	463 ± 13
...	298.15	224.40	[9]	447 ± 9	451 ± 6
116. N-propan-2-ylpropan-2-amine	293.15	224.21	[13]	448 ± 8	476 ± 11
...	298.15	226.35	[13]	458 ± 14	465 ± 11
117. trifluoromethylbenzene	293.15	187.08	[13]	322 ± 9	290 ± 9
...	298.15	188.80	[13]	316 ± 10	312 ± 5

Table S10: Classical heat capacity at constant pressure - continued

Name	Experiment			GAFF	OPLS/AA
	T	c_P	Ref.	c_P^{class}	c_P^{class}
118. benzonitrile	288.15	163.00	[13]	294 ± 7	248 ± 3
119. benzaldehyde	298.15	172.00	[9]	291 ± 7	289 ± 4
120. toluene	298.15	157.20	[9]	309 ± 8	292 ± 6
121. methoxybenzene	293.15			339 ± 4	335 ± 4
...	298.15	208.60	[9]	338 ± 9	333 ± 6
122. phenylmethanol	297.15	216.44	[13]	349 ± 6	378 ± 8
123. 2-methylphenol	308.15	234.03	[13]	361 ± 10	372 ± 13
124. 3-methylphenol	320.00	233.79	[13]	356 ± 6	380 ± 11
125. 4-methylphenol	313.15	229.41	[13]	348 ± 6	359 ± 13
...	320.00	232.03	[13]	355 ± 6	355 ± 7
126. diethyl propanedioate	293.15	284.24	[13]	501 ± 12	506 ± 11
127. 2,4-dimethylpentan-3-one	293.15	233.78	[13]	460 ± 8	457 ± 10
...	298.15	235.51	[13]	460 ± 5	442 ± 9
128. heptan-2-one	293.15	241.05	[13]	489 ± 12	465 ± 4
...	298.15	243.60	[9]	467 ± 6	455 ± 8
129. ethenylbenzene	298.15	182.50	[9]	331 ± 8	333 ± 8
130. 1-phenylethanone	293.15			393 ± 7	356 ± 7
...	298.15	204.60	[9]	392 ± 8	360 ± 6
131. methyl benzoate	298.15	221.30	[9]	368 ± 8	380 ± 9
132. methyl 2-hydroxybenzoate	298.15	247.51	[13]	401 ± 10	397 ± 10
...	320.00	262.63	[13]	421 ± 13	409 ± 9
133. ethylbenzene	298.15	185.50	[9]	372 ± 7	366 ± 8
134. 1,2-dimethylbenzene	293.15	184.85	[13]	348 ± 7	358 ± 7
...	298.15	188.00	[9]	362 ± 11	360 ± 11
135. 1,2-dimethoxybenzene	298.15			441 ± 4	435 ± 6
136. 2,4,6-trimethylpyridine	295.15	213.05	[13]	379 ± 12	390 ± 12
...	298.15	214.00	[9]	394 ± 9	385 ± 6
137. octan-1-ol	298.15	305.50	[9]	561 ± 11	607 ± 13
...	320.00	333.97	[13]	624 ± 19	773 ± 22
138. 1-butoxybutane	293.15	276.56	[13]	580 ± 11	562 ± 11
...	298.15	251.90	[9]	563 ± 16	561 ± 12
139. N-butylbutan-1-amine	293.15			590 ± 14	632 ± 12
...	298.15	292.80	[9]	612 ± 10	611 ± 9

Table S10: Classical heat capacity at constant pressure - continued

Name	Experiment			GAFF c_P^{class}	OPLS/AA c_P^{class}
	T	c_P	Ref.		
140. isoquinoline	303.15	197.45	[13]	340 ± 8	319 ± 4
...	320.00	203.57	[13]	359 ± 6	378 ± 9
141. quinoline	288.15	191.49	[13]	369 ± 6	346 ± 6
...	298.15	200.00	[9]	362 ± 9	353 ± 9
142. (1-methylethyl)benzene	298.15	198.90	[9]	422 ± 10	407 ± 7
143. 1,2,4-trimethylbenzene	293.15	213.10	[13]	423 ± 15	413 ± 9
...	298.15	214.94	[13]	424 ± 13	413 ± 9
144. 2,6-dimethylheptan-4-one	293.15			570 ± 13	558 ± 12
...	298.15	297.30	[11]	552 ± 12	575 ± 18
145. 1-chloronaphthalene	298.15	222.14	[13]	357 ± 7	387 ± 11
146. phenoxybenzene	303.15	269.87	[13]	504 ± 15	445 ± 11

4 Polynomial Fits to Experimental Data

Figure S2: (part 1) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.

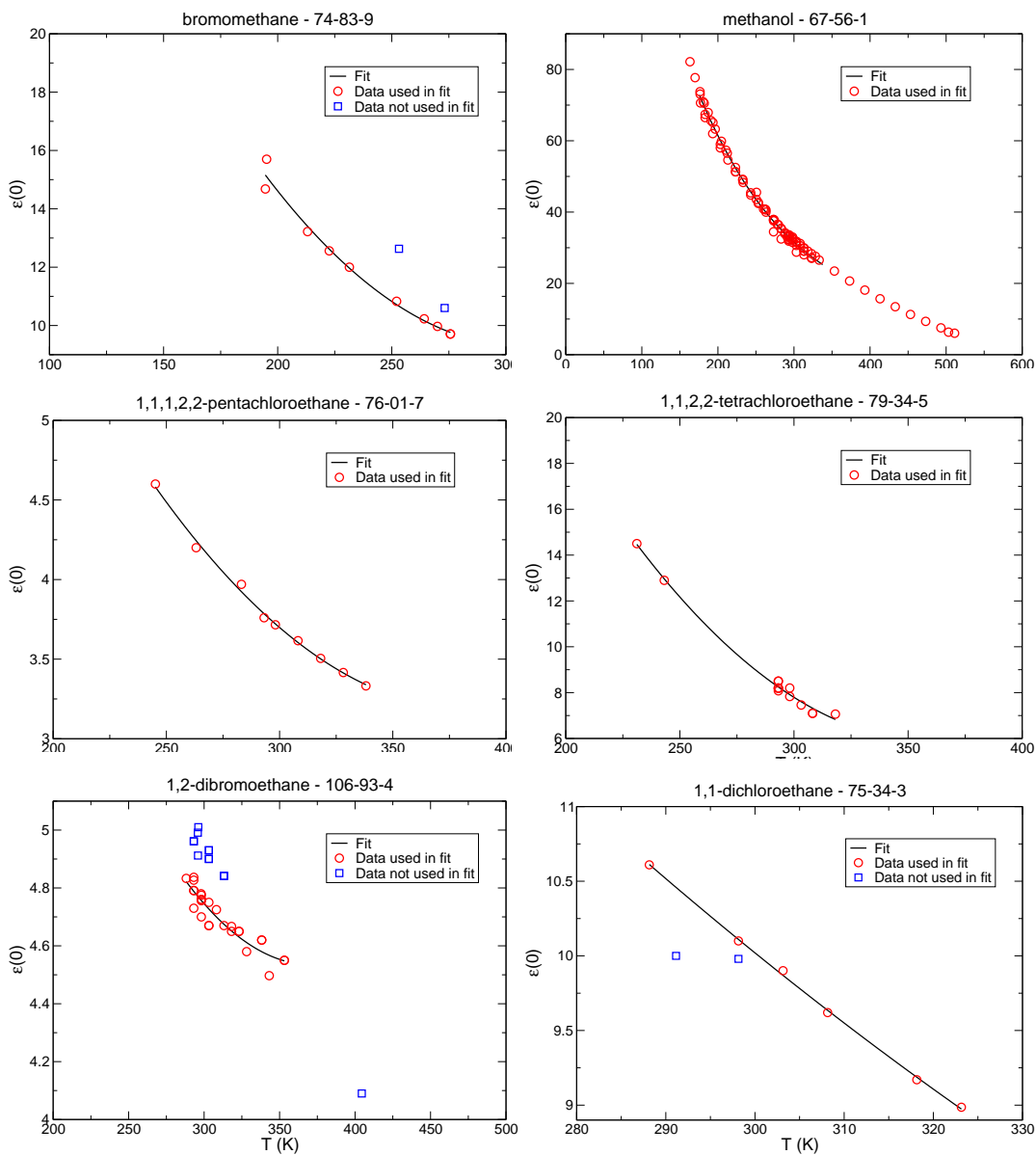


Figure S2: (part 2) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.

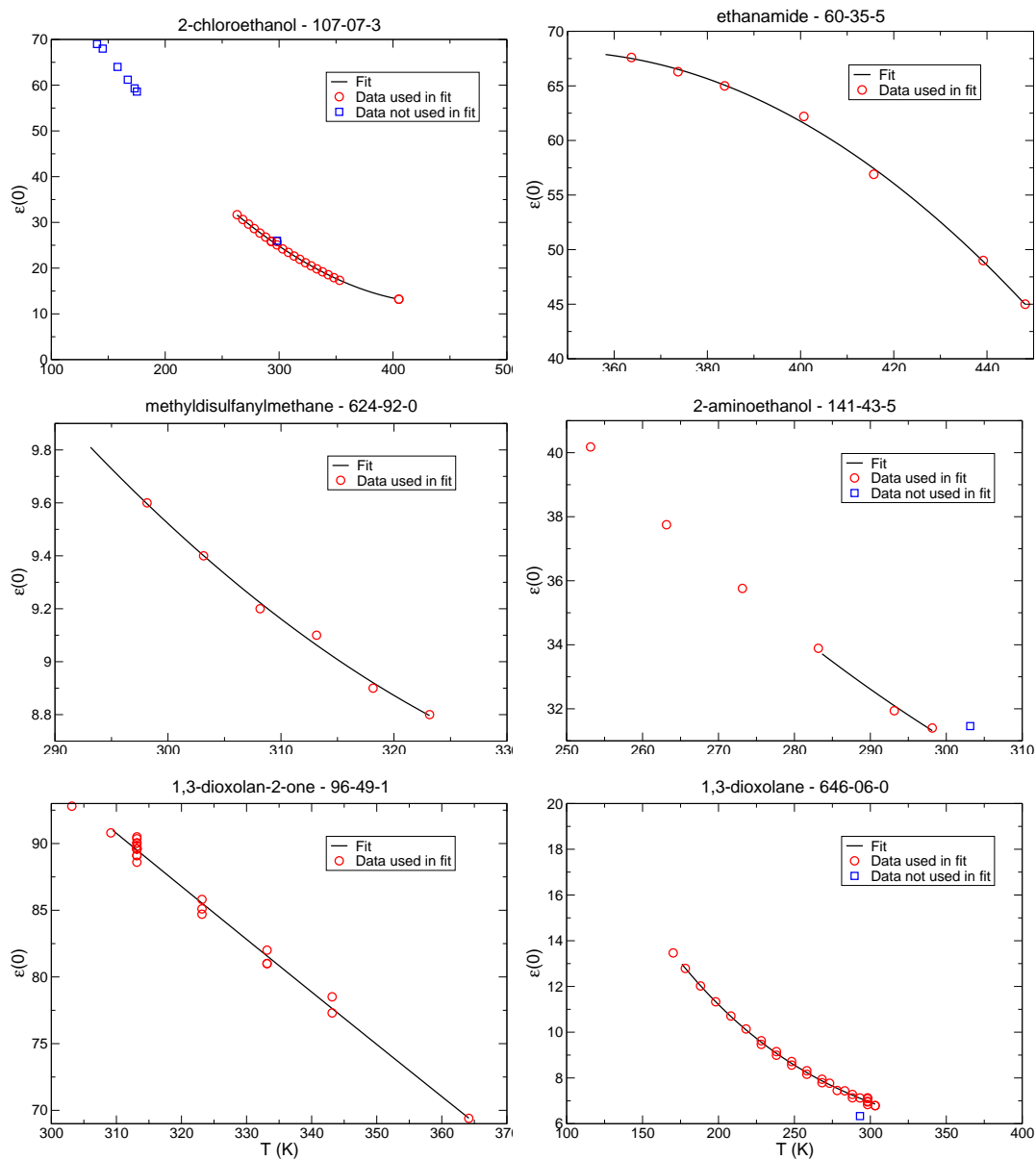


Figure S2: (part 3) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.

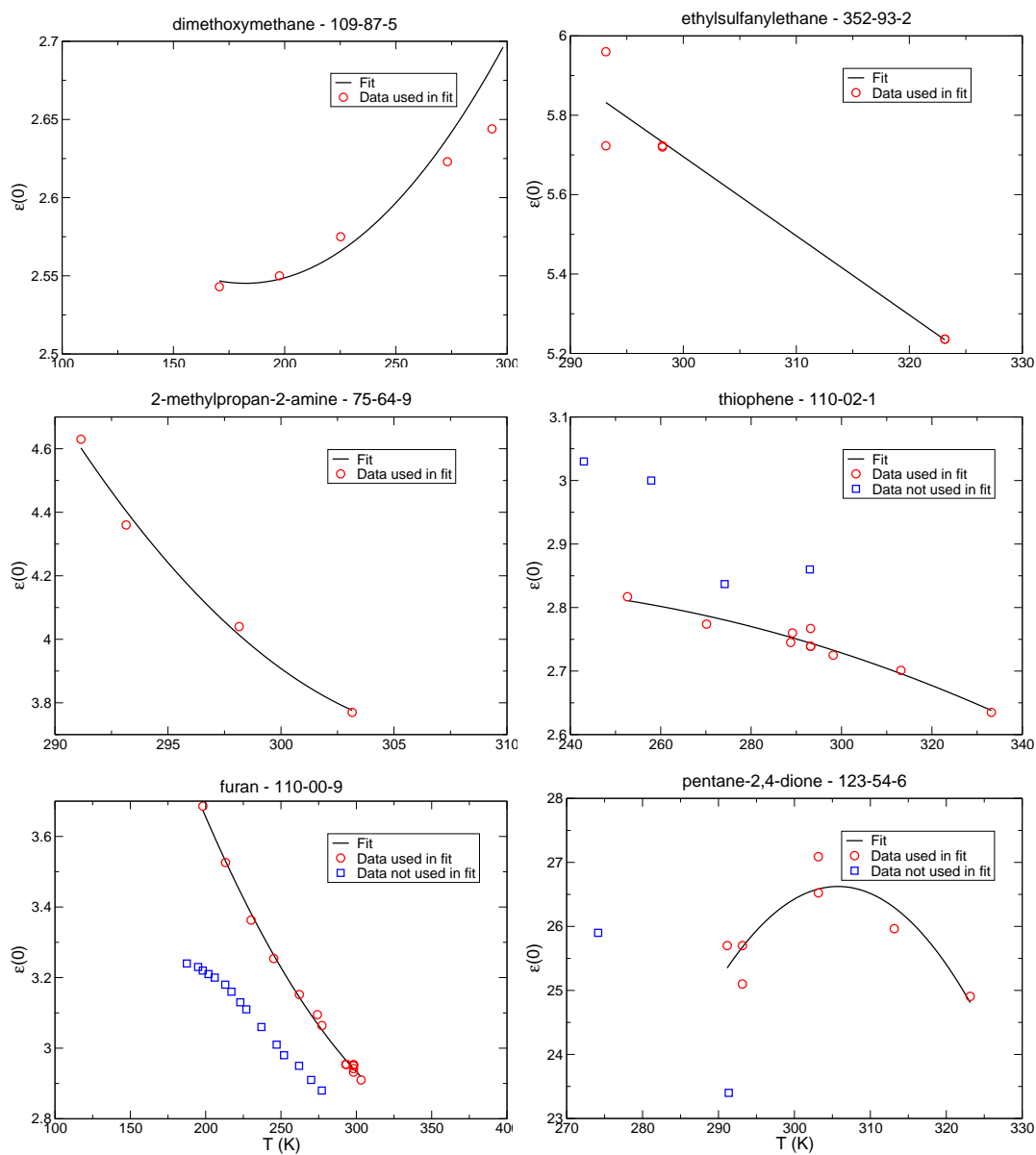


Figure S2: (part 4) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.

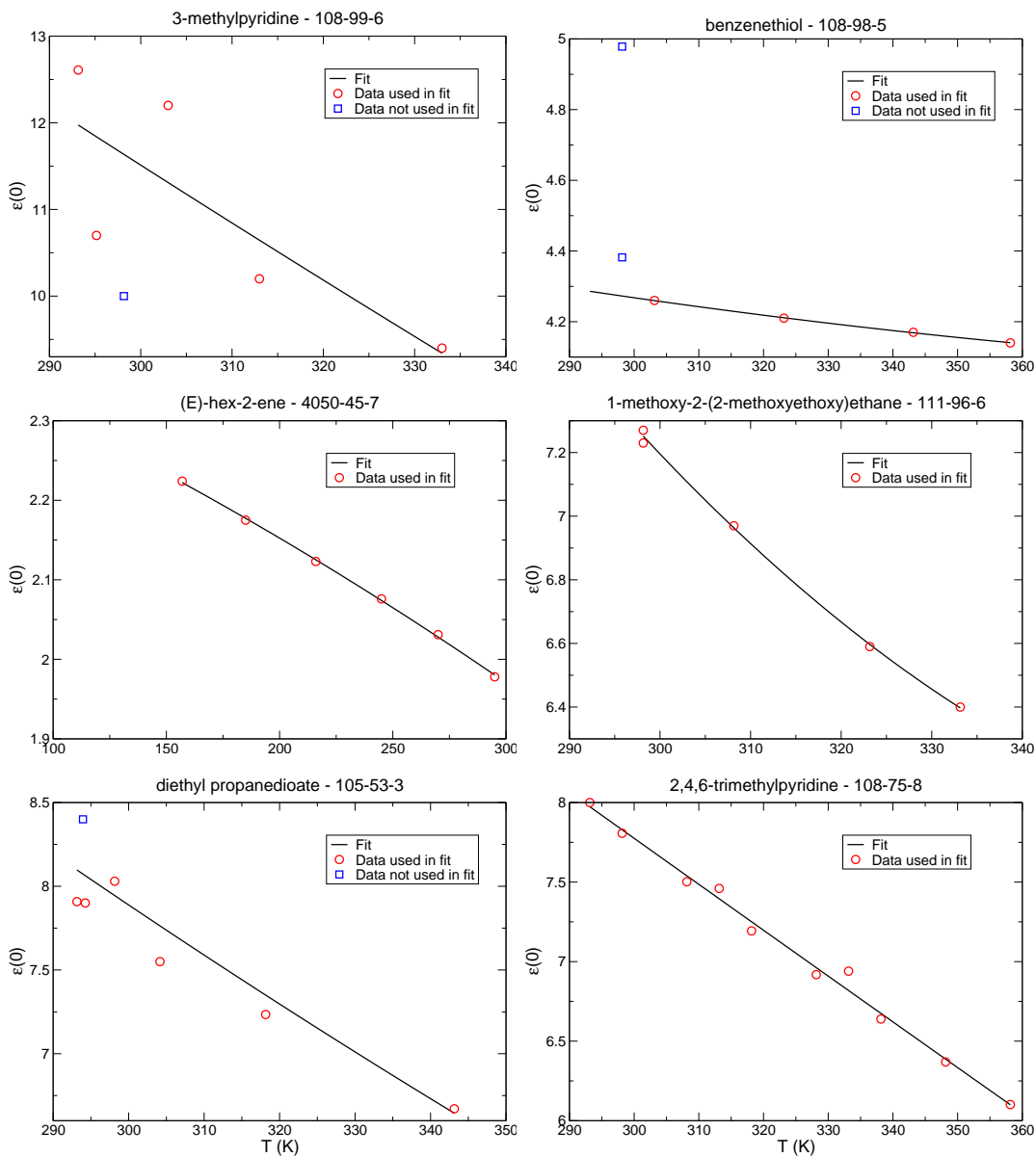


Figure S2: (part 5) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.

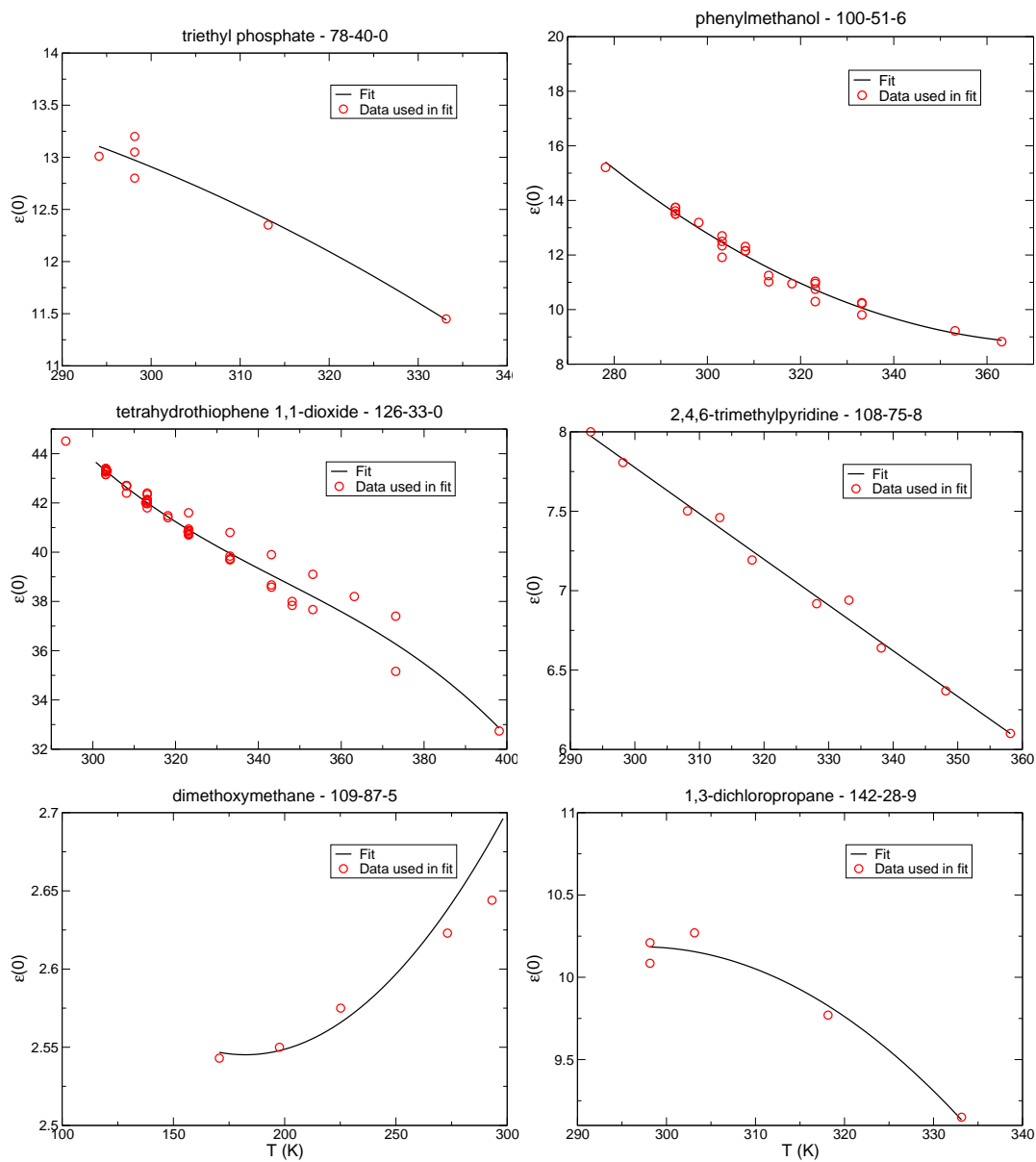


Figure S2: (part 6) Polynomial curves fitted to dielectric constant measurements for different molecules. For parameters see Table 4 in the main text.

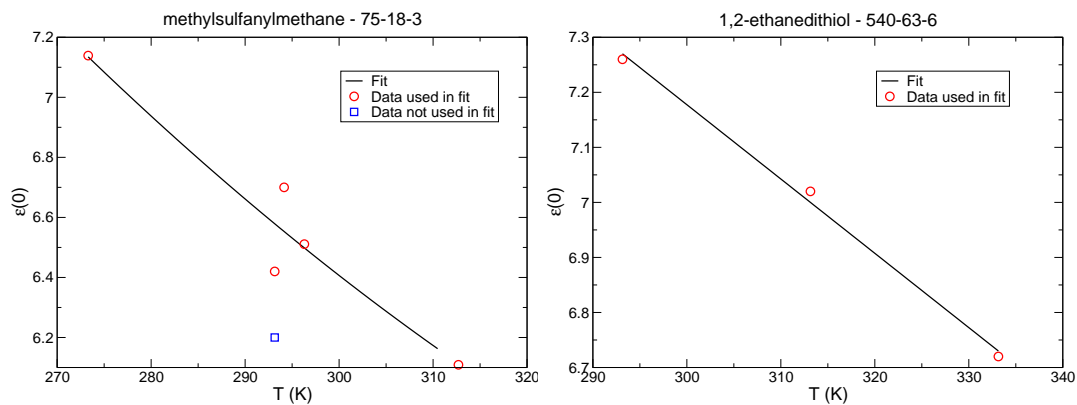


Table S11: References used for deriving fits of dielectric constants as a function of temperature to experimental data.

Molecule	References
ethylsulfanylethane	[19]
1,1-dichloroethane	[19]
2-aminoethanol	[24, 19, 25]
furan	[19, 26, 27, 28, 29]
2-chloroethanol	[30, 19, 31]
benzenethiol	[19, 32]
2,4,6-trimethylpyridine	[19]
1-methoxy-2-(2-methoxyethoxy)ethane	[19]
bromomethane	[19]
1,3-dioxolan-2-one	[19, 30, 23]
1,2-dibromoethane	[19, 23]
methanol	[19]
triethyl phosphate	[19]
2-methylpropan-2-amine	[19]
1,3-dichloropropane	[19, 33]
1,3-dioxolane	[34, 23, 35, 36, 37]
1,1,1,2,2-pentachloroethane	[19]
thiophene	[19]
dimethoxymethane	[19]
phenylmethanol	[19]
1,1,2,2-tetrachloroethane	[19, 23]
ethanamide	[19]
(E)-hex-2-ene	[19]
pentane-2,4-dione	[38, 39, 19, 40, 41, 42]
methylsulfanylmethane	[19, 23, 43]
1,2-ethanedithiol	[19]
diethyl propanedioate	[30, 44, 45]
methyldisulfanylmethane	[19]
3-methylpyridine	[32, 46, 19]
tetrahydrothiophene 1,1-dioxide	[19]

Figure S3: (part 1) Polynomial curves fitted to heat capacity at constant pressure measurements for different molecules. For parameters see Table 5 in the main text.

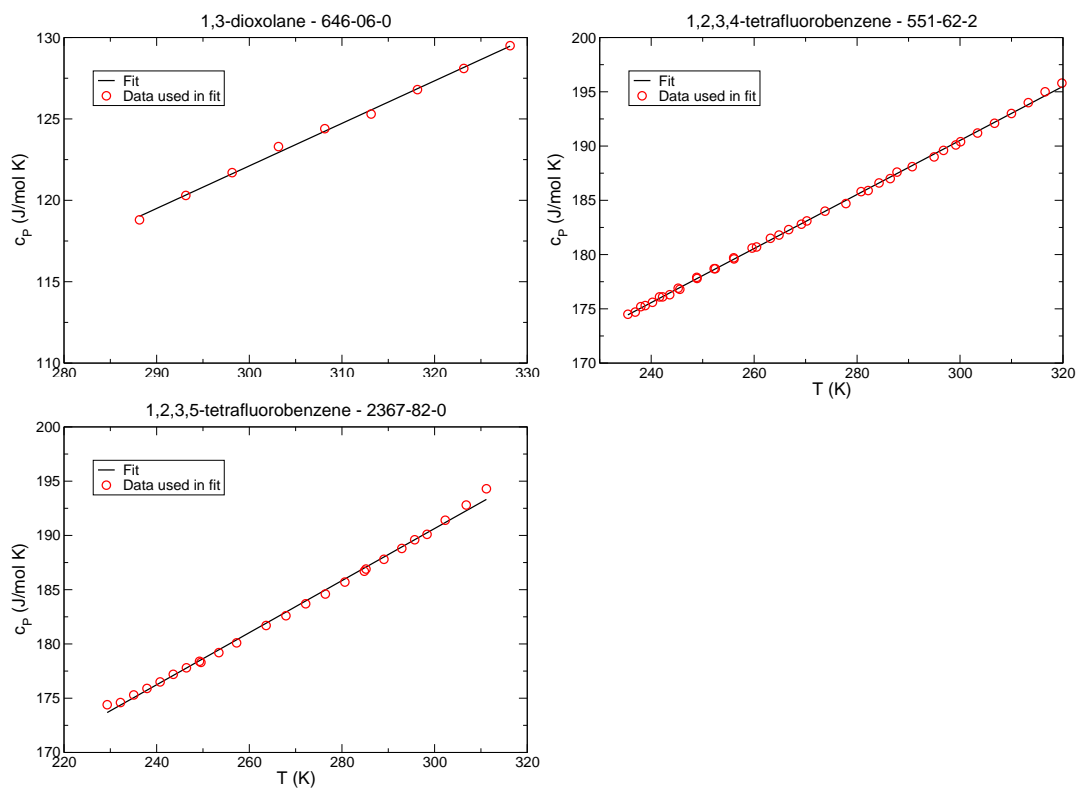


Table S12: References used for deriving fits of isothermal compressibilities as a function of temperature to experimental data.

Molecule	References
1,3-dioxolane	[23]
1,2,3,5-tetrafluorobenzene	[23]
1,2,3,4-tetrafluorobenzene	[23]

Figure S4: (part 1) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

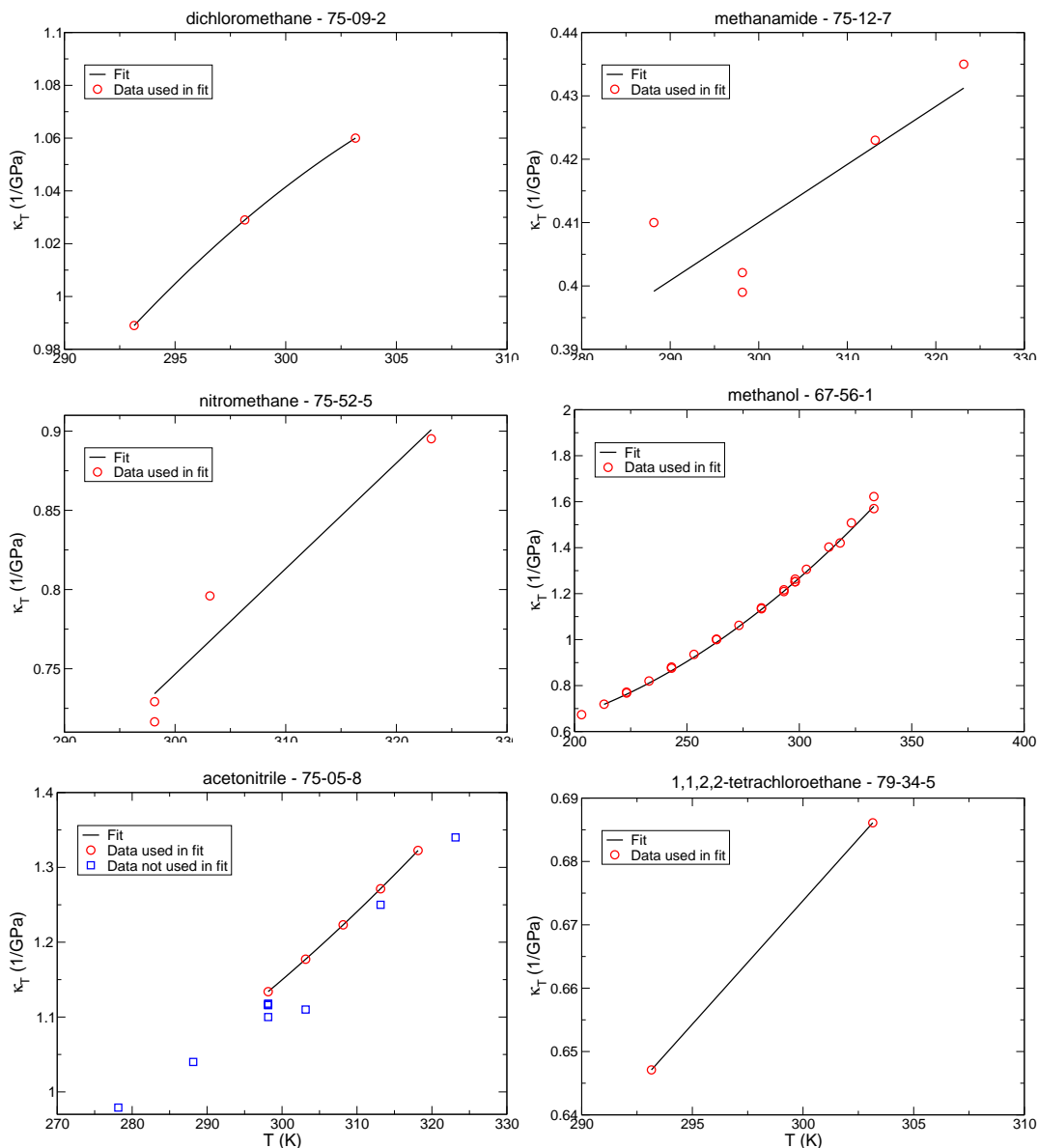


Figure S4: (part 2) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

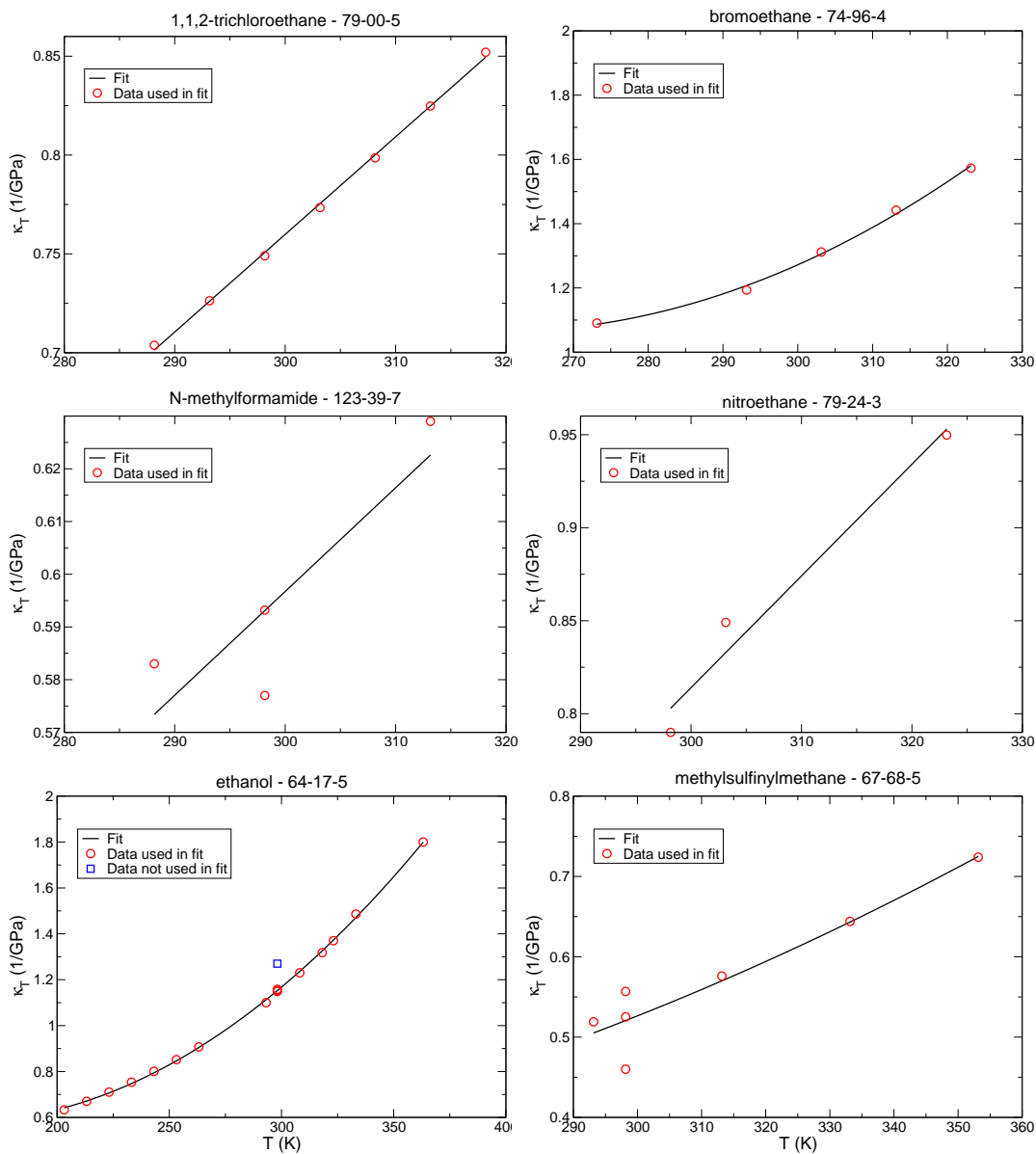


Figure S4: (part 3) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

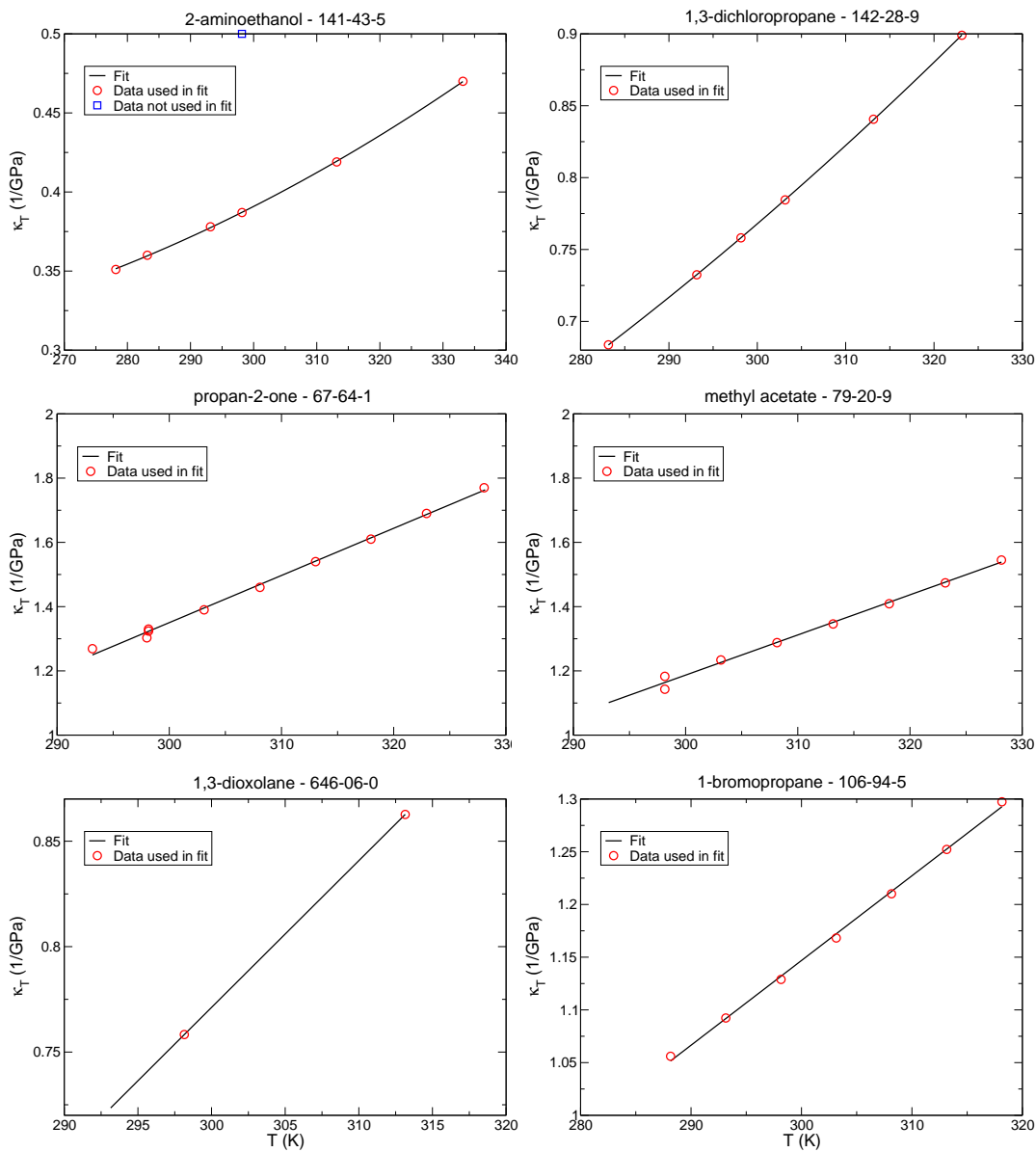


Figure S4: (part 4) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

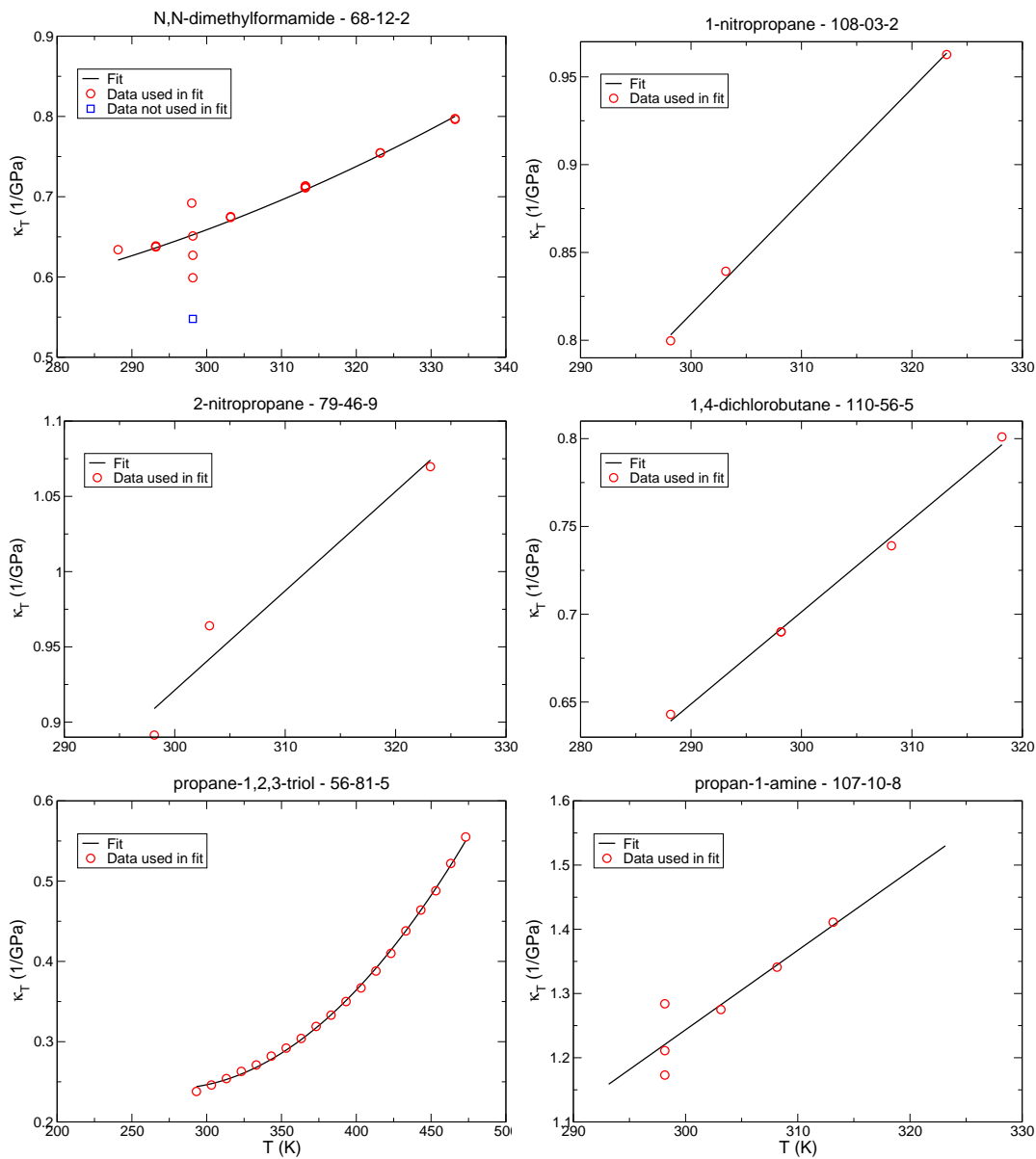


Figure S4: (part 5) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

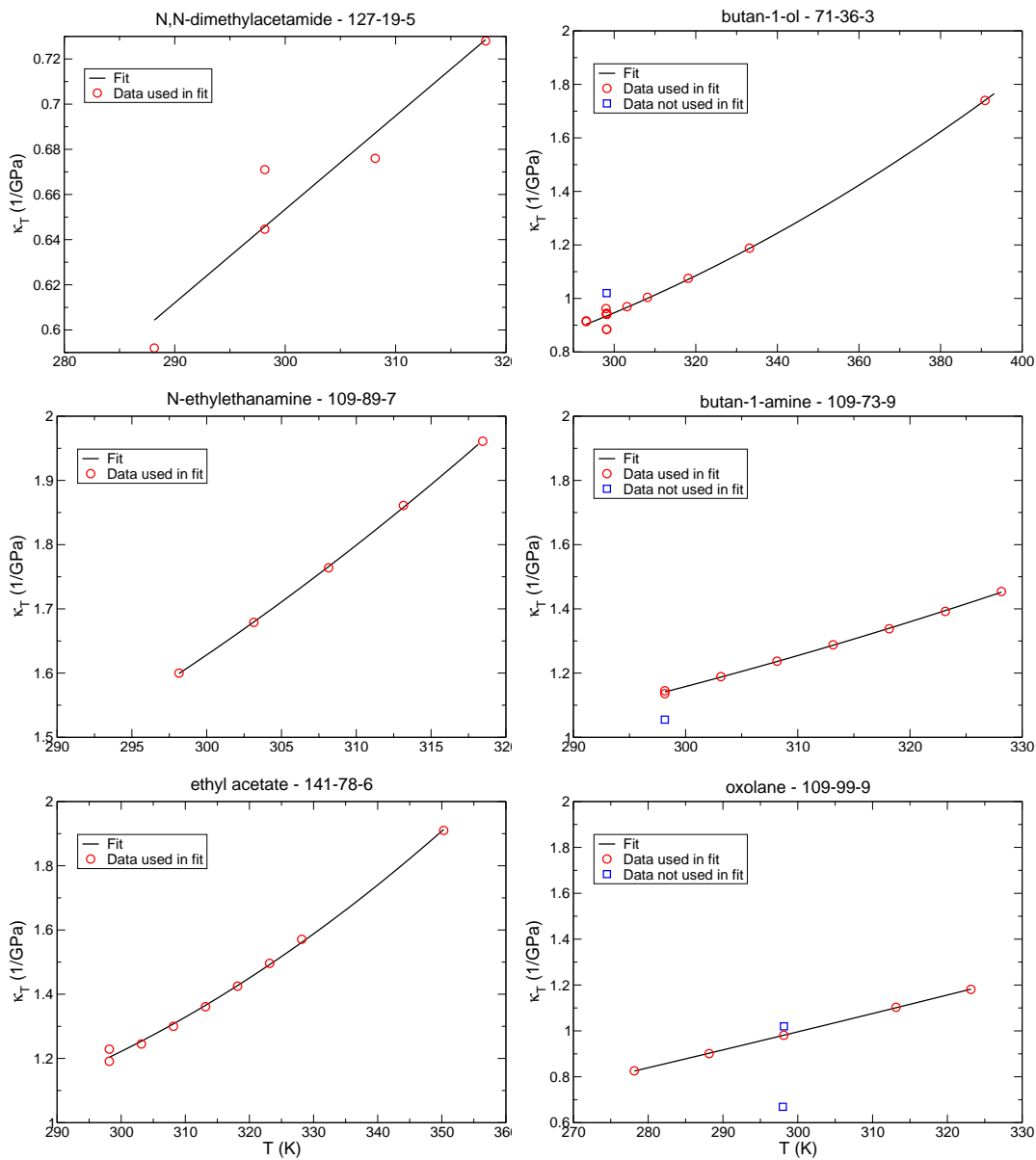


Figure S4: (part 6) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

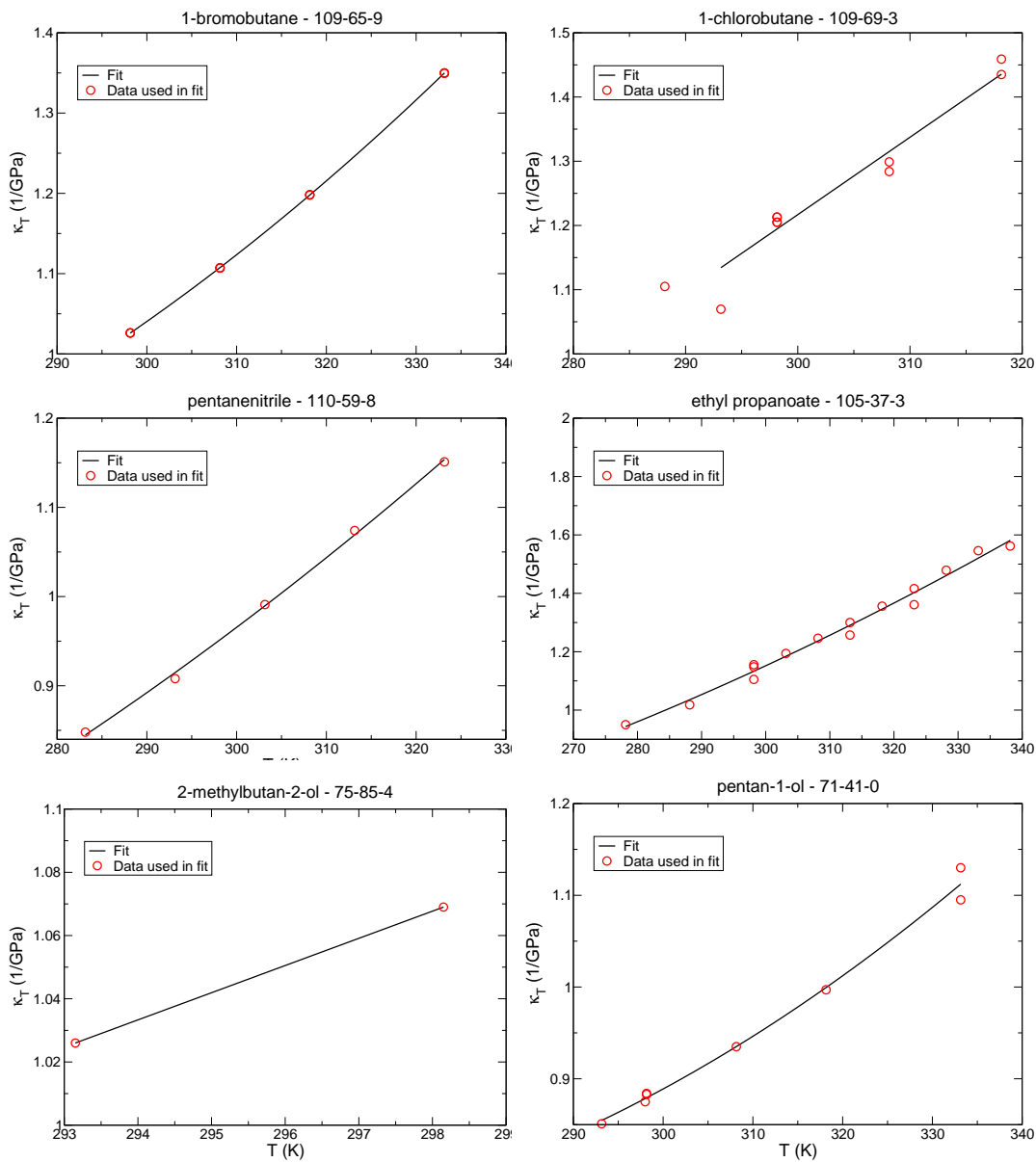


Figure S4: (part 7) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

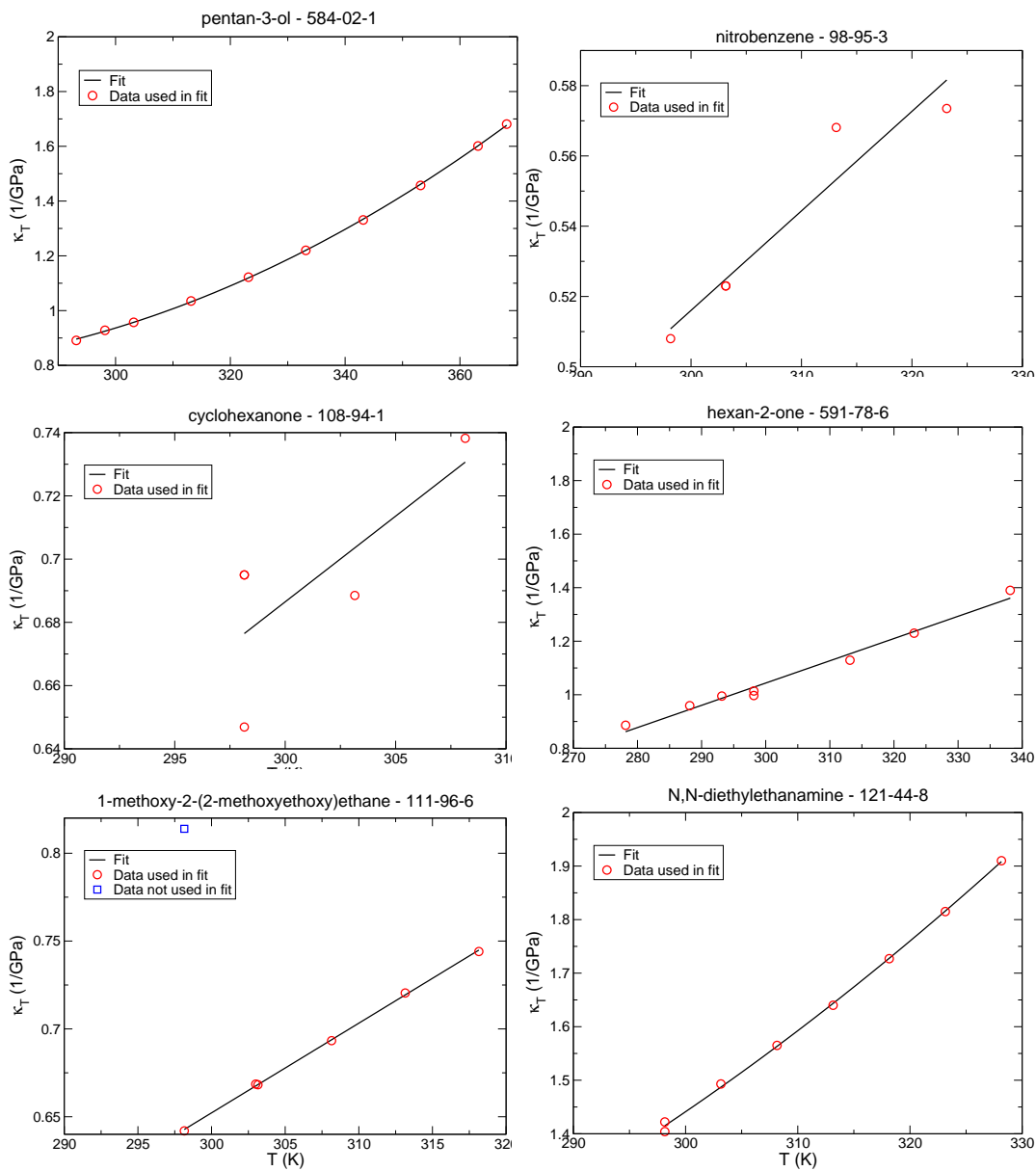


Figure S4: (part 8) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

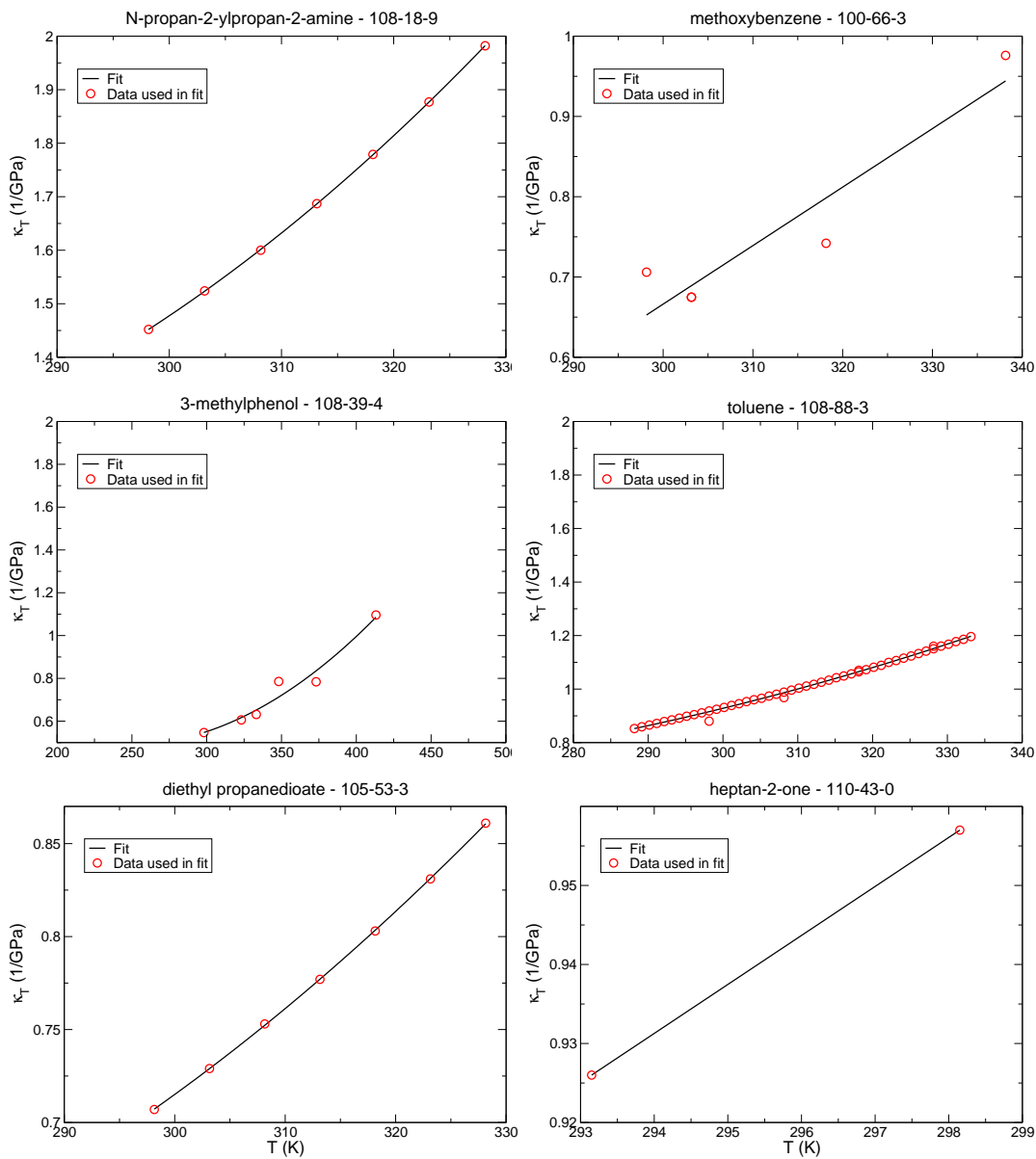


Figure S4: (part 9) Polynomial curves fitted to isothermal compressibility measurements for different molecules. For parameters see Table 6 in the main text.

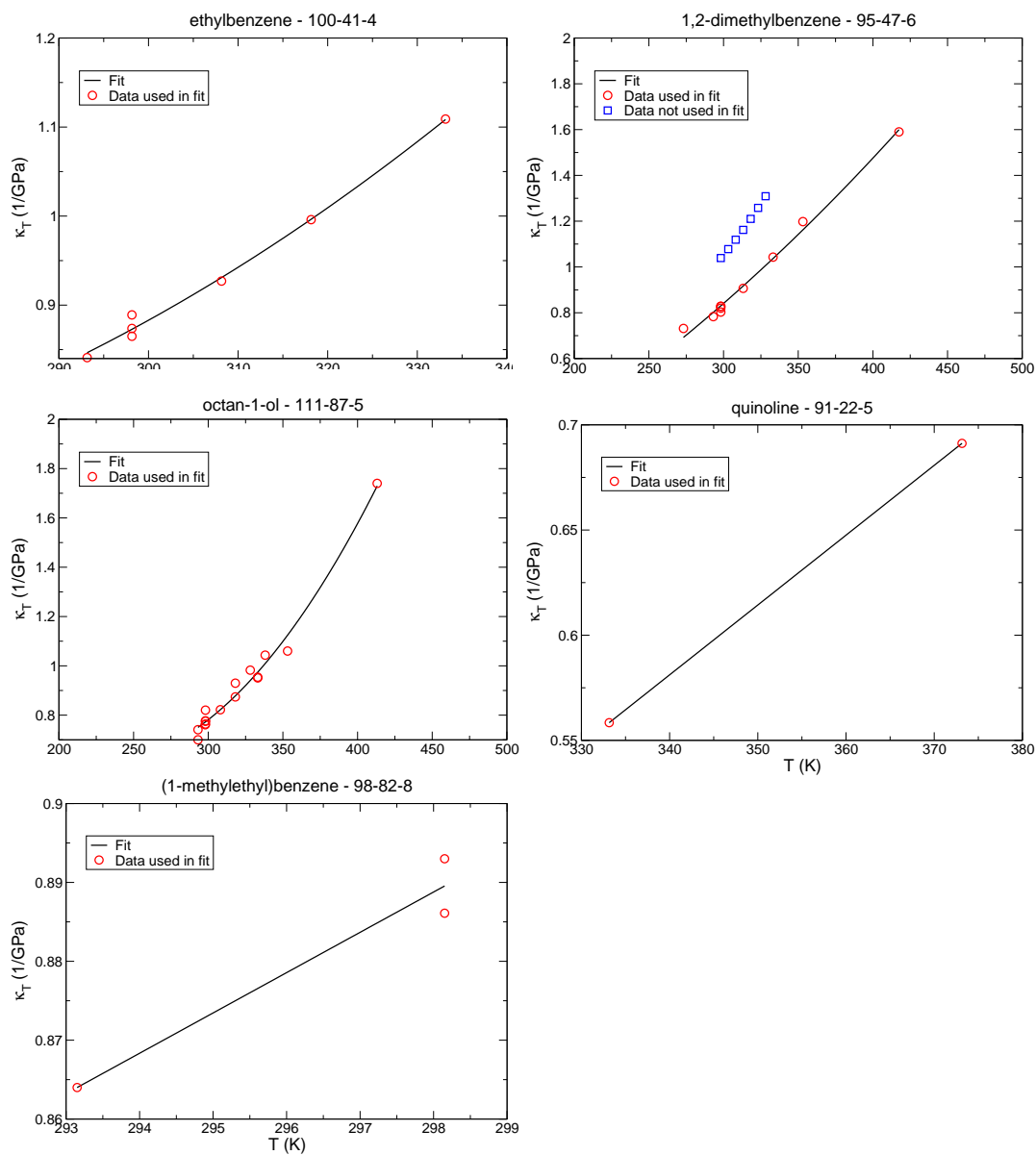


Table S13: References used for deriving fits of isothermal compressibilities as a function of temperature to experimental data.

Molecule	References
pentan-1-ol	[23]
1,4-dichlorobutane	[47]
2-aminoethanol	[23]
dichloromethane	[23]
methylsulfinylmethane	[23]
acetonitrile	[23]
1-chlorobutane	[23, 47]
ethanol	[23]
1-methoxy-2-(2-methoxyethoxy)ethane	[23]
hexan-2-one	[47]
heptan-2-one	[23]
N,N-diethylethanamine	[23]
nitromethane	[23, 47]
propane-1,2,3-triol	[23]
N,N-dimethylformamide	[23]
1,3-dioxolane	[23]
1,3-dichloropropane	[23]
nitrobenzene	[47]
1,2-dimethylbenzene	[23]
ethyl propanoate	[23]
1,1,2,2-tetrachloroethane	[23]
N-propan-2-ylpropan-2-amine	[23]
N-ethylethanamine	[23]
3-methylphenol	[23]
N-methylformamide	[23]
(1-methylethyl)benzene	[23]
diethyl propanedioate	[23]
octan-1-ol	[23]

Table S13: References used for deriving fits of isothermal compressibilities as a function of temperature to experimental data (continued).

Molecule	References
cyclohexanone	[23]
N,N-dimethylacetamide	[23, 47]
quinoline	[23]
pentan-3-ol	[23]
2-methylbutan-2-ol	[23]
methanamide	[23, 47]
propan-2-one	[47]
methoxybenzene	[23]
pentanenitrile	[23]
1-nitropropane	[47]
toluene	[23]
methanol	[23]
butan-1-ol	[23]
oxolane	[23]
1-bromopropane	[47]
2-nitropropane	[47]
ethylbenzene	[23]
methyl acetate	[23]
propan-1-amine	[23]
1-bromobutane	[23]
nitroethane	[47]
1,1,2-trichloroethane	[47]
bromoethane	[47]
butan-1-amine	[23]
ethyl acetate	[23]

References

- [1] Lin, S. T.; Blanco, M.; Goddard, III, W. A. *J. Chem. Phys.* **2003**, *119*, 11792–11805.
- [2] Lin, S.-T.; Maiti, P. K.; Goddard, III, W. A. *J. Phys. Chem. B* **2010**, *114*, 8191–8198.
- [3] Pascal, T. A.; Lin, S.-T.; Goddard, III, W. A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 169–181.
- [4] Huang, S.-N.; Pascal, T. A.; Goddard, III, W. A.; Maiti, P. K.; Lin, S.-T. *J. Chem. Theory Comput.* **2011**, *7*, 1893–1901.
- [5] Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. *J. Chem. Theory Comput.* **2008**, *4*, 435–447.
- [6] Berens, P. H.; Mackay, D. H. J.; White, G. M.; Wilson, K. R. *J. Chem. Phys.* **1983**, *79*, 2375–2389.
- [7] Carnahan, N.; Starling, K. *J. Chem. Phys.* **1970**, *53*, 600–&.
- [8] McQuarrie, D. A. *Statistical Mechanics*; Harper & Row: New York, 1976.
- [9] Marcus, Y. *The Properties of Solvents*; Wiley, 1998.
- [10] Frenkel, M.; Hong, X.; Dong, Q.; Yan, X.; Chirico, R. D. *Landolt-Börnstein - Group IV Physical Chemistry, Densities of Halohydrocarbons*; Springer: Berlin / Heidelberg, 2000.
- [11] Lide, D. R. *CRC Handbook of Chemistry and Physics 90th edition*; CRC Press: Cleveland, Ohio, 2009.
- [12] Yaws, C. L. *Thermophysical Properties of Chemicals and Hydrocarbons*; William Andrew Inc.: Beaumont, Texas, 2008.
- [13] Design institute for physical properties, project 801. American Institute for Chemical Engineering. <http://www.knovel.com>, **2010**.
- [14] Wohlfahrt, C.; Springer Verlag: <http://www.springermaterials.com>, 2008; chapter Surface Tension of Pure Liquids and Binary Liquid Mixtures.
- [15] Hales, J. L.; Townsend, R. *J. Chem. Thermodynamics* **1974**, *6*, 111–116.
- [16] Finger, G. C.; Reed, F. H.; Oesterling, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 152–153.
- [17] Chickos, J.; Acree, W. *J. Phys. Chem. Ref. Data* **2003**, *32*, 519–878.
- [18] Findlay, T. J. V. *J. Chem. Eng. Data* **1969**, *14*, 229–231.

- [19] Wohlfahrt, C.; Springer Verlag: <http://www.springermaterials.com>, 2008; chapter Static Dielectric Constants of Pure Liquids and Binary Liquid Mixtures.
- [20] Yaws, C. L. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*; Knovel: Beaumont, Texas, 2003.
- [21] Knovel. *Knovel Critical Tables (2nd Edition)*; Knovel, 2008.
- [22] Yaws, C. L. *Yaws' Handbook of Thermodynamic Properties for Hydrocarbons and Chemicals*; Knovel, 2009.
- [23] Thermophysical properties of pure substances & mixtures. DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V.. <http://i-systems.dechema.de/detherm>, **2011**.
- [24] Gaboriaud, R. C. R. *Seances Acad. Sci. Ser. C*. **1967**, *264*, 157–160,.
- [25] Sengwa, R.; Sankhla, S.; Khatri, V.; Choudhary, S. *Fluid Phase Equilib.* **2010**, *293*, 137–140.
- [26] Murakami, S.; Koyama, M.; Fujishiro., R. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1540–1545.
- [27] Smyth, C.; Wall, W. *J. Am. Chem. Soc.* **1932**, *54*, 3230–3240.
- [28] INFOTHERM thermophysical properties database. Homann, J. <http://www.fiz-chemie.de/infotherm>, **2011**.
- [29] B. Harris, J. L. F.; Sullivan, E. *J. Chem. Soc.* **1953**, page 1622.
- [30] Knovel metadatabase. Corporation, K. <http://www.knovel.com>, **2011**.
- [31] Grimm, F.; Patrick, W. *J. Am. Chem. Soc.* **1923**, *45*, 2794–2802.
- [32] Ruzicka, K. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
- [33] Conner, W.; Smyth, C. *65* **382**, (1943a), The Dielectric Dispersion and Absorption of Water and Some Organic Liquids.
- [34] Sinha, A.; Roy, M. N. *140* **39-44**, (2008), Ion–pair and triple–ion studies of some tetraalkylammonium halides in pure 1,3–dioxolane at 298.
- [35] Ue, M.; Takeda, M.; Takehara, M.; Mori, S. *J. Electrochem. Soc.* **1997**, *144*, 2684–2688.
- [36] J., W. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
- [37] Matsuda, Y.; Morita, M.; Yamada, K.; Hirai, K. *J. Electrochem. Soc* **1985**, *132*, 2538–2543.
- [38] Eggers, H. E. *J. Phys. Chem.* **1904**, *8*, 15–36.
- [39] Maryott, A. A.; Smith, E. R. *NBS Circular* **1951**, *514*, 5–39.

- [40] Walden. *Zeitschrift fuer Physikalische Chemie, Stoechiometrie und Verwandtschaftslehre* **1910**, *70*, 575.
- [41] P., W. *Z. Phys. Chem. Leipzig* **1903**, *46*, 103–188.
- [42] Naoum, M.; Botros, M. *Indian J. Chem. Sect. A* **1986**, *25*, 1084–1088.
- [43] Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J.-L. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807–5816.
- [44] Ketelaar. *Rec. Trav. Chim. Pays-Bas* **1957**, *76*, 437.
- [45] Dobrosserdow. *Chem. Zentralbl.* **1911**, *82*, 955.
- [46] Ladenburg. *Zeitschrift fuer Elektrochemie und Angewandte Physikalische Chemie*, **1900**, *7*, 816.
- [47] <http://www.reaxys.com>, **2011**.