Round Robin Study: Molecular Simulation of Thermodynamic Properties from Models with Internal Degrees of Freedom

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Abstract

Thermodynamic properties are often modeled by classical force fields which describe the interactions on the atomistic scale. Molecular simulations are used for retrieving thermodynamic data from such models and many simulation techniques and computer codes are available for that purpose. In the present round robin study, the following fundamental question is addressed: Will different user groups working with different simulation codes obtain coinciding results within the statistical uncertainty of their data? A set of 24 simple simulation tasks is defined and solved by five user groups working with eight molecular simulation codes: DL_POLY, GROMACS, IMC, LAMMPS, *ms*2, NAMD, Tinker, and TOWHEE. Each task consists of the definition of (1) a pure fluid that is described by a force field and (2) the conditions under which that property is to be determined. The fluids are four simple alkanes: ethane, propane, n-butane, and iso-butane. All force fields consider internal degrees of freedom: OPLS, TraPPE, and a modified OPLS version with bond stretching vibrations. Density and potential energy are determined as a function of temperature and pressure on a grid which is specified such that all states are liquid. The user groups worked independently and reported their results to a central instance. The full set of results was disclosed to all user groups only at the end of the study. During the study, the central instance gave only qualitative feedback. The results reveal the challenges of carrying out molecular simulations. Several iterations were needed to eliminate gross errors. For most simulation tasks, the remaining deviations between the results of the different groups are acceptable from a practical standpoint, but they are often outside of the statistical errors of the individual simulation data. However, there are also cases, where the deviations are unacceptable. This study highlights similarities between computer experiments and laboratory experiments, which are both subject not only to statistical error but also to systematic error.

1 Introduction

Classical force fields that describe interactions on the atomistic level are widely used to model thermodynamic properties of fluids.[1–6] The theory which relates the force field to the thermodynamic properties is statistical thermodynamics, a well-established branch of science.[7–9] For a long time, the framework of statistical thermodynamics could practically only be applied to simple force fields. However, with the advent of computers and the corresponding development of numerical algorithms and codes, the application range of force fields for modeling thermodynamic properties has expanded drastically. This went along with an increasing number of publicly available codes, an increase in complexity of these codes and algorithms they are based on, an increase in complexity of the input and output data, and an increasing number of users, many of which are not molecular simulations experts. The present discussion focuses on molecular simulations of thermodynamic properties of fluids, but the results can probably be regarded as typical for many other advanced simulations.

The question whether a given force field is a good representation of a real fluid is not important for the present work. The sole interest rests on simulation, i.e. the way of retrieving the desired result from a given model. A schematic showing the steps of a simulation process is presented in Figure 1. Assume that a molecular model of a certain fluid is given and that a certain property of that fluid is of interest, e.g. its density at 300 K and 0.1 MPa, then there is a certain true value of that property x^{mod} for the given model. To obtain information on it, the model needs to be studied by simulation. Assume further that everything has to be done from scratch then appropriate algorithms from statistical thermodynamics and numerical mathematics have to be chosen and a corresponding computer code has to be written and implemented on a suitable computer. Only then simulations can be carried out, which will eventually yield a result x^{sim} for the property of interest.

It is important to realize that, apart from trivial cases, x^{mod} cannot be obtained, only x^{sim} can. All steps in the chain depicted in Figure 1 may lead to deviations between x^{sim} and x^{mod}. This is troublesome in many ways. E.g., such differences affect the modeling

process itself, which is an iterative procedure in which force field parameters are adjusted by comparing x^{sim} to corresponding experimental values x^{exp}.[10] Deviations between x^{mod} and x^{sim}, hence, directly affect parametrization and transferability of model parameters between different simulation codes.

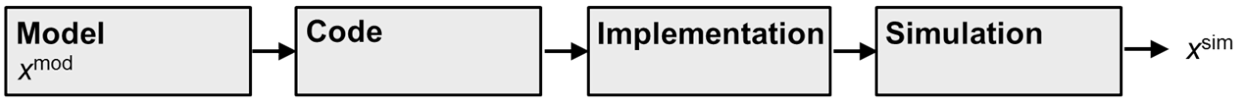

Figure 1: Schematic for the route from model to simulation result. The property x^{mod} described by the model is of interest and to obtain information on it, simulations have to be carried out. x^{mod} is not directly accessible, only the simulation result x^{sim} is. Errors may occur in every step of the route.

In the discussion below, for brevity, we use terms like: "the simulation results for n-butane", acknowledging that this refers not to real n-butane but rather to some model of butane.

The situation depicted in Figure 1 is similar to that encountered in laboratory work in which real world objects are studied with experimental equipment. Let a real world quantity x^{real} be of interest. In order to get information on it, an experiment has to be carried out, which yields x^{exp} as a result. It is fully accepted for laboratory experiments that there are differences between x^{real} and x^{exp}. These inevitable deviations are usually classified in systematic errors and statistical errors, also called random errors.[11]

The same holds for computer experiments. There are inevitable deviations between x^{sim} and x^{mod}, and they can be classified in systematic errors and statistical errors. The existence of statistical errors is accepted for computer simulations and they are regularly quantified together with the molecular simulation results. The attitude towards systematic errors in computer simulation is more complicated. Their existence is not put into question, but many scientists consider them as resulting from faults, which can and have to be avoided.[12,13]

With the present study, we try to contribute to shaking this belief. Once some level of complexity is reached, not only statistical but also systematic errors become unavoidable in computer simulation. Measures need to be taken to reduce both statistical and systematic

errors to a limit which is acceptable from a practical standpoint. With sufficient effort, this is possible in many cases. However, because there are always limits to the affordable effort, there will always be limits to the error level which can be reached in simulations.

Statistical errors can be assessed by repetition. In computer simulations this is often easier than in laboratory experiments. Assessing systematic errors is much harder. The present round robin study responds to that challenge. Systematic errors of computer simulations are explicitly addressed by applying a straightforward technique: The same set of simulation tasks was given to different user groups working with different codes and the results were compared. The question was whether they agree within the statistical uncertainty of the individual data.

Five academic groups participated in the present round robin study, cf. Table 1. During the study, the user groups were connected only through a central instance and worked independently. A set of relatively simple molecular simulation tasks was defined, details are given below.

Table 1: User groups which participated in the present round robin study. The central instance was at University of Kaiserslautern.

AA	RWTH Aachen University
BS	Technische Universität of Braunchschweig
FM	Fraunhofer Institute of Industrial Mathematics
KL	University of Kaiserslautern
PB	University of Paderborn

The participating groups worked with different well-established molecular simulation codes, of which the source codes are publicly available, cf. Table 2. In the early stages of this round robin study, two commercial molecular simulation tools were considered as well, of which the source codes are confidential. After having obtained very poor initial results and after unsuccessful contacts with the providers of these codes, both were excluded from the study. We do not wish to interfere with commercial interests and will therefore not disclose the names of these codes. The fact is nevertheless mentioned here because it indicates that the question whether a source code is disclosed to the scrutiny of the scientific

community or not is deeply related to their reliability.

Three different force fields with internal degrees of freedom (OPLS,[14,15] TraPPE,[14] and a modified OPLS version with bond stretching potential taken from the AMBER force field,[16] in the following named OPLSAMBER) were applied to model four simple alkanes: ethane, propane, n-butane, and iso-butane. The task was to use these force fields to determine the density and potential energy for a given set of liquid states, specified by a grid of temperature-pressure pairs.

The present results can be used as a benchmark for testing new algorithms and software. Such benchmarks are up to now hardly available. In fact, the initial motivation of the present work was to obtain such a benchmark for testing a new version of the *ms*2 code, which includes the internal degrees of freedom.

Table 2: Molecular simulation codes used in the present study and user groups in which they were applied. MD stands for molecular dynamics, MC for Monte-Carlo.

Code	Type	Reference	Group
DL_POLY	MD	[17]	BS
GROMACS	MD	[18,19]	BS, KL
IMC	MC		PB
LAMMPS	MD	[20]	AA, KL
*ms*2	MD/MC[1]	[21]	KL, PB
NAMD	MD	[22]	FM
Tinker	MD	[23]	AA
TOWHEE	MC	[24]	BS

Recently, the National Institute of Standards and Technology (NIST) initiated a project to provide simulation reference data.[25] In this endeavor, NIST aims at building a data base of well-documented molecular simulation results obtained with well-established simulation techniques. The documentation includes the statistical uncertainty of the data, whereas, up to now, the aspect of systematic errors in the data is not directly addressed in that project.[25]

The issue addressed here is closely related to the reproducibility of scientific results in a broader sense, where the question is: How reproducible is information on a quantity x^{mod} defined by a model, which is only accessible by computer simulation, if different codes

are used? This has been studied recently in depth in a round robin study for quantum chemical density functional theory (DFT) simulations, a field in which about 15.000 papers are published each year.[26] The authors do not only evaluate the current situation, but also its past evolution and conclude that in their field the level of agreement of the results from different codes has very positively developed over the last decade and is close to reaching a satisfactory level.

The field we are considering here, obtaining precise data for thermodynamic properties from force fields with internal degrees of freedom, is much narrower than the field of quantum chemical DFT. This directly affects the amount of experience with the corresponding simulation codes and the amount of independent testing. It can be expected that this has consequences for the reproducibility of the results obtained with different codes.

The present paper is organized as follows: Initially, general remarks on statistical and systematic errors in molecular simulation are made, showing that systematic errors are the rule, not the exception. Next, the round robin study is explained in detail, including the specification of the simulation tasks. Subsequently, the results are discussed, first for the force fields without bond stretching and then for the OPLSAMBER that includes bond stretching. We conclude with a general discussion of the findings and their consequences.

2 Molecular simulation errors

2.1 Statistical and systematic errors

The results obtained in repetitions of a computer simulation usually differ. Hence, a set of more or less scattering results is obtained. The number for x^{sim} which is reported based on such a set is an average. Furthermore, some measure σ_{x} for the scatter of the data set can be obtained, e.g. the standard deviation. The deviation of the simulation result x^{sim} from the true value x^{mod} is the simulation error, cf. Figure 1. That error is considered to consist of two contributions, the statistical error, which is quantified by σ_{x}, and the systematic error,

which is rarely addressed.

In equilibrium molecular simulations, as they were carried out in the present study, the statistical error is usually determined by the well-known block averaging technique.[27] Its basic idea is to divide the productive period of a simulation run in a number of blocks and to consider each block as a single run. Because the blocks are not truly independent, this is not rigorous, but as long as the blocks are large enough, block averaging is a practically useful approach. The block averages are then subjected to statistical analysis. The numerical results obtained for σ_{x} depend not only on the length of the production run, but also on the choice of the block size so that it is not straightforward to compare numbers for σ_{x} obtained differently. Furthermore, also the definition of σ_{x} may vary for different codes.

In this round robin study systematic errors are assessed by the execution of the same set of simulation tasks in independent environments. In absence of systematic errors, the results obtained on this meta-level should agree within their statistical errors. However, as shown below, they do not. The scatter of the results on that meta-level obviously contains information on the systematic error that must be expected.

In the following, error sources in molecular simulations are briefly discussed. The list is not exhaustive, but illustrates the plethora of error sources, which may be present in all steps of the molecular simulation process, cf. Figure 1.

The impact that a certain error source has on a given simulation result x^{sim} depends on various circumstances. The same error source may e.g. lead to systematic or statistical error (or both), depending on the type of simulation result which is retrieved from the simulation run.

2.2 Algorithmic errors

Statistical thermodynamics provides a solid foundation for molecular simulation. Its core is undisputed and a safe ground. The same holds for many of the algorithms built on that basis. However, when applied in simulations, these algorithms will usually entail errors. E.g., in

equilibrium simulations it is never possible to sample the entire phase space. Hence, the task is to select and run simulations such that the consequences of the errors are acceptable. Only some well-known aspects are mentioned here, more information on the individual aspects is available in the literature.[8,9,13,28,29]

Simulation period: To rigorously apply statistical thermodynamics, simulations of infinite length would have to be carried out to study equilibrium states, which is obviously impossible. Therefore, the simulation period has to be extensive enough to ensure that the error from incomplete sampling is acceptable. To evaluate how long the run has to be, may not be trivial.[30,31]

Evaluation of interactions: For practical reasons, it is generally impossible to evaluate all interactions in the studied system explicitly, even if only pairwise additivity is assumed. The interactions are therefore usually cut off and long-range corrections are applied. This quickly becomes non-trivial, e.g. for inhomogeneous systems, long-range (electrostatic) interactions, or regarding the application of different cut off schemes (center-of-mass, site-based).

System size: The size of the simulation volume is finite. To avoid undesired boundary effects, techniques like periodic imaging are used. Poor choices may lead to artifacts.

Equilibration period: In equilibrium simulations, the equilibration period which precedes productive sampling must be chosen such that the initial configuration, which is often unphysical, has no influence on the results. It may be non-trivial to decide, when this is the case.

Choice and realization of ensemble: Although theoretically the choice of the ensemble should not matter, in practice it does. There are preferences depending on the type of study and there are also well-known issues with thermostats and barostats.[32,33]

In the discussion above only physical aspects of simulations were addressed. Additionally, numerical issues have to be considered which may lead to erroneous simulation results. Among these are errors related to time integration in MD simulations or the construction of Markov chains in MC simulations, which have been extensively discussed in the literature.[8,9]

In many of the cases mentioned above, errors can be avoided or reduced to an acceptable level by carrying out suitable parametric studies. But carrying out such studies for each possible error source for each studied simulation scenario is practically impossible. This is especially true for large, time consuming simulations. Experienced users will nevertheless generally be able to achieve trustworthy results, but there is no general guarantee that this is the case. The ground may become shaky without anybody noticing it. As illustrated above, many choices have to be made, which cannot be rigorously assessed so that algorithmic errors must be expected and accepted.

2.3 Software errors

Writing complex codes inevitably entails errors. They sometimes lead to very undesirable consequences such as the retraction of scientific papers.[34] There are estimates for the number of errors per 1000 lines of code, which can be obtained from different sources, e.g. by monitoring bug fixes. For large codes, as they are used in molecular simulation, that number is expected to be in the range of 2 to 70 per 1000 lines of code.[35] Numbers at the low end of that range may be expected for comparatively simple codes with a large user community as well as professional development and maintenance. Numbers at the high end can be anticipated for complex codes used by small communities with unsystematic maintenance. For molecular simulation codes, which are generally developed and used in comparatively small academic communities, there should not be too much optimism in this respect. For a typical molecular simulation code of about 100.000 lines, hence, several 100 up to several 1000 errors have to be expected. Fortunately, not all software bugs have an influence on every simulation result. But assuming that there is no influence of software bugs on molecular simulation results would be naive.

The above discussion shows how important professional maintenance of molecular simulation software is, including a feedback system from the user community. Good software requires a continuous effort in debugging. The discussion also highlights the potential ad-

vantage of open source over proprietary codes, if a suitable maintenance system and a strong core development team are established.

2.4 Implementation bugs

Molecular simulation is computationally intensive and therefore usually deployed across multiple compute units. However, parallelization renders algorithms more intricate, thereby increasing the likelihood of algorithmic errors and software bugs. E.g., a shared memory parallelization of a linked-cell algorithm is prone to suffer from race conditions, which can lead to unexpected behavior.[36]

Molecular simulation codes are usually written in compiled languages, such as C or Fortran to achieve high levels of computational performance. Compilers are extremely complex pieces of software, involving millions of lines of code and a large parameter space defining their behavior. Arguably, the behavior of a compiler cannot be fully predicted, leading to a number of potential pitfalls. When using e.g. high optimization levels, compilers will aggressively rearrange or even delete commands, which may have unexpected consequences.

2.5 Errors in the evaluation of simulation results

The amount of data generated in molecular simulations is extremely large. Most of the primary data are discarded already during the simulation run and post-processing of the data is required. This may include sophisticated steps like identification of events and visualization. For simplicity, these steps are considered here as an integral part of the simulation process itself, cf. Figure 1. But it is acknowledged that errors may also occur in the evaluation of molecular simulation data.

2.6 User error

The input data of the simulation is classified here as follows:

1. Specifying the model
2. Specifying the scenario
3. Controlling the algorithms (physical, numerical)
4. Controlling the compilation
5. Controlling the actual simulation run
6. Controlling the evaluation of the simulation results

Any input data is prone to user error.

The importance of user errors has recently been discussed by Wong-ekkabut and Karttunen in a paper entitled: *The good, the bad, and the user in soft matter simulations*,[37] in which they give many non-trivial examples for user errors and conclude that the user is the "most significant error source" and that "one does not become a theorist by buying chalk, experimentalist by buying a microscope, or a computational scientist by downloading software". Based on the experience from the present work, we fully agree and add only that user errors are not a privilege of rookies but regularly happen to experienced users as many examples show.[34]

3 Round robin study

3.1 Procedure

The user groups and simulation codes participating in the present round robin study are summarized in Tables 1 and 2. The procedure is illustrated in Figure 2. The central instance was at University of Kaiserslautern and it connected the user groups during the simulation phase of the study, in which the user groups worked independently. Communication between the groups took place only during the preliminary phase, before the simulations were performed, and during the wrap-up phase.

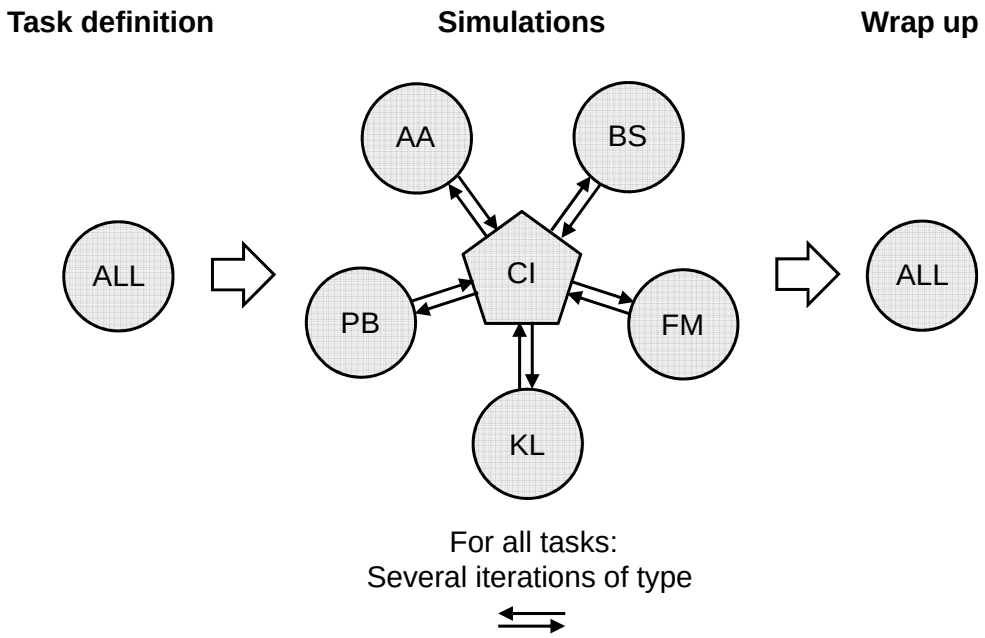

Figure 2: Overview of the round robin study. During the simulation phase the five user groups (AA, BS, FM, KL, PB) worked independently, connected only by the central instance (CI).

In the preliminary phase of the round robin study, the tasks were defined. Each task is a physical problem to be solved by simulation. More information on the tasks is given in the next section. In addition, simulation settings were specified in the preliminary phase. All production runs were carried out in the isobaric-isothermal (NpT) ensemble with 512 molecules. The cut-off radius was calculated with respect to the center of mass and was 14 Å, except for Tinker with 15 Å and IMC with almost half of the edge length of the simulation volume. Statistical errors were estimated by block averaging with a block size of 5000 time steps for MD simulations and at least $1.5 \cdot 10^6$ trial displacements for MC simulations. The reported numbers are the standard deviation σ of the block averages. More information is given in the Supporting Information.

Accounting for differences between the codes and the on-site situation of the participating user groups, e.g. regarding computer access, the choices for simulation settings were only recommended and could always be overruled by the general guideline that all groups should work to the best of their knowledge with their codes, while respecting the agreed feedback times of the round robin study. A list of the employed hardware, compilers and parallelization strategies is given in the Supporting Information.

It turned out to be necessary to carry out several iterations because an inspection of the results submitted to the central instance after the first iteration partially revealed very large differences, cf. Supporting Information for an example. Most of these differences could later be traced back to different types of input errors or faulty communication. E.g., it turned out to be particularly cumbersome that in different codes different types and implementations of intramolecular potentials functions are used. Some of the errors would in the end probably have been eliminated also by a user group working on its own, e.g. by checking internal consistency. But other errors would have remained hidden, had the simulations not been carried out in a round robin study. This also illustrates the need for carrying out several iterations in this round robin study. After every iteration, the results were compared by the central instance and qualitative feedback was given to the participating groups. The

feedback consisted only in an indication of those results which deviated strongly from a set of results obtained by other user groups, which showed much better mutual agreement.

Within each iteration step, the reaction to feedback from the central instance was in the sole responsibility of the respective user group. It generally consisted of checking the input parameters and carrying out new simulations with modified parameters. It has to be mentioned that even cryptic feedback, as it was given, may contain valuable information for the search for errors, namely when only certain results of the respective group were challenged, whereas others were (implicitly) confirmed. This procedure eliminated most gross errors over time.

During every iteration, each user group executed the assigned tasks within several weeks. Subsequently, the results from all groups were reported to the central instance, which evaluated them and gave feedback as described above. Based on that feedback, the next iteration was started. The criterion to end the iterations was simply a time-out after about six months. Only the final results are reported below. They would have changed further, had the iterations continued.

3.2 Tasks

The idea was to select a set of comparatively simple molecular simulation tasks and to focus on the quantitative accuracy of the results. The tasks were exactly the same for all groups, but not all codes could be used for all tasks. They consisted of finding numbers for the specific density ρ and the molar potential energy u of different fluid models for a range of liquid state points. The molar potential energy u was calculated from the contributions of all pair-potentials, i.e. intra- and intermolecular, excluding the kinetic energy. For brevity, ρ is referred to as density and u as energy in the following.

Four substances were considered in the study: ethane, propane, n-butane, and iso-butane. They have an increasing complexity with respect to the intramolecular interactions, but are similar with respect to the intermolecular interactions. 12 state points at temperatures

of 98, 173, 248, and 298 K and pressures of 5, 41, and 70 MPa were chosen, where all considered substances are liquid. The large number of state points allows for assessing the internal consistency of the corresponding data set.

Table 3 gives an overview of the considered force fields, their parameters are reported in the Supporting Information. All force fields describe the alkyl groups on the basis of the united atom approach and account for the internal degrees of freedom. However, OPLS and TraPPE do not account for bond stretching. Therefore, when ethane is described with these force fields, it is a rigid body, which is realized by constraint algorithms.

Table 3: Studied force fields.

Force field	Description	Reference
OPLS	Optimized potentials for liquid simulations	[14,15]
TraPPE	Transferable potentials for phase equilibria	[14]
OPLSAMBER	OPLS with stretching vibrations from AMBER	[14–16]

To also include a force field with high frequency bond stretching vibrations, the OPLS force field was modified by including the bond stretching potential from the AMBER force field, named OPLSAMBER here. Using that simple combination is not critical here as the aim is not the comparison to experimental data. For intermolecular interactions between unlike sites, the Lorentz-Berthelot combining rules were used throughout.

The following restrictions regarding the application of the present simulations codes to the studied force fields were encountered: IMC, *ms*2*(MC), and NAMD cannot handle fixed bond lengths and were therefore only used for OPLSAMBER. LAMMPS cannot handle models constraining three or more consecutive bond stretching vibrations and was thus not used for n-butane with OPLS and TraPPE. The results obtained with Tinker for the energy are not reported here because the energy calculation was erroneous in this study. The source of this deviation could not be identified until the time-out of this work.

4 Results and discussion

4.1 Overview

Systematic errors were investigated by solving identical simulation tasks with different codes, running on different computers, operated by different user groups. In the following, we simply refer to this as "results of different groups", even though there are cases in which results were produced with different codes by the same user group. The main interest lies on quantitative differences between the results of the different groups, while comparison with experimental data is not of interest.

First, the results for the two force fields without bond stretching (OPLS and TraPPE) and subsequently those for the force field with bond stretching (OPLSAMBER) are discussed because the findings with respect to the systematic errors differ in these groups. As expected, the findings regarding the systematic errors do not differ significantly for data sets obtained for different pressures. Therefore, mainly results at 41 MPa are discussed. The numerical simulation results from the present study including information on the statistical uncertainties as obtained from the respective programs are reported in the Supporting Information.

4.2 Force fields without bond stretching

4.2.1 Density

Before entering a broader discussion of the results, a typical example is presented and discussed in detail. The results for the density of n-butane at 41 MPa obtained with the OPLS force field are chosen for this purpose. Results obtained after the first iteration are shown in the Supporting Information, the final ones in Figure 3. After elimination of the gross errors during the iterations, the results seem to agree very well at a first glance, cf. Figure 3 (top). The scatter of the results is only about $\pm$ 3 kg/m^3, which is acceptable for many applications.

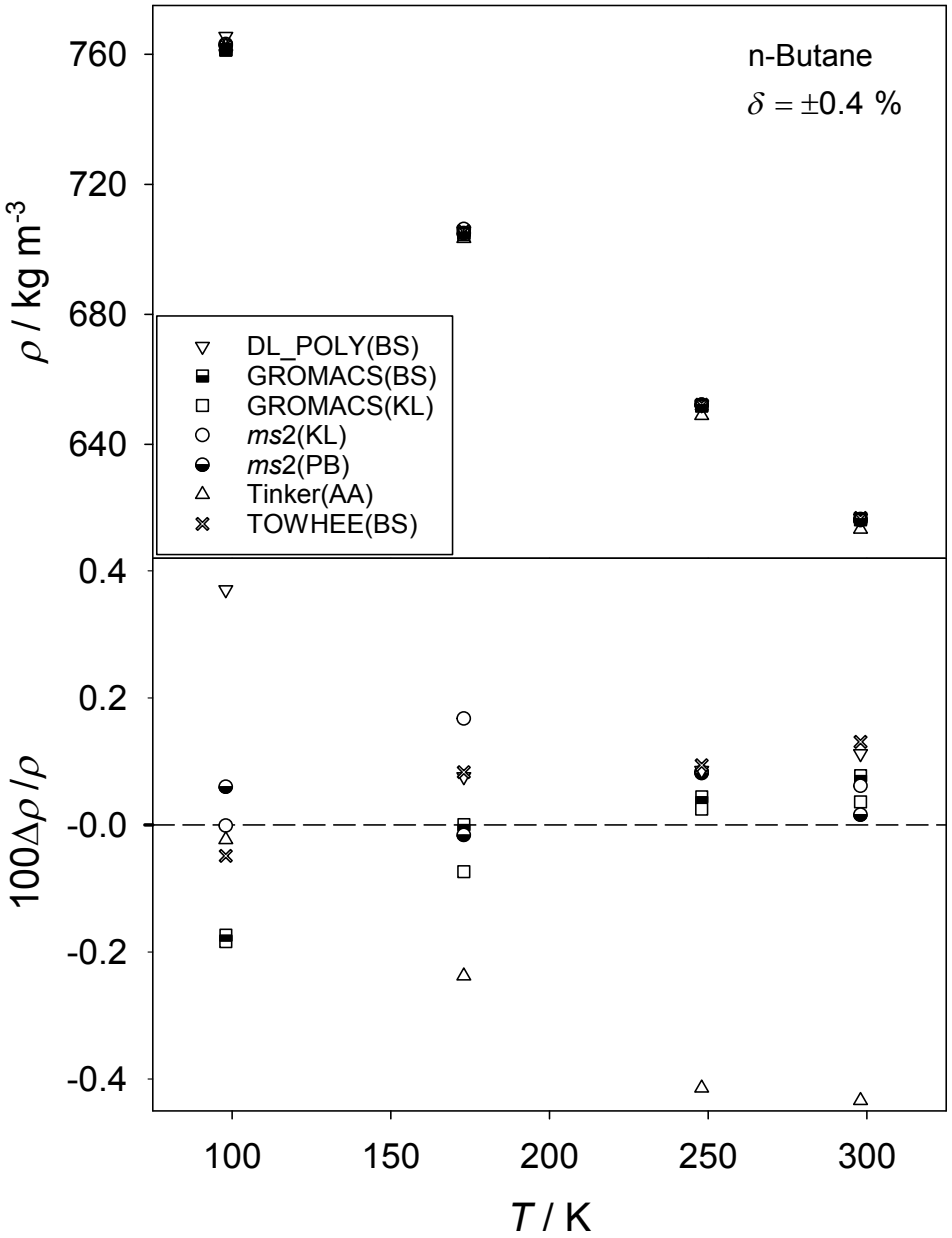

Figure 3: Density of n-butane at 41 MPa from the OPLS force field as a function of temperature. Symbols: results from different groups working with different codes. Top: absolute numbers. Bottom: relative deviations from the arithmetic mean value (dashed line). δ indicates the width of the band in which these relative deviations lie and is taken here as an estimate for the systematic uncertainty of the data.

For a detailed discussion of the results, the arithmetic mean of the results from the different groups was calculated and the relative deviation of the individual results from that arithmetic mean determined. Taking the arithmetic mean as a guess for the true model value of the density, the deviation can be interpreted as the uncertainty resulting from systematic error. The result for the above example is included in Figure 3 (bottom). The deviations lie in a band of $\delta = \pm$ 0.4 % in that case. Two of the programs, GROMACS and $ms2$, were both used by two different groups. The corresponding results agree within $\pm$ 0.2 %.

We refrain here from entering a detailed discussion of results of individual simulation codes or different algorithms. This would inevitably lead to discussing their strengths and weaknesses, and would have to include benchmarking computational performance, which is not in the scope of the present study.

The above results for the deviations have to be compared to the statistical uncertainty of the individual results. The error bars are not included in Figure 3 for clarity. The data obtained for the case studied here at 98 K and 248 K are used to discuss this topic exemplarily in Figure 4. The error bars reported in Figure 4 were determined from an evaluation of the block averages of the production phase and represent the standard deviation σ. The large error bars obtained from DL_POLY and Tinker are related to fluctuations in pressure and temperature for these programs, where they were up to $\pm$ 5 MPa and $\pm$ 5 K for DL_POLY and Tinker and below $\pm$ 0.2 MPa and $\pm$ 0.1 K for the other three programs. At 248 K, all results agree within $\pm$ 0.1 %, with Tinker being the sole exception. At 98 K, the results agree within $\pm$ 0.2 %, again with one exception, i.e. DL_POLY. However, the comparably large deviations of Tinker and DL_POLY from the average of all results are still within the large error bars for these simulations. But for many of the other results, which have distinctly smaller error bars, the deviation of the results from the mean of all results clearly exceeds the error bar. Not even the results obtained with the same code by different groups agree within their error bars in all cases.

Regarding the data obtained at 248 K, cf. Figure 4 (bottom), it can be argued that

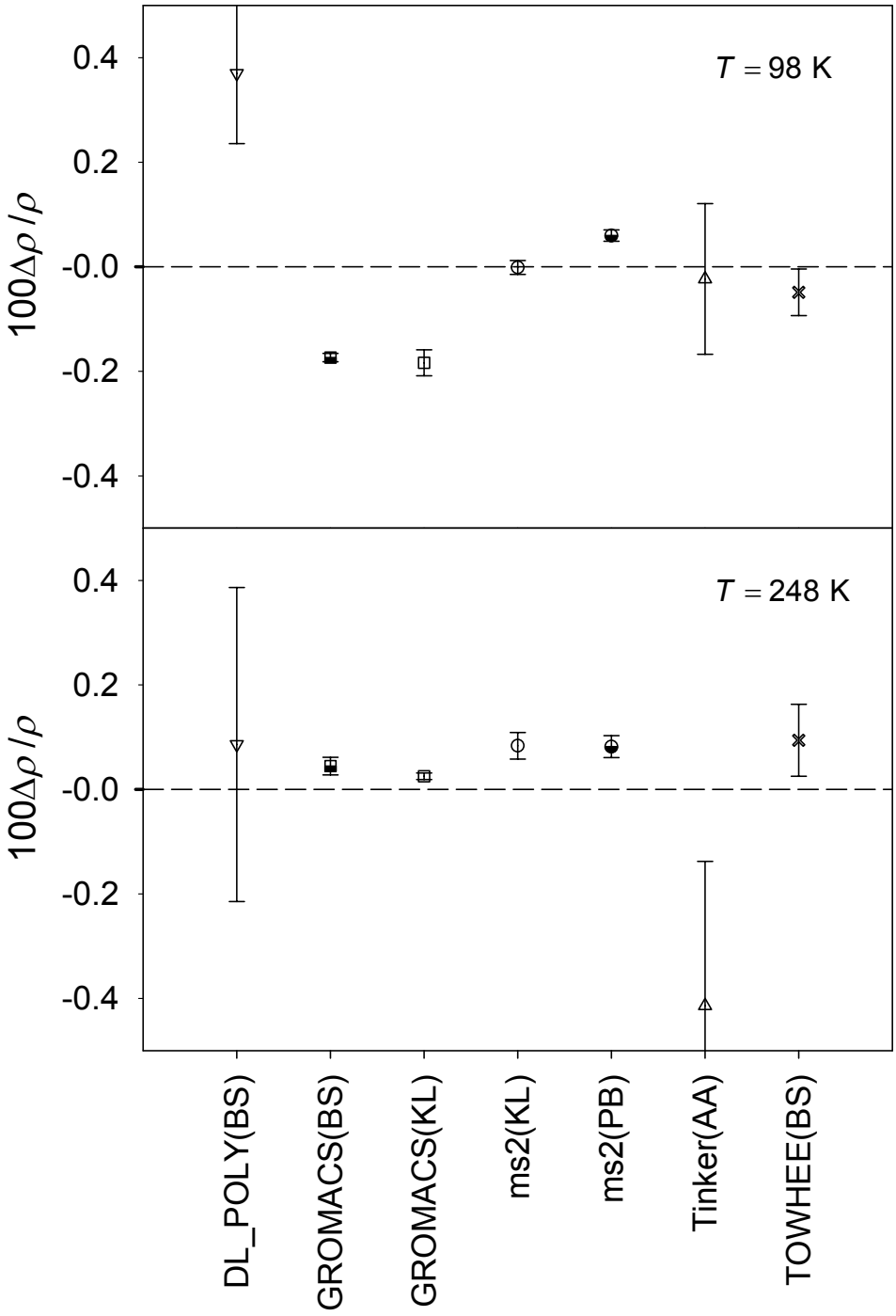

Figure 4: Statistical uncertainty of the data obtained for the density of n-butane at 41 MPa and 98 K (top) and 248 K (bottom) from the OPLS force field. Symbols: mean values with error bars determined from block averages of the production phase. The large error bars of the DL_POLY and Tinker data are due to the chosen barostat. Dashed line: arithmetic mean of all results.

after removal of the Tinker result, a more favorable picture would be obtained. The average of all results would be shifted upwards and the deviation of the remaining results from the average would be within the error bars in most cases. However, this statement is biased by arbitrarily disregarding one result. But even if such a bias was accepted, which we do not, and a similar procedure would be repeated for the data obtained at 98 K, the results would still not match within their error bars, cf. Figure 4 (top). The results shown in Figure 4 are typical. In general, the results from the different simulation codes do not agree within their statistical uncertainty.

It should be noted that we simply report and evaluate the data as they were obtained in the final iteration. Further improvements would have been possible, if more time would have been given for the round robin study. E.g., in the above case, the groups working with Tinker and DL_POLY could have revisited the particular simulations and could have worked on the barostat parameters or other settings. But this merely shows that it is fairly easy to adjust simulation settings to obtain a desired value, which is obviously unacceptable.

Furthermore, one could argue that some programs are more reliable than others, and therefore should be preferred. While this may be true, we refrain from an assessment of simulation codes, a task which is out of the scope of the present study. We also note that the discussion of the quality of the codes would have to be lead, if the sole aim of the study would have been the determination of reference data. Nevertheless, the unbiased data from the present study can well be used as reference data, although reference values with even smaller error bars could probably be obtained in a dedicated study.

The results obtained for the density of the other three substances with the OPLS force field at 41 MPa are shown in Figures 5, 6 and 7. They basically confirm the results for n-butane. Also values for δ are reported, which indicate the width of the band in which the relative deviations of the individual results around their arithmetic mean lie. The value of δ is taken here as an estimate for the systematic uncertainty of the simulation data. For the discussed case the results here are $\delta = \pm$ 0.4 % for n-butane (cf. Figure 3), $\pm$ 0.2 % for

ethane and propane, cf. Figures 5 and 6, and ± 0.6 % for iso-butane, cf. Figure 7. Note that even the small value for ethane exceeds the statistical uncertainty of the simulation data in most cases.

The corresponding results for the TraPPE force field as well as the data for the other pressure levels obtained with the OPLS and TraPPE force fields are presented in the Supporting Information in numerical form. They all confirm the statements above.

4.2.2 Energy

The data obtained for the molar potential energy u of the studied alkanes as a function of the temperature with the OPLS force field are presented in Figure 8.

Figure 8 contains numbers for δ, which characterize the scatter of the results from the different groups. They are taken here as a measure for the systematic error, i.e. $\delta = \pm$ 0.2 % for ethane and propane, ± 1.0 % for iso-butane, and ± 1.6 % for n-butane. The statistical uncertainties of the individual results are similar to those for the density, i.e. about ± 0.05 % for GROMACS and *ms*2, ± 0.1 % for TOWHEE and ± 0.3 to 1.2 % for DL_POLY. As for the density, the deviations between the results from the different groups are generally outside of the statistical uncertainty of the individual results. The results from the TraPPE force field are similar and listed numerically in the Supporting Information.

4.3 Force fields with bond stretching

4.3.1 Density

Figure 9 shows the results for the density of the alkanes obtained with the OPLSAMBER force field for which all simulation codes could be used. The scatter of the data obtained by the different groups is much larger than for the force fields without bond stretching, i.e. $\delta = \pm$ 4.9 % for ethane, ± 3.6 % for propane, ± 2.2 % for n-butane, and ± 1.0 % for iso-butane, and, hence, roughly one order of magnitude larger than those found in the studies presented above. The results for the density deviate by up to about 50 kg/m^3, which is

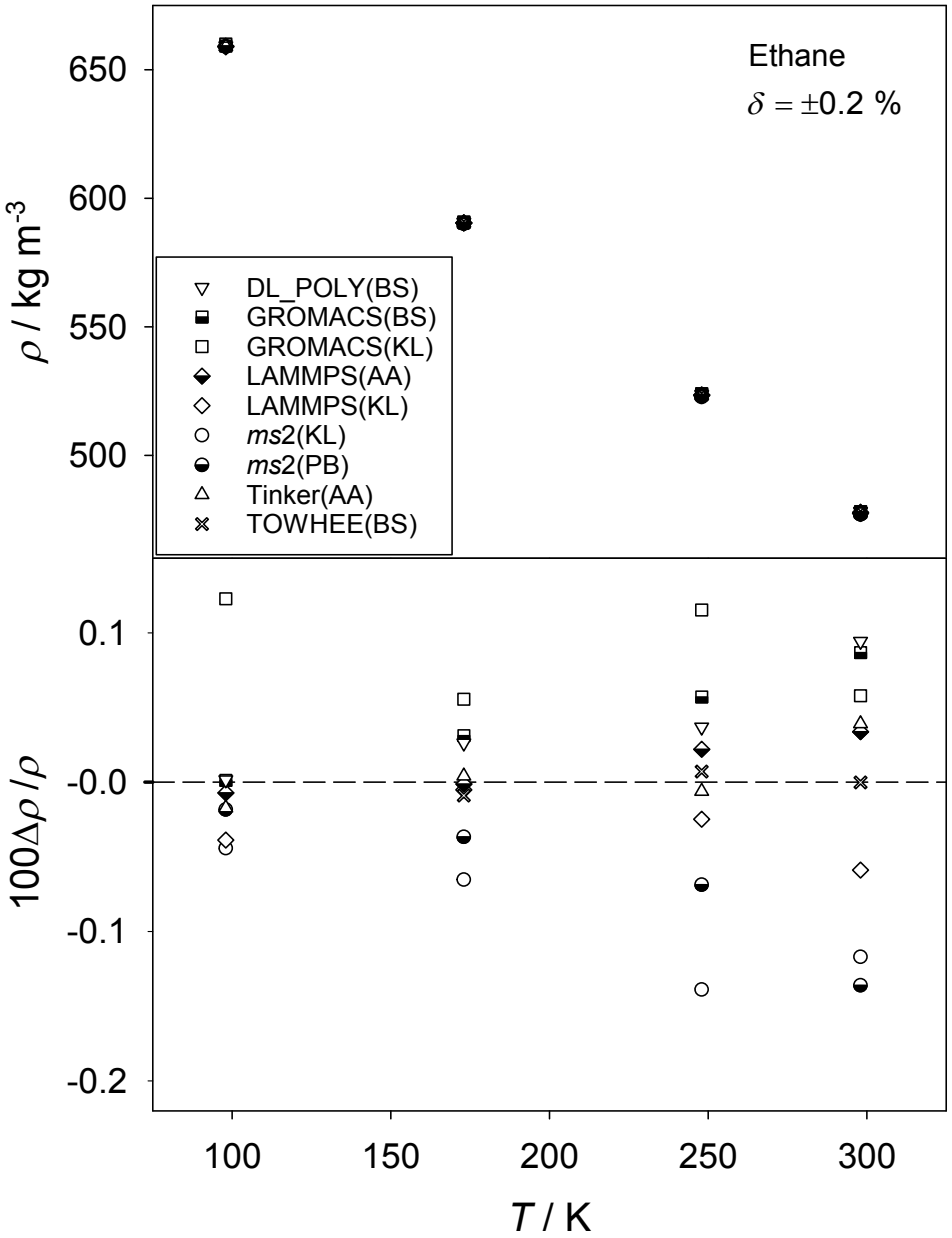

Figure 5: Density of ethane at 41 MPa from the OPLS force field as a function of temperature. Symbols: Results from different groups working with different codes. Top: absolute numbers. Bottom: relative deviations from the arithmetic mean value (dashed line). δ is the width of the band in which the relative deviations of the individual results from their arithmetic mean lie.

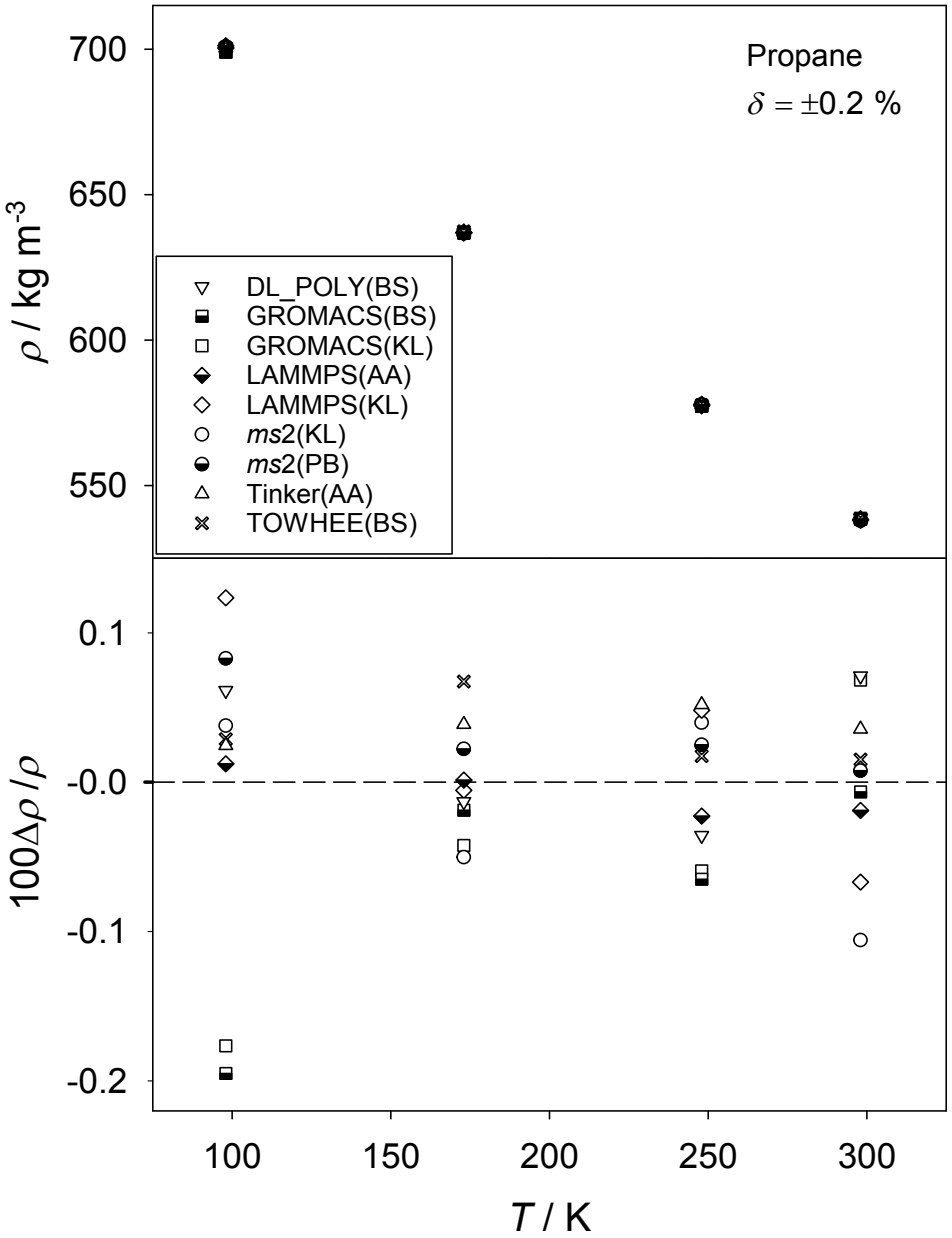

Figure 6: Density of propane at 41 MPa from the OPLS force field as a function of temperature. Symbols: Results from different groups working with different codes. Top: absolute numbers. Bottom: relative deviations from the arithmetic mean value (dashed line). δ is the width of the band in which the relative deviations of the individual results from their arithmetic mean lie.

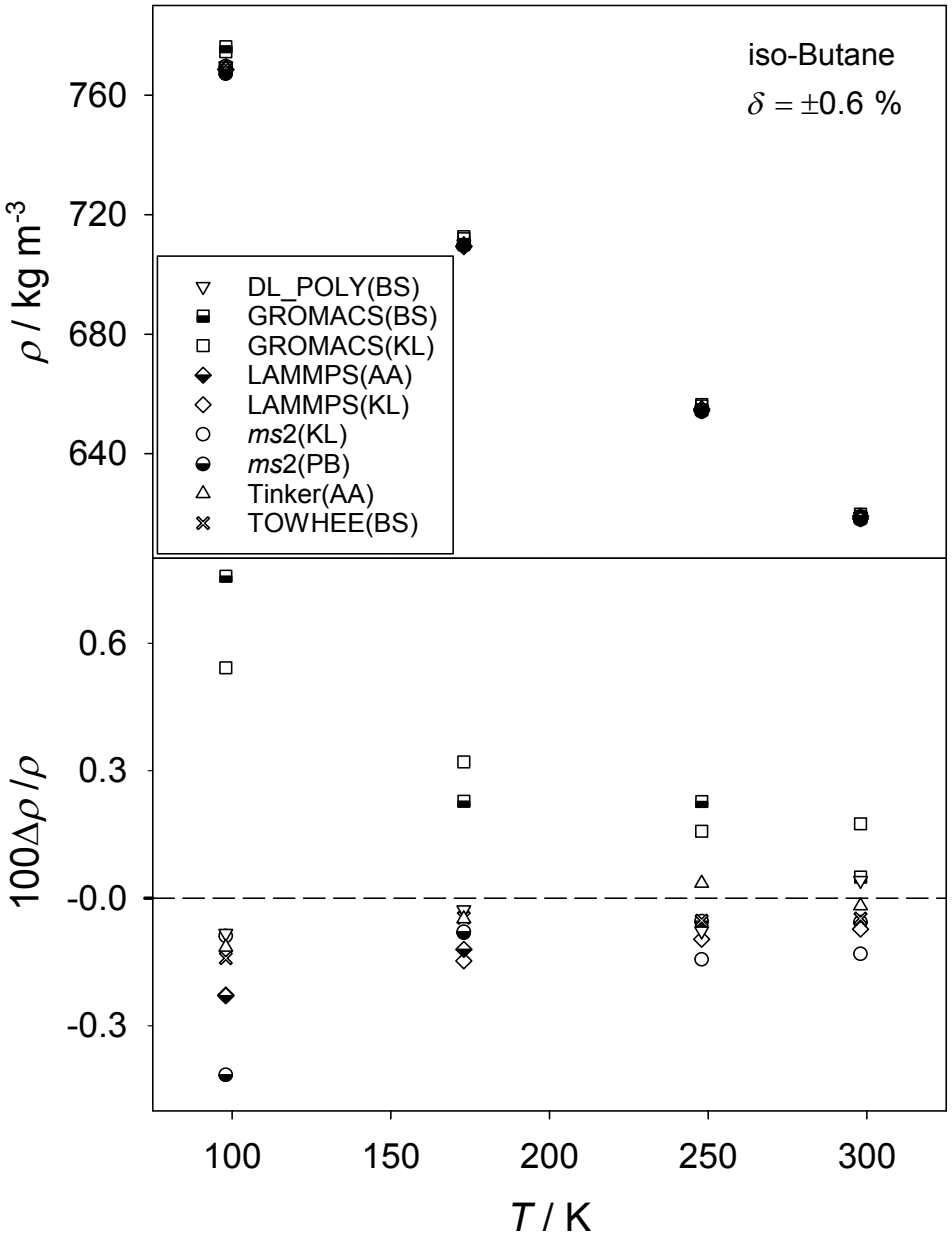

Figure 7: Density of iso-butane at 41 MPa from the OPLS force field as a function of temperature. Symbols: Results from different groups working with different codes. Top: absolute numbers. Bottom: relative deviations from the arithmetic mean value (dashed line). δ is the width of the band in which the relative deviations of the individual results from their arithmetic mean lie.

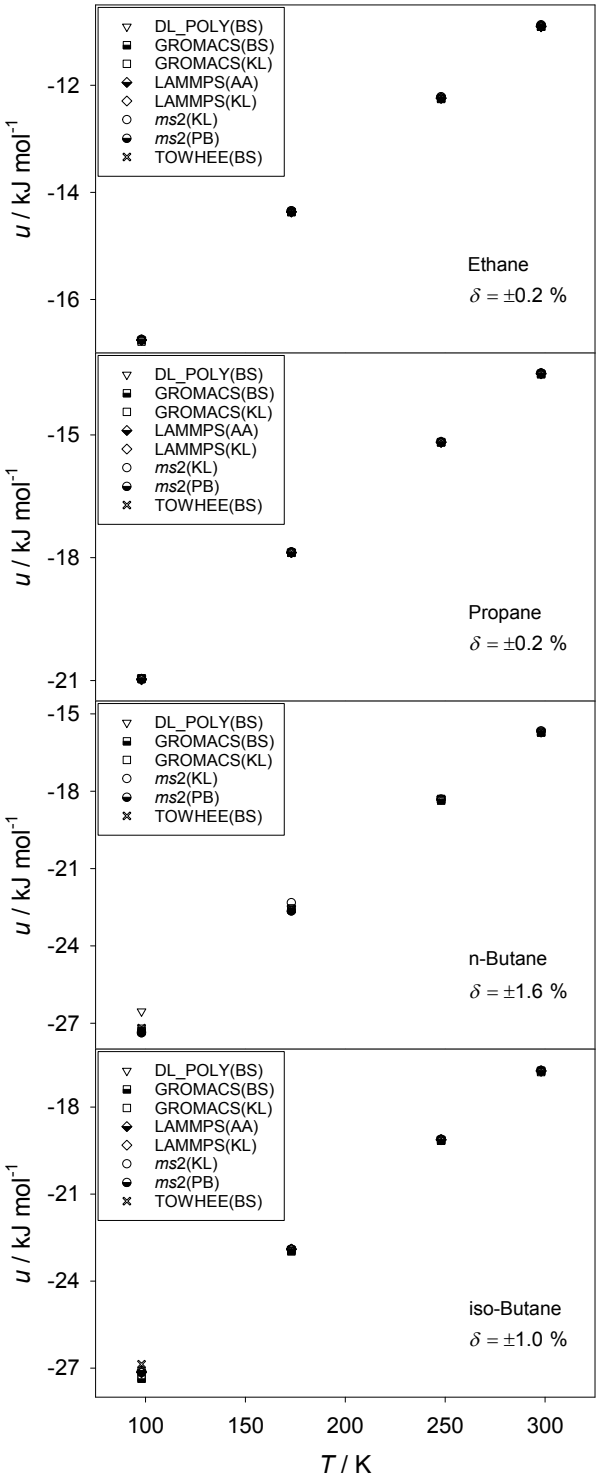

Figure 8: Energy of ethane, propane, n-butane, and iso-butane (from top to bottom) at 41 MPa from the OPLS force field as a function of temperature. Symbols: Results from different groups working with different codes. δ is the width of the band in which the relative deviations of the individual results from their arithmetic mean lie.

unacceptable for many applications. It is pointed out that the results presented in Figure 9 are those at the end of the iterations of the round robin study, i.e. after elimination of gross errors.

The statistical uncertainties are exemplarily shown in Figure 10 for n-butane at 41 MPa and 173 K and 248 K. The error bars of the individual results obtained by the different groups have the same order of magnitude as for the force fields considered in Section 4.2 and range between about $\pm$ 0.05 and $\pm$ 0.5 %. The deviations between the results obtained by the different groups are, hence, much larger than the individual statistical uncertainties. This holds even in cases in which the same program was used by different groups. The results for the other pressure levels are similar.

The only difference between the OPLS and OPLSAMBER force field is the consideration of the bond stretching. It is evident to assume that this is the cause of the large deviations. In the MD simulations shown in Figure 10 different time steps were used. In the range of 0.12 - 1.2 fs no systematic influence of the time step was observed. E.g. the LAMMPS results shown in Figure 10 agree, even though they were obtained with time steps differing by a factor of 10.

Another interesting finding that might shed light on the reasons of the discrepancies is the following: for both OPLS and TraPPE an increase of the deviations between the results from the different groups as measured by δ was observed for increasing complexity of the molecule, i.e. going from ethane to the butanes, cf. Section 4.2. The opposite trend was found for OPLSAMBER, cf. Figure 9.

In general, with increasing model complexity also the complexity of the model evaluation increases, which in turn leads to an increase of the number of potential sources of systematic error of the simulation result.

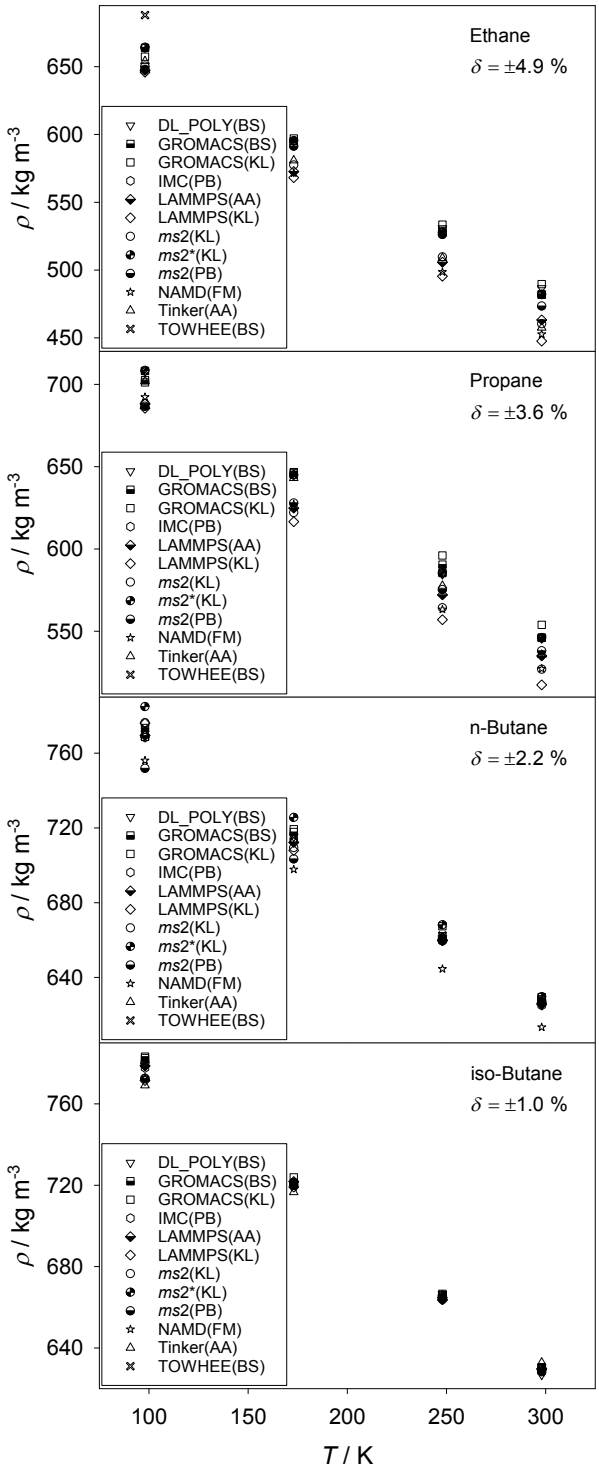

Figure 9: Density of ethane, propane, n-butane, and iso-butane (from top to bottom) at 41 MPa from the OPLSAMBER force field as a function of temperature. Symbols: Results from different groups working with different codes. δ is the width of the band in which the relative deviations of the individual results from their arithmetic mean lie.

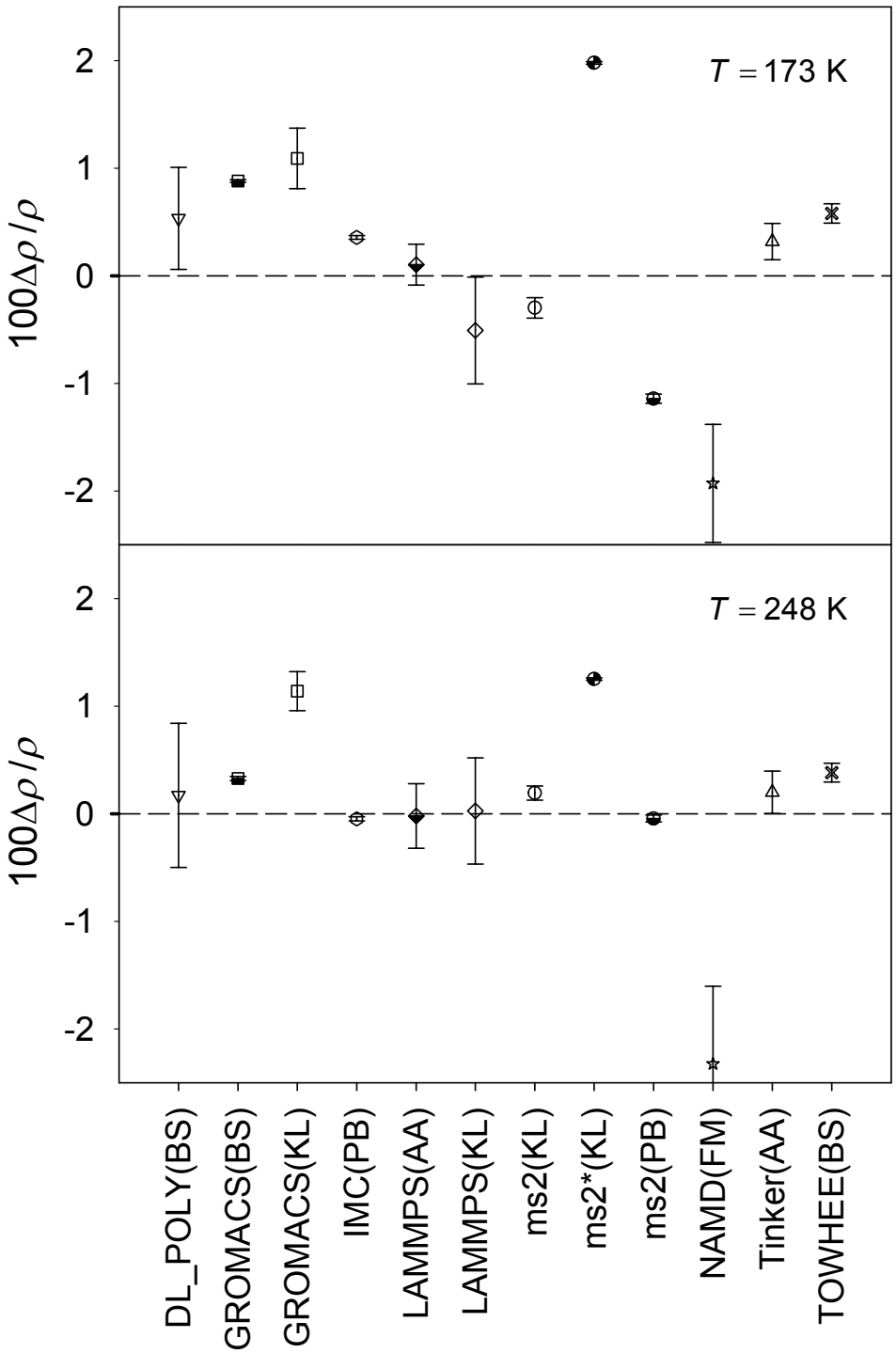

Figure 10: Statistical uncertainty of the data obtained for the density of n-butane at 41 MPa and 173 (top) and 248 K (bottom) from the OPLSAMBER force field. Symbols: mean values with error bars determined from block averages of the production phase. Dashed line: arithmetic mean of all results.

4.3.2 Energy

The results obtained from the OPLSAMBER force field for the energy at 41 MPa are presented in Figure 11. Again, the results for the other pressure levels are similar. The results obtained by different groups deviate generally by $\delta = \pm$ 1.4 % for ethane, $\pm$ 1.1 % for propane, $\pm$ 9.7 % for n-butane, and $\pm$ 4.4 % for iso-butane. The statistical uncertainties reported by the different codes are typically in the range of $\pm$ 0.1 to 0.6 %. Hence the deviations between the results from the different groups exceed the statistical uncertainty of the individual results by far, which underpins the above statements on the importance of systematic errors.

5 Conclusions

The present work addresses the issue of systematic errors in molecular simulation. The quality of the models, i.e. the question whether they are a good description of some real fluid or not, is not addressed.

Statistical and systematic errors were assessed by a round robin study. The same set of simulation tasks was given to independently working user groups, which used different molecular simulation codes for solving the tasks. Under ideal circumstances, i.e. in the absence of systematic errors, the results from the different groups should agree within their statistical uncertainties. The results show that this is not the case in reality. The present study is the first of its kind and addresses the issue on a broad front. There were five participating groups, which worked with eight different molecular simulation codes. The tasks were quite simple: the determination of the density and the energy of four pure liquids, i.e. ethane, propane, n-butane, and iso-butane, on a given temperature–pressure grid. Three molecular model types were used, all of them with internal degrees of freedom.

The collected data demonstrate that systematic errors are important in molecular simulations. In many cases, the deviations between the results obtained by the different groups far

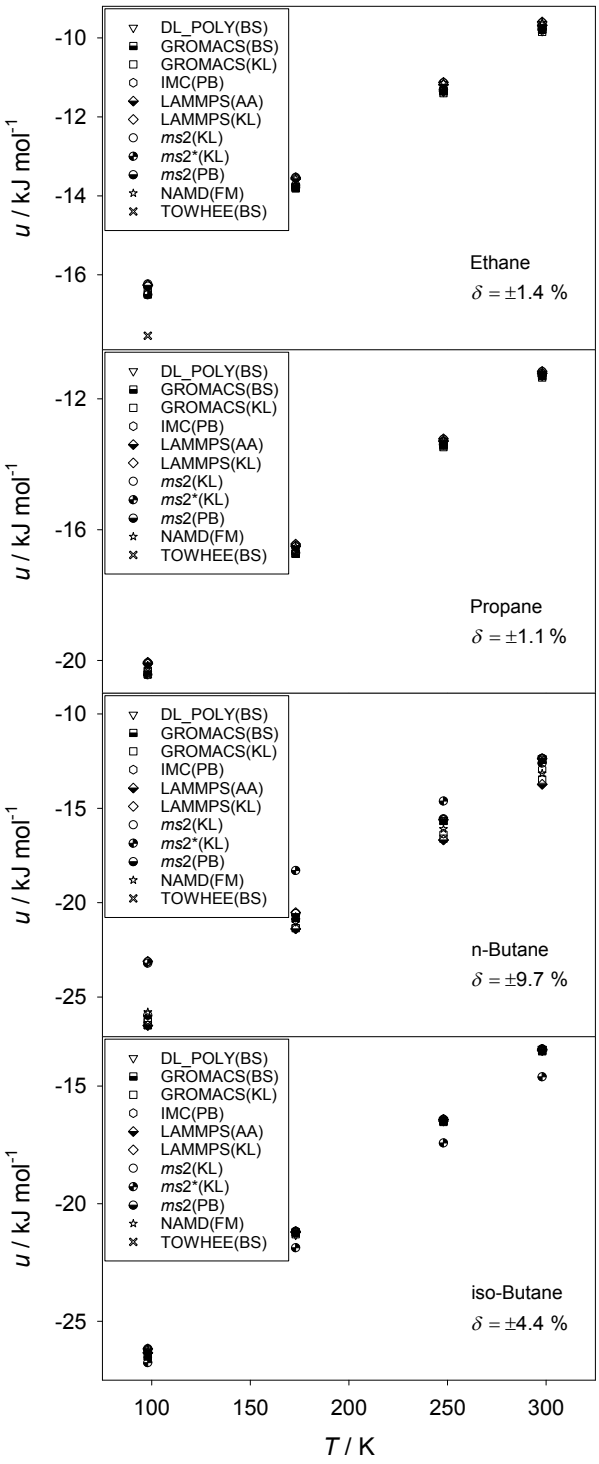

Figure 11: Energy of ethane, propane, n-butane, and iso-butane (from top to bottom) at 41 MPa from the OPLSAMBER force field as a function of temperature. Symbols: Results from different groups working with different codes. δ is the width of the band in which the relative deviations of the individual results from their arithmetic mean lie.

exceed the statistical uncertainty of the individual results. Potential reasons for these errors are plentiful and are briefly discussed. Systematic errors can probably not be completely avoided once a certain degree of simulation complexity is reached. This is highlighted by the fact that the deviations between the results from the different groups were distinctly larger for more complex force fields.

We emphasize that it must be the goal to aim at entirely avoiding systematic errors in molecular simulations. However, there should be no doubt that fully achieving this goal is practically impossible.

Acknowledgement

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Center Stuttgart (HLRS) under the grant MMHBF2. Simulations of both groups were conducted under the auspices of the Boltzmann-Zuse Society of Computational Molecular Engineering (BZS).

Supporting Information Available

The "Supporting Information to Round Robin Study: Molecular Simulation of Thermodynamic Properties from Models with Internal Degrees of Freedom" shows an example for results after the first iteration, includes detailed information on hardware, parallelization and compilers, detailed descriptions of the simulation settings and force field specifications as well as the numerical results of all simulation tasks carried out in this work.

This information is available free of charge via the Internet at http://pubs.acs.org

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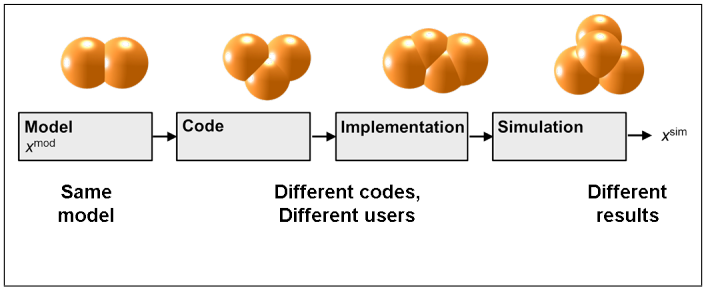
Graphical TOC Entry



Supporting Information to Round Robin Study: Molecular Simulation of Thermodynamic Properties from Models with Internal Degrees of Freedom

Michael Schappals, Andreas Mecklenfeld, Leif Kröger, Vitalie Botan, Andreas Köster, Simon Stephan, Edder Garcia, Gabor Rutkai, Gabriele Raabe, Peter Klein, Kai Leonhard, Colin W. Glass, Johannes Lenhard, Jadran Vrabec, and Hans Hasse*

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Abstract

This supporting information includes detailed information on hardware, parallelization and compilers, detailed descriptions of the simulation settings and force field specifications as well as the numerical results of all simulation tasks carried out in this work.

1 Example for results after the first iteration

Figure 1 shows a typical example for results submitted to the central instance after the first iteration.

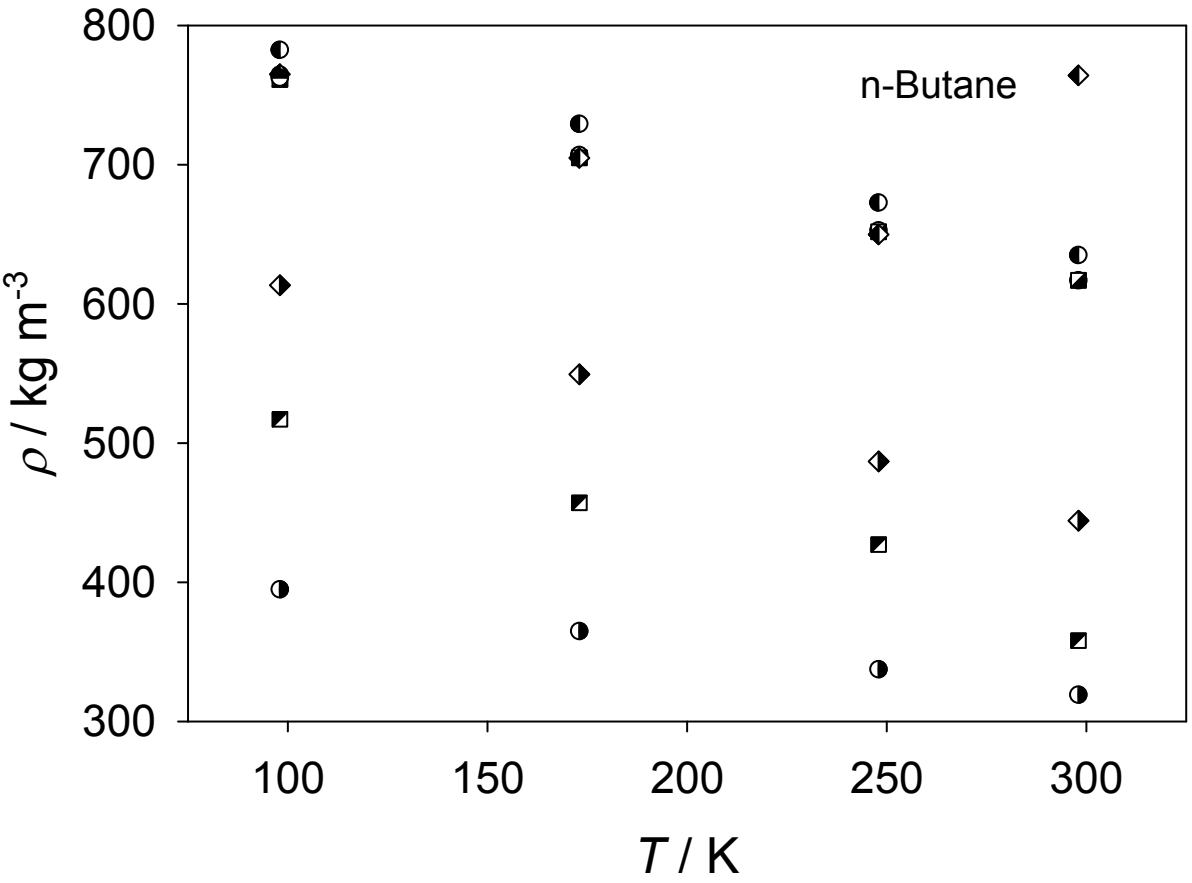

Figure 1: Example for results submitted to the central instance after the first iteration. The task was to simulate the density of n-butane at 41 MPa for the indicated temperatures with the OPLS force field. Different symbols stand for results from different user groups working with different simulation codes. There are seven different symbols, but due to overlap not all of them can be discerned. The extreme differences are in most cases due to input errors that were eliminated later, cf. Figure 3 from the main text.. A declaration of the symbols is not provided because it does not matter here. The choice of symbols is not the same as in the other figures of this work.

2 Hardware, parallelization and compilers

The simulations were carried out by the different user groups on different compute clusters:

- Competence Center High Performance Computing and Visualization (ITWM)
- Institutscluster Verbrennungskraftmaschinen - Verfahrenstechnik (vvtsim)
- North-German Supercomputing Alliance (HLRN)
- Paderborn Center for Parallel Computing (PC^2)
- Regional University Computing Center Kaiserslautern (RHRK)
- RWTH Compute Cluster (RWTH)

All molecular simulation codes were compiled with either INTEL or GNU compilers of different versions and employed various parallelization schemes, cf. Table 1.

Table 1: Compilers, parallelization and execution settings of the molecular simulation codes.

Program	Compiler	Parallelization	Cluster	Cores
DL_POLY(BS)	INTEL 11.0.1	OpenMPI 1.3.3	vvtsim	4
GROMACS(BS)	gcc 4.9.1	MPICH 7.2.5, OpenMP 4.0	HLRN	24
GROMACS(KL)	INTEL 15.0.1	OpenMPI 1.6.5	RHRK	8
IMC(PB)	gcc 4.6.1	none	PC^2	1
LAMMPS(AA)	INTEL 14.0.2	INTEL MPI 14.0.2	RWTH	2
LAMMPS(KL)	INTEL 15.0.3	INTEL MPI 15.0.3	RHRK	12
*ms*2(KL)	INTEL 14.0.2	INTEL MPI 14.0.2	RHRK	8
*ms*2*(KL)	INTEL 14.0.2	INTEL MPI 14.0.2	RHRK	8
*ms*2(PB)	INTEL 15.0.1	OpenMPI 1.10.2	PC^2	4
NAMD(FM)	gcc 4.3.4	Charm++	ITWM	16
Tinker(AA)	gcc 4.8.3	OpenMP 3.1	RWTH	2
TOWHEE(BS)	INTEL 11.0.1	none	vvtsim	1

3 Simulation settings

The number of molecules was 512 throughout. The real-space cutoff was equal to the Lennard-Jones cutoff distance of 14 Å, except for Tinker with 15 Å and IMC with almost

half of the edge length of the simulation volume. The Lorentz-Berthelot mixing rules were used in all programs.

An overview of the simulation settings of the MD simulations is given in Table 2. The temperature was specified either with isokinetic scaling or the Nosé-Hoover thermostat. Different barostats (Berendsen, Andersen, Nosé-Hoover) with different damping parameteres were employed, depending on the program. The bond constraints were realized by the SHAKE algorithm[1] with a tolerance of 10^{-4}. In MD simulations, Newton's equations of motion were solved with either the leap-frog or the velocity Verlet integrator with a time step of 1.2 fs for the OPLS and TraPPE force fields. The statistical uncertainties were estimated by block averaging with a block size of 5.000 time steps for all programs. The MD simulations were conducted as follows: First, an equilibration in the canonical (NVT) ensemble was carried out over $0.25{\cdot}10^6$ time steps. Then the isothermal-isobaric (NpT) ensemble was used, initially in a second equilibration phase of $0.25{\cdot}10^6$ time steps, followed by a production run of $1{\cdot}10^6$ time steps. For the OPLSAMBER force field different time steps between 0.12 - 1.2 fs were applied while increasing the number of the time steps accordingly to yield the same simulation time in all tasks.

Table 2: Algorithms and simulation settings of the MD simulations.

Program	Thermostat	Barostat	Integrator
DL_POLY(BS)	Nosé-Hoover	Nosé-Hoover	Velocity Verlet
GROMACS(BS)	Berendsen	Parrinello-Rahman	Leap-Frog
GROMACS(KL)	Velocity scaling	Berendsen	Leap-Frog
LAMMPS(AA)	Nosé-Hoover	Nosé-Hoover	Velocity Verlet
LAMMPS(KL)	Nosé-Hoover	Nosé-Hoover	Velocity Verlet
*ms*2(KL)	Velocity scaling	Andersen	Leap-Frog
*ms*2(PB)	Velocity scaling	Andersen	Leap-Frog
NAMD(FM)	Velocity scaling	Nosé-Hoover Langevin	Leap-Frog
Tinker(AA)	Nosé-Hoover	Nosé-Hoover	Nosé-Hoover

MC simulations were carried out with an acceptance rate of 50 % employing IMC, *ms*2* and TOWHEE. Trial displacements and other simulation settings are shown in Table 3. Random volume changes were evaluated according to the Metropolis acceptance criterion for

the barostat. Block averaging was used for the determination of the statistical uncertainties as well. One block consisted of $1.5{\cdot}10^6$ trial displacements for IMC and $ms2^*$ and $15{\cdot}10^6$ for TOWHEE. MC simulations with $ms2$ and TOWHEE were carried out using $75{\cdot}10^6$ trial displacements during NVT equilibration as well as in the following NpT equilibration, and $300{\cdot}10^6$ trial displacements for production. Production runs with IMC had the same length, but only a NpT equilibration of $120{\cdot}10^6$ trial displacements was used.

Table 3: Displacements and other simulation settings of the MC codes.

Program	IMC(PB)	$ms2^*$(KL)	TOWHEE(BS)
Acceptance rate	0.5	0.5	0.5
Site move/rotate ratio	0.2	0.6	0.1
Configurational bias/regrowth ratio			0.5
Molecule move/rotate ratio	0.8	0.4	0.4
NVT equilibration	none	$75{\cdot}10^6$	$75{\cdot}10^6$
NpT equilibration	$120{\cdot}10^6$	$75{\cdot}10^6$	$75{\cdot}10^6$
Production	$300{\cdot}10^6$	$300{\cdot}10^6$	$300{\cdot}10^6$

4 Force field parameters

The force field parameters used in the present study are summarized in Tables 4, 5, 6, and 7 and were taken from the literature.[2–4] In addition to the Lennard-Jones (12,6) potential for the intermolecular interactions, the intramolecular interactions were described by up to three potentials: bond stretching, angle bending, and torsion. For ethane only bond stretching is relevant, propane then adds angle bending and n-butane also torsion. Other non-bonded interactions and improper torsion were not considered in this study.

Table 4: Lennard-Jones potential parameters of OPLS and TraPPE.

	CH_3		CH_2		CH		CH_3(ethane)	
	σ [Å]	ε/k_B [K]	σ [Å]	ε/k_B [K]	σ [Å]	ε/k_B [K]	σ [Å]	ε/k_B [K]
TraPPE	3.750	98.00	3.950	46.00	4.680	10.00		
OPLS	3.905	88.06	3.905	59.38	3.850	40.26	3.775	104.167

Bond stretching and angle bending defined by harmonic potentials

$$U_{\mathrm{b}} = 0.5 \cdot k_{\mathrm{b}}(r - r_0)^2, \tag{1}$$

$$U_{\mathrm{a}} = 0.5 \cdot k_{\mathrm{a}}(\theta - \theta_0)^2, \tag{2}$$

are the most common forms.[2–7]

Table 5: Bond stretching potential parameters of OPLS, TraPPE, and OPLSAMBER.

	Sites	r_0 [Å]	$k_{\mathrm{b}}/k_{\mathrm{B}}$ [K/Å^2]
TraPPE	CH_x – CH_y	1.540	-
OPLS	CH_x – CH_y	1.530	-
OPLSAMBER	CH_x – CH_y	1.507	319225

Table 6: Angle bending potential parameters of OPLS and TraPPE.

	Sites	θ_0 [°]	$k_{\mathrm{a}}/k_{\mathrm{B}}$ [K]
TraPPE	CH_x – CH_y – CH_z	114	62500
	CH_3 – CH_1 – CH_3	112	62500
OPLS	CH_x – CH_y – CH_z	112	62500

For torsion, three different potential forms were employed, depending on the program

$$U_{\mathrm{t}} = \sum_{i=0}^{3} c_{\mathrm{i}} \cos(\psi)^i, \tag{3}$$

$$U_{\mathrm{t}} = c_0 + c_1[1 + \cos(\phi)] + c_2[1 - \cos(2\phi)] + c_3[1 + \cos(3\phi)], \tag{4}$$

$$U_{\mathrm{t}} = \sum_{i=0}^{3} c_{\mathrm{i}}[1 + \cos(i \cdot \phi - \phi_0)]. \tag{5}$$

It should be noted that equation 3[5,7] relies on a different definition for the torsion angle than equation 4[2] and 5[4] with $\psi = 0$ and $\phi = \pi$ in the (trans) conformation of an alkane. The definition of ϕ follows the IUPAC convention.[8] Equations 3, 4, and 5 can, however, be transformed into one another if $\phi_0 = 0$.[3]

Table 7: Torsion potential parameters of OPLS and TraPPE according to equation 3.

	c_0/k_B [K]	c_1/k_B [K]	c_2/k_B [K]	c_3/k_B [K]
TraPPE	1009.97	2018.93	136.38	-3165.28
OPLS	1031.36	2037.82	158.52	-3227.70

5 Numerical results

As stated the results obtained with Tinker for the energy are not reported, because the energy calculation was erroneous in this study. Some simulations of DL_POLY and TOWHEE were unstable and are thus also not reported.

5.1 Ethane

Table 8: Results of the different groups for ethane at 5 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	646.13	1.36	-16.529	0.062
	173.0	567.39	2.08	-13.866	0.086
	248.0	477.80	3.32	-11.194	0.011
	298.0	394.04	4.86	-9.009	0.131
GROMACS(BS)	98.0	646.48	0.05	-16.542	0.002
	173.0	567.56	0.09	-13.870	0.003
	248.0	478.40	0.16	-11.207	0.004
	298.0	393.74	0.26	-9.001	0.006
GROMACS(KL)	98.0	647.03	0.16	-16.560	0.006
	173.0	567.23	0.14	-13.860	0.005
	248.0	475.32	2.90	-11.140	0.067
	298.0	354.88	25.00	-8.205	0.500
LAMMPS(AA)	98.0	646.18	0.83	-16.531	0.029
	173.0	567.03	1.57	-13.855	0.046
	248.0	477.72	2.99	-11.192	0.079
	298.0	392.15	7.16	-8.968	0.154
LAMMPS(KL)	98.0	645.96	0.85	-16.532	0.030
	173.0	567.12	1.63	-13.865	0.050
	248.0	477.61	3.22	-11.193	0.082
	298.0	392.37	6.47	-8.977	0.146
ms2(KL)	98.0	645.93	0.12	-16.523	0.003
	173.0	566.68	0.13	-13.843	0.003
	248.0	477.24	0.29	-11.178	0.005
	298.0	376.01	18.57	-9.209	0.044
ms2(PB)	98.0	645.95	0.07	-16.513	0.002
	173.0	566.75	0.09	-13.838	0.003
	248.0	476.76	0.20	-11.160	0.005
	298.0	391.04	0.47	-8.930	0.010
Tinker(AA)	98.0	645.90	1.20		
	173.0	567.00	1.30		
	248.0	478.30	1.60		
	298.0	392.70	2.00		
TOWHEE(BS)	98.0				
	173.0	567.18	0.35	-13.862	0.010
	248.0	477.46	0.28	-11.187	0.007
	298.0	390.83	0.82	-8.938	0.019

Table 9: Results of the different groups for ethane at 41 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	659.22	1.25	-16.759	0.061
	173.0	590.63	1.91	-14.366	0.086
	248.0	523.63	2.48	-12.241	0.102
	298.0	478.16	3.03	-10.908	0.113
GROMACS(BS)	98.0	659.22	0.05	-16.759	0.002
	173.0	590.66	0.07	-14.365	0.002
	248.0	523.73	0.11	-12.245	0.003
	298.0	478.13	0.15	-10.908	0.004
GROMACS(KL)	98.0	660.02	0.09	-16.787	0.003
	173.0	590.80	0.10	-14.371	0.003
	248.0	524.04	0.08	-12.256	0.003
	298.0	477.99	0.12	-10.905	0.003
LAMMPS(AA)	98.0	659.17	0.85	-16.758	0.032
	173.0	590.47	1.17	-14.361	0.037
	248.0	523.55	1.88	-12.241	0.053
	298.0	477.87	6.77	-10.904	0.061
LAMMPS(KL)	98.0	658.96	0.80	-16.758	0.030
	173.0	590.44	1.20	-14.366	0.039
	248.0	523.30	1.86	-12.238	0.054
	298.0	477.43	2.22	-10.893	0.059
ms2(KL)	98.0	658.92	0.13	-16.748	0.003
	173.0	590.09	0.13	-14.347	0.003
	248.0	522.71	0.16	-12.215	0.003
	298.0	477.15	0.20	-10.880	0.003
ms2(PB)	98.0	659.09	0.05	-16.744	0.002
	173.0	590.26	0.07	-14.344	0.002
	248.0	523.07	0.11	-12.219	0.003
	298.0	477.06	0.14	-10.871	0.004
Tinker(AA)	98.0	659.10	1.20		
	173.0	590.50	1.40		
	248.0	523.40	1.40		
	298.0	477.90	1.40		
TOWHEE(BS)	98.0				
	173.0	590.42	0.30	-14.362	0.010
	248.0	523.47	0.37	-12.238	0.011
	298.0	477.71	0.35	-10.897	0.010

Table 10: Results of the different groups for ethane at 70 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	668.53	1.15	-16.907	0.059
	173.0	605.46	1.83	-14.659	0.086
	248.0	546.57	2.30	-12.733	0.102
	298.0	508.63	2.53	-11.570	0.110
GROMACS(BS)	98.0	668.48	0.04	-16.904	0.002
	173.0	605.51	0.06	-14.660	0.002
	248.0	546.79	0.08	-12.738	0.002
	298.0	508.83	0.10	-11.575	0.003
GROMACS(KL)	98.0	669.11	0.09	-16.925	0.004
	173.0	605.44	0.08	-14.659	0.003
	248.0	546.66	0.05	-12.737	0.002
	298.0	508.80	0.15	-11.576	0.004
LAMMPS(AA)	98.0	668.25	0.68	-16.896	0.026
	173.0	605.29	0.97	-14.654	0.032
	248.0	546.39	1.35	-12.727	0.040
	298.0	508.67	1.79	-11.573	0.050
LAMMPS(KL)	98.0	668.09	0.79	-16.898	0.030
	173.0	605.19	1.09	-14.657	0.037
	248.0	546.26	1.38	-12.729	0.041
	298.0	508.34	1.82	-11.568	0.053
ms2(KL)	98.0	668.03	0.10	-16.887	0.002
	173.0	604.92	0.10	-14.639	0.002
	248.0	545.82	0.12	-12.710	0.002
	298.0	508.27	0.15	-11.559	0.003
ms2(PB)	98.0	668.25	0.06	-16.885	0.002
	173.0	604.97	0.06	-14.633	0.002
	248.0	546.12	0.09	-12.711	0.003
	298.0	508.28	0.11	-11.552	0.003
Tinker(AA)	98.0	668.40	1.00		
	173.0	605.30	1.30		
	248.0	546.40	1.50		
	298.0	508.70	1.50		
TOWHEE(BS)	98.0				
	173.0				
	248.0	546.45	0.30	-12.731	0.009
	298.0	508.63	0.35	-11.571	0.010

Table 11: Results of the different groups for ethane at 5 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	648.90	1.01	-15.230	0.051
	173.0	562.59	1.39	-12.577	0.068
	248.0	459.96	1.78	-9.834	0.079
	298.0	337.81	2.52	-7.091	0.094
GROMACS(BS)	98.0	648.85	0.06	-15.227	0.002
	173.0	562.67	0.09	-12.578	0.002
	248.0	460.02	0.18	-9.835	0.004
	298.0	333.74	0.45	-7.010	0.009
GROMACS(KL)	98.0	648.64	0.09	-15.223	0.003
	173.0	562.15	0.46	-12.567	0.010
	248.0	451.41	9.00	-9.667	0.180
	298.0	226.30	5.20	-5.060	0.087
LAMMPS(AA)	98.0	648.75	1.07	-15.225	0.035
	173.0	562.22	1.77	-12.567	0.049
	248.0	459.60	3.51	-9.825	0.078
	298.0	332.81	15.54	-6.992	0.296
LAMMPS(KL)	98.0	648.53	0.89	-15.224	0.029
	173.0	562.13	1.61	-12.569	0.044
	248.0	459.28	4.23	-9.822	0.095
	298.0	329.16	17.21	-6.928	0.326
ms2(KL)	98.0	648.40	0.09	-15.212	0.003
	173.0	561.64	0.11	-12.548	0.003
	248.0	458.30	0.19	-9.794	0.004
	298.0	62.74	3.57	-5.242	0.108
ms2(PB)	98.0	648.36	0.07	-15.212	0.002
	173.0	561.94	0.11	-12.559	0.003
	248.0	459.07	0.27	-9.812	0.006
	298.0	325.68	1.39	-6.861	0.026
Tinker(AA)	98.0	648.50	1.10		
	173.0	562.10	1.40		
	248.0	459.90	1.50		
	298.0	336.20	3.60		
TOWHEE(BS)	98.0	648.53	0.53	-15.220	0.017
	173.0	562.29	0.57	-12.569	0.016
	248.0	459.49	0.74	-9.825	0.017
	298.0	327.11	0.27	-6.899	0.052

Table 12: Results of the different groups for ethane at 41 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	663.38	0.92	-15.466	0.050
	173.0	589.73	1.16	-13.121	0.069
	248.0	517.67	1.34	-11.050	0.080
	298.0	468.73	1.61	-9.750	0.087
GROMACS(BS)	98.0	663.38	0.05	-15.466	0.002
	173.0	589.84	0.07	-13.125	0.002
	248.0	517.42	0.11	-11.044	0.003
	298.0	468.73	0.16	-9.750	0.004
GROMACS(KL)	98.0	663.27	0.05	-15.464	0.002
	173.0	589.61	0.18	-13.118	0.005
	248.0	517.46	0.09	-11.046	0.002
	298.0	468.51	0.23	-9.745	0.006
LAMMPS(AA)	98.0	663.29	0.88	-15.463	0.030
	173.0	589.44	1.24	-13.114	0.036
	248.0	517.16	1.89	-11.036	0.049
	298.0	468.14	2.47	-9.737	0.058
LAMMPS(KL)	98.0	662.95	0.86	-15.459	0.029
	173.0	589.30	1.32	-13.116	0.038
	248.0	517.09	1.97	-11.039	0.050
	298.0	468.18	2.52	-9.741	0.060
ms2(KL)	98.0	662.87	0.09	-15.449	0.003
	173.0	589.07	0.07	-13.102	0.002
	248.0	516.66	0.12	-11.023	0.003
	298.0	467.51	0.16	-9.720	0.004
ms2(PB)	98.0	663.07	0.06	-15.456	0.002
	173.0	589.29	0.08	-13.109	0.002
	248.0	517.03	0.12	-11.034	0.003
	298.0	467.75	0.17	-9.729	0.004
Tinker(AA)	98.0	663.30	1.10		
	173.0	589.50	1.30		
	248.0	517.40	1.60		
	298.0	468.10	1.70		
TOWHEE(BS)	98.0	663.17	0.74	-15.464	0.026
	173.0	589.17	0.49	-13.108	0.015
	248.0	517.20	0.58	-11.039	0.015
	298.0	467.84	0.49	-9.731	0.012

Table 13: Results of the different groups for ethane at 70 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	673.44	0.91	-15.612	0.050
	173.0	606.29	1.09	-13.426	0.069
	248.0	543.93	1.15	-11.569	0.081
	298.0	503.98	1.37	-10.458	0.090
GROMACS(BS)	98.0	673.45	0.05	-15.613	0.002
	173.0	606.56	0.06	-13.433	0.002
	248.0	544.21	0.09	-11.576	0.002
	298.0	504.00	0.11	-10.457	0.003
GROMACS(KL)	98.0	673.53	0.09	-15.617	0.003
	173.0	606.29	0.08	-13.427	0.002
	248.0	544.04	0.12	-11.574	0.003
	298.0	504.15	0.21	-10.461	0.005
LAMMPS(AA)	98.0	673.51	0.75	-15.615	0.026
	173.0	606.20	1.05	-13.424	0.031
	248.0	543.81	1.46	-11.565	0.040
	298.0	503.75	1.98	-10.451	0.052
LAMMPS(KL)	98.0	673.20	0.75	-15.612	0.026
	173.0	605.92	1.16	-13.421	0.035
	248.0	543.60	1.46	-11.566	0.039
	298.0	503.75	1.90	-10.454	0.049
ms2(KL)	98.0	673.14	0.07	-15.602	0.003
	173.0	605.75	0.05	-13.409	0.002
	248.0	543.26	0.10	-11.551	0.003
	298.0	503.49	0.10	-10.442	0.003
ms2(PB)	98.0	673.23	0.05	-15.605	0.002
	173.0	605.91	0.07	-13.415	0.002
	248.0	543.32	0.10	-11.552	0.003
	298.0	503.60	0.11	-10.445	0.003
Tinker(AA)	98.0	673.20	1.10		
	173.0	606.00	1.40		
	248.0	543.60	1.40		
	298.0	504.00	1.50		
TOWHEE(BS)	98.0	673.97	0.84	-15.635	0.029
	173.0	606.08	0.46	-13.422	0.015
	248.0	543.65	0.34	-11.563	0.009
	298.0	503.91	0.55	-10.455	0.015

Table 14: Results of the different groups for ethane at 5 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0				
	248.0	492.13	7.15	-10.439	0.198
	298.0	418.90	10.13	-8.216	0.263
GROMACS(BS)	98.0	652.50	0.14	-16.298	0.003
	173.0	580.91	0.18	-13.409	0.003
	248.0	483.17	0.27	-10.327	0.006
	298.0	402.00	0.43	-7.968	0.010
GROMACS(KL)	98.0	645.03	1.90	-16.185	0.029
	173.0	570.61	3.80	-13.282	0.049
	248.0	483.35	6.30	-10.330	0.081
	298.0	375.37	12.00	-7.538	0.200
Ind.MC(PB)	98.0	650.48	0.08	-16.246	0.003
	173.0	572.09	0.12	-13.278	0.004
	248.0	483.25	0.18	-10.311	0.005
	298.0	399.50	0.40	-7.910	0.009
LAMMPS(AA)	98.0	632.39	0.99	-15.982	0.035
	173.0	545.30	1.75	-12.958	0.050
	248.0	446.51	3.94	-9.842	0.095
	298.0	203.17	64.19	-4.212	1.382
LAMMPS(KL)	98.0	631.46	1.88	-15.981	0.065
	173.0	540.69	4.05	-12.905	0.118
	248.0	433.13	8.60	-9.662	0.210
	298.0	97.84	8.56	-1.938	0.246
ms2(KL)	98.0	634.34	0.18	-15.960	0.003
	173.0	552.65	0.31	-12.930	0.004
	248.0	456.00	0.79	-9.774	0.006
	298.0	306.62	2.51	-5.708	0.177
ms2*(KL)	98.0	651.19	0.08	-16.277	0.003
	173.0	572.29	0.12	-13.294	0.004
	248.0	483.49	0.14	-10.325	0.003
	298.0	399.15	0.37	-7.913	0.008
ms2(PB)	98.0	636.17	0.06	-16.028	0.002
	173.0	570.16	0.09	-13.244	0.003
	248.0	478.43	0.20	-10.232	0.005
	298.0	369.21	0.75	-7.419	0.016
NAMD(FM)	98.0	634.27	3.29	-16.007	0.089
	173.0	544.42	5.47	-12.939	0.149
	248.0	440.08	8.96	-9.743	0.226
	298.0	121.17	15.07	-2.429	0.403
Tinker(AA)	98.0	640.50	0.80		

	173.0	556.80	1.00		
	248.0	463.20	2.90		
	298.0	387.10	10.90		
TOWHEE(BS)	98.0	671.55	1.26	-17.108	0.049
	173.0	572.15	0.59	-13.293	0.018
	248.0	483.22	0.90	-10.321	0.024
	298.0	398.69	0.11	-7.901	0.026

Table 15: Results of the different groups for ethane at 41 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0				
	248.0	530.89	0.47	-11.366	0.166
	298.0	486.69	6.41	-9.826	0.192
GROMACS(BS)	98.0	663.92	0.09	-16.498	0.002
	173.0	597.04	0.11	-13.810	0.002
	248.0	529.00	0.14	-11.352	0.003
	298.0	481.76	0.20	-9.791	0.004
GROMACS(KL)	98.0	657.37	1.50	-16.409	0.019
	173.0	593.43	2.90	-13.776	0.029
	248.0	533.52	4.70	-11.398	0.036
	298.0	489.68	5.50	-9.846	0.034
Ind.MC(PB)	98.0	663.88	0.07	-16.487	0.003
	173.0	595.02	0.10	-13.771	0.004
	248.0	527.92	0.12	-11.330	0.004
	298.0	482.02	0.13	-9.775	0.004
LAMMPS(AA)	98.0	647.39	0.80	-16.265	0.029
	173.0	572.69	1.16	-13.569	0.037
	248.0	505.81	2.04	-11.181	0.056
	298.0	463.26	2.82	-9.678	0.060
LAMMPS(KL)	98.0	645.90	1.66	-16.252	0.059
	173.0	568.18	3.13	-13.537	0.096
	248.0	495.51	5.14	-11.125	0.135
	298.0	447.63	6.63	-9.594	0.159
ms2(KL)	98.0	647.88	0.18	-16.234	0.003
	173.0	577.42	0.22	-13.535	0.003
	248.0	509.66	0.39	-11.138	0.005
	298.0	460.38	0.56	-9.617	0.005
ms2*(KL)	98.0	664.27	0.08	-16.507	0.003
	173.0	595.41	0.09	-13.790	0.003
	248.0	528.03	0.09	-11.344	0.003
	298.0	482.10	0.12	-9.788	0.003

ms2(PB)	98.0	650.41	0.05	-16.291	0.002
	173.0	591.39	0.07	-13.728	0.002
	248.0	526.25	0.12	-11.303	0.004
	298.0	473.44	0.17	-9.706	0.005
NAMD(FM)	98.0	647.95	3.14	-16.270	0.084
	173.0	571.53	4.72	-13.558	0.130
	248.0	498.61	6.68	-11.133	0.176
	298.0	452.69	7.93	-9.610	0.198
Tinker(AA)	98.0	654.10	0.90		
	173.0	580.90	0.80		
	248.0	508.90	1.20		
	298.0	457.50	6.20		
TOWHEE(BS)	98.0	688.06	0.79	-17.543	0.034
	173.0	595.09	0.31	-13.786	0.010
	248.0	528.00	0.60	-11.343	0.017
	298.0	482.12	0.61	-9.789	0.018

Table 16: Results of the different groups for ethane at 70 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0				
	248.0	561.46	6.51	-11.885	0.162
	298.0	515.77	5.80	-10.469	0.179
GROMACS(BS)	98.0	671.11	0.08	-16.616	0.002
	173.0	610.99	0.12	-14.090	0.002
	248.0	550.60	0.13	-11.838	0.003
	298.0	513.62	0.15	-10.468	0.003
GROMACS(KL)	98.0	668.03	1.60	-16.572	0.021
	173.0	608.30	2.80	-14.069	0.023
	248.0	556.08	3.70	-11.863	0.018
	298.0	520.11	4.30	-10.489	0.011
Ind.MC(PB)	98.0	672.79	0.07	-16.618	0.003
	173.0	609.86	0.09	-14.065	0.003
	248.0	550.78	0.10	-11.820	0.004
	298.0	512.90	0.11	-10.449	0.004
LAMMPS(AA)	98.0	657.12	0.80	-16.429	0.030
	173.0	589.89	1.18	-13.923	0.038
	248.0	533.82	1.68	-11.764	0.040
	298.0	498.09	2.42	-10.425	0.053
LAMMPS(KL)	98.0	656.11	1.47	-16.423	0.053
	173.0	584.92	2.72	-13.889	0.087
	248.0	524.01	4.27	-11.733	0.114

	298.0	484.85	5.22	-10.420	0.130
ms2(KL)	98.0	657.89	0.13	-16.400	0.003
	173.0	593.59	0.23	-13.882	0.003
	248.0	533.77	0.34	-11.725	0.003
	298.0	496.04	0.41	-10.406	0.003
ms2*(KL)	98.0	673.12	0.07	-16.638	0.003
	173.0	609.79	0.09	-14.071	0.003
	248.0	550.90	0.08	-11.833	0.002
	298.0	512.87	0.09	-10.460	0.002
ms2(PB)	98.0	660.23	0.06	-16.453	0.002
	173.0	605.42	0.06	-14.013	0.002
	248.0	548.55	0.10	-11.790	0.003
	298.0	509.12	0.12	-10.417	0.003
NAMD(FM)	98.0	657.47	2.98	-16.429	0.079
	173.0	588.15	4.47	-13.901	0.125
	248.0	527.34	5.91	-11.736	0.157
	298.0	489.01	6.53	-10.418	0.172
Tinker(AA)	98.0	663.20	0.90		
	173.0	596.40	1.00		
	248.0	534.60	1.10		
	298.0	494.70	1.20		
TOWHEE(BS)	98.0	672.37	0.61	-16.614	0.024
	173.0	609.73	0.52	-14.073	0.017
	248.0	550.73	0.41	-11.829	0.012
	298.0	512.85	0.54	-10.461	0.016

5.2 Propane

Table 17: Results of the different groups for propane at 5 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	686.72	1.08	-20.678	0.073
	173.0				
	248.0	539.59	2.49	-14.142	0.121
	298.0	482.48	3.35	-11.957	0.142
GROMACS(BS)	98.0	684.91	0.08	-20.643	0.003
	173.0	614.12	0.10	-17.301	0.003
	248.0	539.42	0.23	-14.139	0.006
	298.0	481.18	0.36	-11.946	0.010
GROMACS(KL)	98.0	685.21	0.20	-20.653	0.005
	173.0	614.43	0.23	-17.311	0.004
	248.0	539.76	0.26	-14.157	0.004
	298.0	480.98	0.20	-11.937	0.003
LAMMPS(AA)	98.0	687.23	0.73	-20.703	0.036
	173.0	615.15	1.21	-17.320	0.048
	248.0	540.55	2.04	-14.170	0.076
	298.0	482.20	3.37	-11.954	0.105
LAMMPS(KL)	98.0	688.04	1.71	-20.705	0.049
	173.0	615.13	1.49	-17.312	0.051
	248.0	540.63	2.85	-14.153	0.086
	298.0	481.80	4.14	-11.944	0.111
ms2(KL)	98.0	687.42	0.09	-20.680	0.003
	173.0	615.12	0.27	-17.300	0.005
	248.0	540.31	0.30	-14.141	0.006
	298.0	481.25	0.45	-11.913	0.009
ms2(PB)	98.0	686.84	0.08	-20.678	0.003
	173.0	615.02	0.10	-17.304	0.003
	248.0	539.94	0.19	-14.134	0.005
	298.0	481.43	0.28	-11.931	0.007
Tinker(AA)	98.0	687.50	1.20		
	173.0	615.50	1.50		
	248.0	540.80	2.20		
	298.0	483.20	2.50		
TOWHEE(BS)	98.0	687.60	0.47	-20.700	0.020
	173.0	615.64	0.28	-17.321	0.011
	248.0	540.61	0.56	-14.156	0.019
	298.0	482.11	0.52	-11.944	0.015

Table 18: Results of the different groups for propane at 41 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	700.76	1.13	-20.950	0.073
	173.0	636.87	1.44	-17.870	0.084
	248.0	577.39	2.24	-15.180	0.124
	298.0	538.79	2.56	-13.507	0.135
GROMACS(BS)	98.0	698.96	0.05	-20.944	0.002
	173.0	636.83	0.09	-17.879	0.003
	248.0	577.22	0.13	-15.178	0.003
	298.0	538.37	0.17	-13.510	0.004
GROMACS(KL)	98.0	699.09	0.08	-20.944	0.001
	173.0	636.68	0.10	-17.878	0.002
	248.0	577.26	0.19	-15.182	0.003
	298.0	538.78	0.06	-13.522	0.003
LAMMPS(AA)	98.0	700.41	0.76	-20.965	0.034
	173.0	636.96	1.03	-17.875	0.040
	248.0	577.47	1.37	-15.176	0.056
	298.0	538.31	1.81	-13.506	0.063
LAMMPS(KL)	98.0	701.19	1.08	-20.982	0.038
	173.0	636.92	1.31	-17.873	0.041
	248.0	577.88	1.90	-15.174	0.054
	298.0	538.05	2.27	-13.495	0.066
ms2(KL)	98.0	700.59	0.13	-20.961	0.004
	173.0	636.63	0.17	-17.858	0.003
	248.0	577.83	0.20	-15.171	0.003
	298.0	537.84	0.26	-13.490	0.004
ms2(PB)	98.0	700.91	0.08	-20.970	0.002
	173.0	637.10	0.08	-17.867	0.003
	248.0	577.74	0.13	-15.171	0.003
	298.0	538.45	0.16	-13.493	0.004
Tinker(AA)	98.0	700.50	1.00		
	173.0	637.20	1.50		
	248.0	577.90	1.90		
	298.0	538.60	2.20		
TOWHEE(BS)	98.0	700.53	0.38	-20.966	0.017
	173.0	637.38	0.30	-17.881	0.012
	248.0	577.70	0.34	-15.176	0.012
	298.0	538.49	0.36	-13.504	0.014

Table 19: Results of the different groups for propane at 70 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	710.05	0.93	-21.146	0.069
	173.0	650.92	1.17	-18.201	0.083
	248.0	597.74	1.88	-15.702	0.125
	298.0	564.47	2.28	-14.194	0.140
GROMACS(BS)	98.0	708.65	0.05	-21.119	0.002
	173.0	650.76	0.08	-18.200	0.002
	248.0	597.85	0.11	-15.703	0.003
	298.0	564.93	0.14	-14.198	0.004
GROMACS(KL)	98.0	708.70	0.18	-21.130	0.004
	173.0	650.60	0.23	-18.200	0.002
	248.0	598.26	0.27	-15.714	0.003
	298.0	564.67	0.00	-14.206	0.004
LAMMPS(AA)	98.0	709.70	0.72	-21.154	0.034
	173.0	650.94	0.87	-18.204	0.039
	248.0	598.00	1.20	-15.700	0.046
	298.0	564.58	1.51	-14.192	0.056
LAMMPS(KL)	98.0	710.03	0.95	-21.147	0.033
	173.0	650.96	1.23	-18.202	0.041
	248.0	598.19	1.41	-15.705	0.044
	298.0	565.10	1.61	-14.188	0.054
ms2(KL)	98.0	709.50	0.15	-21.123	0.004
	173.0	650.66	0.16	-18.186	0.003
	248.0	598.25	0.17	-15.691	0.003
	298.0	564.83	0.20	-14.174	0.004
ms2(PB)	98.0	709.66	0.06	-21.136	0.003
	173.0	650.93	0.08	-18.195	0.002
	248.0	597.99	0.10	-15.691	0.003
	298.0	564.82	0.14	-14.188	0.003
Tinker(AA)	98.0	709.70	1.00		
	173.0	651.00	1.40		
	248.0	598.30	1.70		
	298.0	564.90	1.80		
TOWHEE(BS)	98.0	709.88	0.53	-21.142	0.025
	173.0	651.49	0.32	-18.214	0.014
	248.0	598.44	0.24	-15.708	0.010
	298.0	564.86	0.28	-14.195	0.011

Table 20: Results of the different groups for propane at 5 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	728.30	1.10	-20.392	0.072
	173.0	648.60	2.00	-16.978	0.102
	248.0	568.23	3.07	-13.806	0.124
	298.0	502.05	7.94	-11.516	0.204
GROMACS(BS)	98.0	725.55	0.07	-20.353	0.002
	173.0	649.34	0.12	-16.995	0.003
	248.0	567.75	0.21	-13.800	0.005
	298.0	503.05	0.41	-11.544	0.010
GROMACS(KL)	98.0	724.93	0.21	-20.340	0.003
	173.0	649.19	0.14	-16.996	0.004
	248.0	568.26	0.31	-13.808	0.005
	298.0	503.58	0.32	-11.561	0.009
LAMMPS(AA)	98.0	728.02	0.88	-20.391	0.036
	173.0	650.09	1.30	-17.002	0.047
	248.0	568.47	2.33	-13.817	0.073
	298.0	503.85	4.33	-11.560	0.125
LAMMPS(KL)	98.0	728.83	1.23	-20.412	0.038
	173.0	650.71	1.86	-17.007	0.053
	248.0	568.45	2.84	-13.805	0.076
	298.0	504.14	4.54	-11.550	0.110
ms2(KL)	98.0	727.70	0.12	-20.380	0.004
	173.0	650.15	0.23	-16.990	0.005
	248.0	568.13	0.31	-13.788	0.006
	298.0	504.50	0.54	-11.540	0.009
ms2(PB)	98.0	727.88	0.07	-20.385	0.002
	173.0	650.14	0.13	-16.991	0.003
	248.0	568.80	0.20	-13.795	0.005
	298.0	503.23	0.32	-11.529	0.008
Tinker(AA)	98.0	728.20	1.20		
	173.0	651.00	1.60		
	248.0	568.50	2.50		
	298.0	503.90	2.80		
TOWHEE(BS)	98.0	727.87	0.49	-20.387	0.021
	173.0	650.41	0.46	-17.005	0.017
	248.0	568.78	0.31	-13.811	0.009
	298.0	503.50	0.53	-11.537	0.002

Table 21: Results of the different groups for propane at 41 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	741.92	1.09	-20.672	0.072
	173.0	671.72	1.65	-17.541	0.099
	248.0	607.84	2.26	-14.829	0.121
	298.0	565.10	2.59	-13.132	0.131
GROMACS(BS)	98.0	739.34	0.06	-20.628	0.002
	173.0	672.11	0.08	-17.548	0.002
	248.0	607.26	0.14	-14.821	0.003
	298.0	564.56	0.20	-13.136	0.005
GROMACS(KL)	98.0	739.61	0.23	-20.637	0.006
	173.0	671.73	0.23	-17.540	0.005
	248.0	607.62	0.11	-14.829	0.003
	298.0	565.08	0.17	-13.138	0.006
LAMMPS(AA)	98.0	741.39	0.78	-20.659	0.033
	173.0	672.70	1.10	-17.552	0.039
	248.0	607.78	1.60	-14.826	0.053
	298.0	564.71	2.15	-13.121	0.069
LAMMPS(KL)	98.0	742.08	0.85	-20.674	0.033
	173.0	672.72	1.37	-17.549	0.044
	248.0	608.12	2.00	-14.826	0.055
	298.0	564.96	2.54	-13.128	0.069
ms2(KL)	98.0	741.75	0.14	-20.663	0.003
	173.0	672.51	0.24	-17.536	0.004
	248.0	607.86	0.21	-14.805	0.003
	298.0	564.36	0.24	-13.109	0.004
ms2(PB)	98.0	741.18	0.06	-20.656	0.002
	173.0	672.73	0.08	-17.542	0.003
	248.0	608.26	0.14	-14.815	0.004
	298.0	565.10	0.16	-13.121	0.004
Tinker(AA)	98.0	741.10	1.20		
	173.0	673.00	1.60		
	248.0	608.10	1.90		
	298.0	564.80	2.10		
TOWHEE(BS)	98.0	742.04	0.40	-20.687	0.018
	173.0	673.00	0.39	-17.555	0.016
	248.0	607.99	0.32	-14.822	0.013
	298.0	565.04	0.33	-13.130	0.011

Table 22: Results of the different groups for propane at 70 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	750.94	1.01	-20.832	0.071
	173.0	687.02	3.67	-17.869	0.124
	248.0	628.96	1.98	-15.348	0.122
	298.0	593.07	2.34	-13.815	0.134
GROMACS(BS)	98.0	749.61	0.06	-20.815	0.002
	173.0	686.55	0.09	-17.869	0.002
	248.0	629.23	0.12	-15.356	0.003
	298.0	592.68	0.15	-13.829	0.003
GROMACS(KL)	98.0	749.33	0.01	-20.814	0.007
	173.0	686.74	0.09	-17.872	0.003
	248.0	629.48	0.24	-15.357	0.005
	298.0	592.78	0.36	-13.828	0.004
LAMMPS(AA)	98.0	750.93	0.71	-20.843	0.029
	173.0	687.23	0.92	-17.876	0.038
	248.0	629.60	1.36	-15.343	0.043
	298.0	592.80	1.62	-13.821	0.052
LAMMPS(KL)	98.0	751.04	0.84	-20.836	0.034
	173.0	687.36	1.19	-17.873	0.037
	248.0	629.67	1.86	-15.348	0.047
	298.0	592.51	1.90	-13.816	0.052
ms2(KL)	98.0	750.72	0.12	-20.819	0.004
	173.0	687.61	0.12	-17.861	0.002
	248.0	629.51	0.16	-15.333	0.003
	298.0	592.58	0.25	-13.805	0.003
ms2(PB)	98.0	750.74	0.06	-20.828	0.002
	173.0	687.23	0.08	-17.865	0.003
	248.0	629.75	0.11	-15.338	0.003
	298.0	592.96	0.16	-13.811	0.004
Tinker(AA)	98.0	751.30	1.20		
	173.0	687.30	1.60		
	248.0	629.90	1.70		
	298.0	592.80	1.90		
TOWHEE(BS)	98.0	750.88	0.62	-20.827	0.003
	173.0	687.56	0.42	-17.878	0.016
	248.0	629.80	0.38	-15.352	0.014
	298.0	593.14	0.20	-13.823	0.008

Table 23: Results of the different groups for propane at 5 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0				
	248.0	546.27	5.79	-12.362	0.224
	298.0	490.88	7.66	-9.787	0.278
GROMACS(BS)	98.0	694.22	0.07	-20.146	0.003
	173.0	630.01	0.13	-16.267	0.004
	248.0	551.35	0.22	-12.427	0.006
	298.0	491.53	0.34	-9.792	0.010
GROMACS(KL)	98.0	688.64	2.00	-20.038	0.037
	173.0	625.23	3.20	-16.203	0.045
	248.0	561.02	3.70	-12.554	0.046
	298.0	500.81	3.80	-9.921	0.053
Ind.MC(PB)	98.0	695.43	0.08	-21.371	0.004
	173.0	623.71	0.11	-18.309	0.004
	248.0	548.79	0.15	-15.450	0.005
	298.0	491.09	0.23	-13.461	0.007
LAMMPS(AA)	98.0	673.80	1.28	-19.764	0.040
	173.0	598.23	1.96	-15.816	0.058
	248.0	524.47	3.19	-12.058	0.079
	298.0	460.87	5.28	-9.335	0.127
LAMMPS(KL)	98.0	671.23	1.76	-19.721	0.074
	173.0	591.28	3.91	-15.738	0.128
	248.0	509.01	7.37	-11.887	0.201
	298.0	441.41	12.51	-9.072	0.300
ms2(KL)	98.0	673.20	0.21	-19.744	0.004
	173.0	597.60	0.28	-15.803	0.005
	248.0	521.15	0.68	-12.014	0.009
	298.0	458.26	1.14	-9.294	0.021
ms2*(KL)	98.0	695.42	0.09	-20.163	0.004
	173.0	623.81	0.08	-16.177	0.003
	248.0	549.43	0.13	-12.401	0.004
	298.0	492.03	0.17	-9.796	0.004
ms2(PB)	98.0	674.86	0.08	-19.782	0.003
	173.0	607.34	0.12	-15.932	0.004
	248.0	537.14	0.22	-12.224	0.006
	298.0	480.40	0.32	-9.612	0.008
NAMD(FM)	98.0	679.28	2.98	-19.854	0.104
	173.0	602.11	4.54	-15.868	0.163
	248.0	525.78	6.59	-12.097	0.226
	298.0	457.31	9.67	-9.305	0.293
Tinker(AA)	98.0	689.80	0.90		

	173.0	624.80	1.50		
	248.0	537.70	1.30		
	298.0	483.90	5.30		
TOWHEE(BS)	98.0	695.38	0.64	-20.169	0.030
	173.0	623.71	0.61	-16.174	0.025
	248.0	549.25	0.39	-12.397	0.015
	298.0	491.51	0.49	-9.780	0.015

Table 24: Results of the different groups for propane at 41 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0				
	248.0	584.60	4.85	-13.384	0.201
	298.0	545.74	5.77	-11.289	0.233
GROMACS(BS)	98.0	702.50	0.11	-20.337	0.003
	173.0	646.72	0.11	-16.740	0.003
	248.0	590.46	0.13	-13.427	0.004
	298.0	546.13	0.18	-11.306	0.005
GROMACS(KL)	98.0	701.19	1.90	-20.313	0.032
	173.0	646.15	3.00	-16.739	0.035
	248.0	596.03	2.40	-13.473	0.018
	298.0	553.88	2.90	-11.347	0.016
Ind.MC(PB)	98.0	707.99	0.08	-20.384	0.004
	173.0	644.97	0.09	-16.689	0.004
	248.0	585.10	0.11	-13.353	0.004
	298.0	545.75	0.13	-11.260	0.004
LAMMPS(AA)	98.0	688.26	1.02	-20.094	0.034
	173.0	624.90	1.67	-16.503	0.048
	248.0	572.11	3.18	-13.284	0.059
	298.0	535.02	3.58	-11.217	0.066
LAMMPS(KL)	98.0	685.47	1.62	-20.054	0.069
	173.0	616.56	3.15	-16.438	0.108
	248.0	557.03	5.43	-13.219	0.145
	298.0	517.39	6.37	-11.160	0.173
ms2(KL)	98.0	688.23	0.12	-20.085	0.003
	173.0	622.13	0.26	-16.468	0.004
	248.0	564.23	0.68	-13.237	0.005
	298.0	526.91	0.72	-11.169	0.005
ms2*(KL)	98.0	708.45	0.07	-20.437	0.003
	173.0	644.97	0.07	-16.715	0.003
	248.0	585.39	0.09	-13.391	0.003
	298.0	546.11	0.08	-11.295	0.003

ms2(PB)	98.0	686.66	0.07	-20.071	0.002
	173.0	627.96	0.10	-16.527	0.003
	248.0	575.30	0.13	-13.301	0.004
	298.0	538.08	0.19	-11.232	0.005
NAMD(FM)	98.0	692.29	2.81	-20.152	0.098
	173.0	627.14	4.08	-16.527	0.149
	248.0	563.26	5.90	-13.251	0.199
	298.0	527.16	6.67	-11.204	0.228
Tinker(AA)	98.0	701.90	0.90		
	173.0	643.10	1.20		
	248.0	577.60	1.70		
	298.0	535.70	2.40		
TOWHEE(BS)	98.0	708.16	0.73	-20.430	0.034
	173.0	645.11	0.53	-16.727	0.023
	248.0	585.40	0.36	-13.391	0.013
	298.0	546.02	0.40	-11.294	0.015

Table 25: Results of the different groups for propane at 70 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0	658.00	3.33	-17.036	0.138
	248.0	602.24	4.54	-13.897	0.188
	298.0	569.40	5.30	-11.972	0.223
GROMACS(BS)	98.0	712.49	0.06	-20.530	0.002
	173.0	660.25	0.10	-17.056	0.003
	248.0	608.58	0.11	-13.924	0.003
	298.0	573.08	0.15	-11.971	0.004
GROMACS(KL)	98.0	710.06	1.80	-20.490	0.031
	173.0	660.15	2.60	-17.062	0.026
	248.0	612.98	2.40	-13.943	0.012
	298.0	581.04	1.90	-11.992	0.006
Ind.MC(PB)	98.0	716.64	0.09	-21.773	0.004
	173.0	658.86	0.09	-19.181	0.004
	248.0	605.49	0.10	-16.974	0.004
	298.0	571.72	0.10	-15.659	0.004
LAMMPS(AA)	98.0	698.38	0.93	-20.300	0.034
	173.0	639.80	1.56	-16.881	0.039
	248.0	593.45	2.77	-13.844	0.052
	298.0	562.64	3.07	-11.946	0.060
LAMMPS(KL)	98.0	696.03	1.46	-20.271	0.065
	173.0	633.60	3.25	-16.852	0.101
	248.0	582.02	4.92	-13.844	0.129

	298.0	549.52	6.08	-11.983	0.145
ms2(KL)	98.0	697.62	0.14	-20.279	0.003
	173.0	638.45	0.32	-16.865	0.003
	248.0	586.43	0.58	-13.834	0.004
	298.0	555.61	0.69	-11.941	0.004
ms2*(KL)	98.0	717.53	0.07	-20.602	0.004
	173.0	658.83	0.06	-17.039	0.002
	248.0	605.72	0.08	-13.910	0.003
	298.0	571.96	0.08	-11.971	0.003
ms2(PB)	98.0	696.11	0.06	-20.300	0.002
	173.0	638.98	0.10	-16.872	0.003
	248.0	595.18	0.13	-13.854	0.003
	298.0	564.81	0.17	-11.941	0.004
NAMD(FM)	98.0	701.16	2.65	-20.334	0.093
	173.0	642.20	4.09	-16.896	0.143
	248.0	588.50	5.09	-13.854	0.186
	298.0	555.18	5.73	-11.961	0.209
Tinker(AA)	98.0	710.50	0.80		
	173.0	656.20	1.10		
	248.0	595.40	1.20		
	298.0	562.00	2.40		
TOWHEE(BS)	98.0	717.61	0.48	-20.614	0.024
	173.0	659.06	0.40	-17.051	0.016
	248.0	605.57	0.39	-13.904	0.016
	298.0	571.90	0.31	-11.973	0.013

5.3 n-Butane

Table 26: Results of the different groups for n-butane at 5 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	753.48	1.15	-26.246	0.088
	173.0	687.41	1.61	-22.064	0.134
	248.0	624.43	2.28	-17.399	0.175
	298.0	579.14	3.03	-14.426	0.208
GROMACS(BS)	98.0	749.93	0.06	-26.919	0.003
	173.0	686.63	0.10	-22.057	0.004
	248.0	624.24	0.15	-17.408	0.006
	298.0	578.71	0.26	-14.447	0.009
GROMACS(KL)	98.0	749.60	0.08	-27.019	0.004
	173.0	686.72	0.15	-22.021	0.006
	248.0	624.24	0.11	-17.421	0.008
	298.0	579.40	0.19	-14.445	0.009
ms2(KL)	98.0	762.18	0.07	-23.551	0.005
	173.0	688.11	0.18	-21.800	0.029
	248.0	624.55	0.19	-17.394	0.008
	298.0	579.47	0.23	-14.411	0.012
ms2(PB)	98.0	751.24	0.07	-27.050	0.004
	173.0	687.12	0.11	-22.120	0.005
	248.0	624.24	0.16	-17.454	0.008
	298.0	579.56	0.20	-14.416	0.008
Tinker(AA)	98.0	751.10	1.20		
	173.0	685.90	1.70		
	248.0	621.00	2.20		
	298.0	576.30	2.40		
TOWHEE(BS)	98.0	751.80	0.60	-26.993	0.037
	173.0	687.71	0.35	-22.054	0.025
	248.0	625.00	0.29	-17.438	0.016
	298.0	579.49	0.51	-14.425	0.020

Table 27: Results of the different groups for n-butane at 41 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	765.50	1.02	-26.539	0.086
	173.0	705.61	1.49	-22.549	0.136
	248.0	652.16	1.96	-18.304	0.180
	298.0	617.27	2.12	-15.708	0.205
GROMACS(BS)	98.0	761.35	0.06	-27.210	0.003
	173.0	705.08	0.09	-22.547	0.005
	248.0	651.89	0.11	-18.363	0.006
	298.0	617.05	0.15	-15.724	0.007
GROMACS(KL)	98.0	761.28	0.19	-27.306	0.011
	173.0	704.56	0.10	-22.556	0.018
	248.0	651.76	0.04	-18.299	0.008
	298.0	616.80	0.11	-15.719	0.015
ms2(KL)	98.0	762.67	0.10	-27.347	0.006
	173.0	706.25	0.13	-22.325	0.024
	248.0	652.14	0.17	-18.306	0.009
	298.0	616.95	0.18	-15.685	0.009
ms2(PB)	98.0	763.13	0.08	-27.372	0.004
	173.0	704.96	0.09	-22.647	0.004
	248.0	652.13	0.14	-18.323	0.007
	298.0	616.67	0.16	-15.660	0.007
Tinker(AA)	98.0	762.50	1.10		
	173.0	703.40	1.60		
	248.0	648.90	1.80		
	298.0	613.90	2.10		
TOWHEE(BS)	98.0	762.31	0.34	-27.187	0.010
	173.0	705.66	0.42	-22.584	0.031
	248.0	652.21	0.45	-18.316	0.024
	298.0	617.38	0.35	-15.697	0.014

Table 28: Results of the different groups for n-butane at 70 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	773.75	0.99	-26.728	0.086
	173.0	717.44	1.56	-22.965	0.134
	248.0	669.19	1.76	-18.789	0.184
	298.0	638.60	2.05	-16.361	0.202
GROMACS(BS)	98.0	770.17	0.06	-27.405	0.003
	173.0	717.03	0.09	-22.857	0.004
	248.0	669.04	0.11	-18.850	0.006
	298.0	638.14	0.13	-16.346	0.007
GROMACS(KL)	98.0	769.98	0.16	-27.515	0.009
	173.0	716.63	0.06	-22.932	0.016
	248.0	668.81	0.09	-18.820	0.011
	298.0	637.80	0.12	-16.382	0.004
ms2(KL)	98.0	781.89	0.11	-23.977	0.006
	173.0	717.90	0.18	-22.673	0.022
	248.0	669.20	0.13	-18.816	0.009
	298.0	638.05	0.15	-16.351	0.012
ms2(PB)	98.0	770.68	0.05	-27.492	0.003
	173.0	717.01	0.09	-23.014	0.004
	248.0	669.12	0.10	-18.853	0.005
	298.0	638.34	0.13	-16.314	0.007
Tinker(AA)	98.0	771.40	1.00		
	173.0	715.70	1.50		
	248.0	666.30	1.90		
	298.0	635.30	2.00		
TOWHEE(BS)	98.0	770.91	0.74	-27.394	0.045
	173.0	717.72	0.76	-22.915	0.041
	248.0	669.19	0.30	-18.828	0.015
	298.0	638.40	0.35	-16.350	0.022

Table 29: Results of the different groups for n-butane at 5 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	778.06	1.19	-24.037	0.088
	173.0	704.52	1.79	-20.164	0.141
	248.0	633.19	2.54	-15.534	0.183
	298.0	581.50	3.00	-12.512	0.199
GROMACS(BS)	98.0	774.15	0.16	-25.132	0.006
	173.0	703.91	0.25	-20.197	0.008
	248.0	632.69	0.22	-15.546	0.020
	298.0	580.98	0.23	-12.491	0.018
GROMACS(KL)	98.0	774.68	0.09	-25.057	0.003
	173.0	704.02	0.11	-20.234	0.004
	248.0	633.05	0.19	-15.550	0.007
	298.0	580.58	0.28	-12.523	0.009
ms2(KL)	98.0	782.19	0.12	-21.637	0.005
	173.0	705.68	0.16	-20.012	0.025
	248.0	633.35	0.23	-15.517	0.011
	298.0	580.56	0.31	-12.447	0.012
ms2(PB)	98.0	776.45	0.08	-25.167	0.004
	173.0	704.75	0.12	-20.167	0.005
	248.0	633.74	0.17	-15.507	0.007
	298.0	581.83	0.28	-12.477	0.010
Tinker(AA)	98.0	776.20	1.40		
	173.0	704.50	1.80		
	248.0	632.20	2.30		
	298.0	579.40	2.70		
TOWHEE(BS)	98.0	775.92	0.73	-25.077	0.037
	173.0	705.47	0.73	-20.194	0.041
	248.0	633.77	0.63	-15.537	0.028
	298.0	581.78	0.72	-12.515	0.030

Table 30: Results of the different groups for n-butane at 41 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	790.76	1.15	-24.349	0.087
	173.0	725.28	1.69	-20.738	0.131
	248.0	665.52	2.00	-16.533	0.173
	298.0	627.20	2.41	-13.889	0.195
GROMACS(BS)	98.0	787.17	0.09	-25.443	0.003
	173.0	723.94	0.12	-20.776	0.028
	248.0	664.71	0.22	-16.442	0.026
	298.0	626.49	0.10	-13.914	0.032
GROMACS(KL)	98.0	787.43	0.07	-25.364	0.003
	173.0	724.29	0.10	-20.766	0.004
	248.0	665.47	0.14	-16.512	0.007
	298.0	626.22	0.19	-13.937	0.008
ms2(KL)	98.0	790.00	0.10	-25.279	0.005
	173.0	725.32	0.14	-20.556	0.020
	248.0	665.80	0.14	-16.500	0.010
	298.0	626.73	0.20	-13.885	0.012
ms2(PB)	98.0	788.39	0.09	-25.437	0.004
	173.0	724.69	0.10	-20.712	0.006
	248.0	665.69	0.13	-16.500	0.007
	298.0	626.07	0.16	-13.876	0.008
Tinker(AA)	98.0	788.80	1.20		
	173.0	724.20	1.70		
	248.0	664.10	1.80		
	298.0	625.10	2.10		
TOWHEE(BS)	98.0	788.83	0.82	-25.397	0.058
	173.0	725.17	0.57	-20.747	0.029
	248.0	665.84	0.64	-16.510	0.028
	298.0	626.98	0.79	-13.907	0.033

Table 31: Results of the different groups for n-butane at 70 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	800.31	1.00	-24.553	0.085
	173.0	738.32	1.53	-21.168	0.136
	248.0	684.46	1.97	-17.082	0.183
	298.0	650.72	2.05	-14.578	0.201
GROMACS(BS)	98.0	795.97	0.18	-25.618	0.007
	173.0	737.55	0.15	-21.096	0.024
	248.0	683.87	0.15	-17.068	0.001
	298.0	650.66	0.22	-14.620	0.003
GROMACS(KL)	98.0	796.28	0.07	-25.533	0.003
	173.0	737.68	0.08	-21.107	0.004
	248.0	684.26	0.12	-17.053	0.005
	298.0	650.76	0.14	-14.622	0.007
ms2(KL)	98.0	804.00	0.09	-22.096	0.004
	173.0	738.34	0.11	-20.959	0.021
	248.0	684.40	0.14	-17.019	0.011
	298.0	650.57	0.15	-14.589	0.010
ms2(PB)	98.0	798.28	0.09	-25.660	0.004
	173.0	738.18	0.11	-21.093	0.005
	248.0	684.53	0.11	-17.036	0.006
	298.0	650.55	0.14	-14.590	0.007
Tinker(AA)	98.0	797.80	1.20		
	173.0	737.40	1.70		
	248.0	683.20	1.90		
	298.0	648.60	2.20		
TOWHEE(BS)	98.0	798.03	1.46	-25.588	0.082
	173.0	738.65	0.46	-21.101	0.033
	248.0	684.85	0.59	-17.045	0.029
	298.0	650.72	0.57	-14.595	0.023

Table 32: Results of the different groups for n-butane at 5 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0	701.26	3.55	-20.482	0.185
	248.0	637.12	4.75	-14.826	0.262
	298.0	588.35	6.50	-11.139	0.322
GROMACS(BS)	98.0	763.68	0.09	-26.284	0.004
	173.0	700.97	0.10	-20.498	0.004
	248.0	637.72	0.17	-14.808	0.007
	298.0	591.73	0.31	-11.202	0.011
GROMACS(KL)	98.0	756.89	1.80	-26.004	0.054
	173.0	705.02	1.80	-20.909	0.044
	248.0	641.98	0.91	-15.769	0.019
	298.0	594.25	1.20	-12.292	0.026
Ind.MC(PB)	98.0	759.16	0.11	-28.588	0.006
	173.0	696.86	0.14	-25.176	0.007
	248.0	632.68	0.14	-21.964	0.006
	298.0	587.87	0.17	-19.884	0.006
LAMMPS(AA)	98.0	758.19	1.87	-26.209	0.048
	173.0	696.74	1.22	-20.855	0.055
	248.0	631.90	2.20	-15.794	0.082
	298.0	587.30	2.94	-12.480	0.108
LAMMPS(KL)	98.0	764.64	3.63	-22.811	0.145
	173.0	689.18	3.35	-20.042	0.161
	248.0	632.03	3.58	-14.697	0.186
	298.0	592.15	4.92	-11.185	0.221
ms2(KL)	98.0	764.81	0.71	-22.880	0.028
	173.0	691.82	0.94	-20.048	0.035
	248.0	634.11	0.31	-14.681	0.012
	298.0	591.04	0.54	-11.130	0.016
ms2*(KL)	98.0	773.85	0.11	-22.938	0.008
	173.0	708.52	0.07	-17.822	0.006
	248.0	640.92	0.14	-13.958	0.022
	298.0	593.23	0.12	-11.568	0.021
ms2(PB)	98.0	738.63	0.12	-25.638	0.004
	173.0	685.92	0.35	-19.920	0.012
	248.0	631.19	0.24	-14.690	0.008
	298.0	590.80	0.25	-11.124	0.008
NAMD(FM)	98.0	744.14	2.68	-25.482	0.118
	173.0	677.76	4.00	-20.116	0.191
	248.0	615.73	5.54	-15.110	0.260
	298.0	572.33	6.38	-11.762	0.313
Tinker(AA)	98.0	757.10	1.30		

	173.0	696.60	1.80		
	248.0	633.80	1.90		
	298.0	590.50	2.20		
TOWHEE(BS)	98.0	761.37	0.89	-26.183	0.047
	173.0	698.22	0.55	-20.341	0.039
	248.0	635.65	0.68	-14.780	0.033
	298.0	590.99	0.64	-11.190	0.034

Table 33: Results of the different groups for n-butane at 41 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0	715.34	3.38	-20.982	0.184
	248.0	661.01	4.42	-15.626	0.242
	298.0	626.74	5.03	-12.357	0.295
GROMACS(BS)	98.0	773.49	0.07	-26.490	0.003
	173.0	717.81	0.09	-20.801	0.006
	248.0	662.05	0.13	-15.668	0.006
	298.0	628.42	0.16	-12.429	0.007
GROMACS(KL)	98.0	768.71	1.60	-26.302	0.043
	173.0	719.30	2.00	-21.353	0.042
	248.0	667.41	1.20	-16.607	0.020
	298.0	629.48	0.43	-13.480	0.008
Ind.MC(PB)	98.0	768.37	0.08	-26.274	0.005
	173.0	714.07	0.12	-21.306	0.006
	248.0	659.57	0.13	-16.342	0.006
	298.0	625.01	0.12	-12.926	0.005
LAMMPS(AA)	98.0	769.52	1.02	-26.511	0.059
	173.0	712.28	1.35	-21.386	0.052
	248.0	659.75	1.98	-16.676	0.065
	298.0	625.64	2.30	-13.728	0.074
LAMMPS(KL)	98.0	776.03	3.38	-23.110	0.142
	173.0	707.92	3.53	-20.526	0.161
	248.0	660.06	3.26	-15.603	0.167
	298.0	626.17	3.66	-12.365	0.191
ms2(KL)	98.0	776.30	0.61	-23.132	0.026
	173.0	709.42	0.68	-20.579	0.023
	248.0	661.15	0.43	-15.588	0.009
	298.0	627.07	0.21	-12.354	0.013
ms2*(KL)	98.0	784.90	0.08	-23.209	0.005
	173.0	725.62	0.09	-18.299	0.006
	248.0	668.16	0.08	-14.616	0.010
	298.0	629.64	0.08	-12.607	0.010

ms2(PB)	98.0	751.84	0.11	-25.970	0.003
	173.0	703.41	0.30	-20.581	0.009
	248.0	659.59	0.21	-15.556	0.007
	298.0	627.07	0.19	-12.363	0.007
NAMD(FM)	98.0	756.10	2.60	-25.798	0.117
	173.0	697.81	3.91	-20.749	0.182
	248.0	644.54	4.76	-16.092	0.239
	298.0	613.36	5.52	-13.152	0.282
Tinker(AA)	98.0	769.70	1.20		
	173.0	713.80	1.20		
	248.0	661.20	1.30		
	298.0	626.70	2.10		
TOWHEE(BS)	98.0	773.13	0.63		
	173.0	715.66	0.64	-20.851	0.040
	248.0	662.41	0.57	-15.662	0.033
	298.0	627.19	0.40	-12.397	0.023

Table 34: Results of the different groups for n-butane at 70 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0	727.59	3.04	-21.271	0.183
	248.0	678.41	4.07	-16.149	0.243
	298.0	649.10	4.73	-13.069	0.290
GROMACS(BS)	98.0	781.06	0.11	-26.649	0.004
	173.0	729.76	0.09	-21.185	0.004
	248.0	679.32	0.13	-16.146	0.006
	298.0	649.26	0.14	-13.058	0.006
GROMACS(KL)	98.0	776.73	1.80	-26.485	0.048
	173.0	730.62	2.20	-21.663	0.044
	248.0	683.17	0.79	-17.090	0.013
	298.0	648.40	0.42	-14.101	0.009
Ind.MC(PB)	98.0	776.20	0.10	-28.883	0.006
	173.0	726.09	0.11	-26.049	0.006
	248.0	676.27	0.12	-23.398	0.006
	298.0	645.96	0.12	-21.820	0.005
LAMMPS(AA)	98.0	778.07	1.22	-26.699	0.040
	173.0	725.17	1.41	-21.723	0.046
	248.0	676.75	1.79	-17.206	0.062
	298.0	643.38	2.36	-14.374	0.063
LAMMPS(KL)	98.0	784.64	3.62	-23.334	0.129
	173.0	720.25	4.18	-20.874	0.198
	248.0	676.94	3.81	-16.111	0.157

	298.0	647.37	3.23	-13.035	0.184
ms2(KL)	98.0	786.49	0.74	-23.332	0.025
	173.0	721.53	0.57	-20.974	0.019
	248.0	677.29	0.26	-16.063	0.017
	298.0	647.39	0.30	-12.983	0.010
ms2*(KL)	98.0	792.79	0.08	-23.366	0.005
	173.0	737.28	0.08	-18.631	0.008
	248.0	684.10	0.11	-15.255	0.019
	298.0	650.09	0.11	-13.436	0.023
ms2(PB)	98.0	761.09	0.10	-26.210	0.003
	173.0	717.19	0.29	-20.909	0.007
	248.0	676.14	0.22	-16.088	0.007
	298.0	646.31	0.14	-13.005	0.006
NAMD(FM)	98.0	764.36	2.48	-25.990	0.116
	173.0	709.63	3.82	-21.101	0.176
	248.0	663.25	4.49	-16.673	0.230
	298.0	635.37	4.74	-13.856	0.266
Tinker(AA)	98.0	777.50	0.70		
	173.0	726.70	1.10		
	248.0	679.20	1.30		
	298.0	646.50	1.90		
TOWHEE(BS)	98.0	781.02	0.39	-26.621	0.039
	173.0	727.69	0.83	-21.182	0.050
	248.0	679.13	0.56	-16.154	0.024
	298.0	648.04	0.51	-13.040	0.030

5.4 iso-Butane

Table 35: Results of the different groups for iso-butane at 5 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	754.74	0.82	-26.779	0.086
	173.0	690.00	1.84	-22.318	0.128
	248.0	625.09	2.38	-18.174	0.158
	298.0	580.42	2.90	-15.471	0.181
GROMACS(BS)	98.0	765.06	0.06	-27.090	0.003
	173.0	694.10	0.10	-22.405	0.003
	248.0	628.39	0.18	-18.233	0.005
	298.0	582.26	0.28	-15.506	0.007
GROMACS(KL)	98.0	764.52	0.31	-27.081	0.010
	173.0	695.59	0.33	-22.458	0.007
	248.0	628.68	0.38	-18.257	0.007
	298.0	582.74	0.33	-15.524	0.008
LAMMPS(AA)	98.0	756.28	1.71	-26.819	0.064
	173.0	692.38	1.49	-22.371	0.054
	248.0	626.92	2.73	-18.209	0.084
	298.0	580.91	3.28	-15.468	0.100
LAMMPS(KL)	98.0	756.68	1.52	-26.841	0.055
	173.0	692.18	1.63	-22.367	0.059
	248.0	627.46	2.57	-18.219	0.083
	298.0	580.49	2.96	-15.463	0.092
ms2(KL)	98.0	757.29	0.13	-26.845	0.005
	173.0	692.16	0.22	-22.356	0.006
	248.0	626.90	0.31	-18.190	0.006
	298.0	580.48	0.38	-15.447	0.008
ms2(PB)	98.0	756.90	0.10	-26.843	0.004
	173.0	691.94	0.11	-22.354	0.004
	248.0	627.22	0.19	-18.205	0.005
	298.0	582.20	0.22	-15.488	0.006
Tinker(AA)	98.0	757.10	1.00		
	173.0	692.90	1.80		
	248.0	627.20	2.80		
	298.0	580.40	2.80		
TOWHEE(BS)	98.0	757.81	0.45	-26.866	0.025
	173.0	692.20	0.41	-22.365	0.019
	248.0	626.65	0.46	-18.190	0.019
	298.0	580.62	0.49	-15.463	0.019

Table 36: Results of the different groups for iso-butane at 41 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	769.75	1.11	-27.164	0.087
	173.0	710.15	1.69	-22.914	0.131
	248.0	654.46	1.90	-19.120	0.162
	298.0	618.97	2.19	-16.766	0.180
GROMACS(BS)	98.0	776.23	0.08	-27.368	0.003
	173.0	711.96	0.08	-22.951	0.003
	248.0	656.46	0.13	-19.148	0.003
	298.0	619.02	0.19	-16.765	0.005
GROMACS(KL)	98.0	774.57	0.16	-27.319	0.005
	173.0	712.62	0.18	-22.979	0.004
	248.0	656.00	0.16	-19.165	0.004
	298.0	619.79	0.33	-16.795	0.005
LAMMPS(AA)	98.0	768.62	1.43	-27.136	0.051
	173.0	709.49	1.10	-22.898	0.046
	248.0	654.99	1.82	-19.130	0.066
	298.0	619.07	2.38	-16.756	0.073
LAMMPS(KL)	98.0	768.63	1.37	-27.139	0.055
	173.0	709.29	1.51	-22.902	0.052
	248.0	654.33	1.82	-19.123	0.069
	298.0	618.26	1.97	-16.750	0.065
ms2(KL)	98.0	769.70	0.20	-27.162	0.007
	173.0	709.76	0.30	-22.902	0.006
	248.0	654.02	0.28	-19.111	0.005
	298.0	617.90	0.29	-16.735	0.005
ms2(PB)	98.0	767.19	0.09	-27.091	0.003
	173.0	709.78	0.11	-22.904	0.003
	248.0	654.61	0.15	-19.118	0.004
	298.0	618.36	0.15	-16.749	0.004
Tinker(AA)	98.0	769.50	1.20		
	173.0	710.00	1.80		
	248.0	655.20	2.20		
	298.0	618.60	2.40		
TOWHEE(BS)	98.0	769.30	0.64	-26.866	0.025
	173.0	710.02	0.31	-22.917	0.017
	248.0	654.62	0.34	-19.127	0.014
	298.0	618.41	0.52	-16.747	0.022

Table 37: Results of the different groups for iso-butane at 70 MPa from the OPLS force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	777.87	1.07	-27.353	0.092
	173.0	722.27	1.60	-23.258	0.129
	248.0	671.43	1.83	-19.650	0.161
	298.0	640.28	2.21	-17.445	0.182
GROMACS(BS)	98.0	783.11	0.06	-27.498	0.003
	173.0	724.06	0.12	-23.290	0.003
	248.0	673.08	0.12	-19.676	0.003
	298.0	639.83	0.13	-17.437	0.004
GROMACS(KL)	98.0	782.20	0.33	-27.481	0.007
	173.0	723.90	0.27	-23.301	0.006
	248.0	672.66	0.23	-19.682	0.004
	298.0	640.28	0.27	-17.454	0.006
LAMMPS(AA)	98.0	777.29	1.22	-27.339	0.048
	173.0	721.72	1.17	-23.243	0.043
	248.0	671.61	1.62	-19.652	0.054
	298.0	640.07	2.24	-17.434	0.064
LAMMPS(KL)	98.0	777.19	1.23	-27.333	0.048
	173.0	722.28	1.30	-23.257	0.046
	248.0	671.08	1.58	-19.651	0.055
	298.0	639.30	1.99	-17.430	0.057
ms2(KL)	98.0	777.39	0.10	-27.333	0.004
	173.0	721.97	0.26	-23.245	0.006
	248.0	670.78	0.25	-19.638	0.004
	298.0	639.09	0.30	-17.409	0.005
ms2(PB)	98.0	776.60	0.06	-27.317	0.003
	173.0	721.68	0.10	-23.239	0.003
	248.0	671.38	0.12	-19.646	0.003
	298.0	639.73	0.15	-17.420	0.004
Tinker(AA)	98.0	777.30	1.10		
	173.0	721.80	1.60		
	248.0	671.60	2.20		
	298.0	640.00	2.00		
TOWHEE(BS)	98.0	777.67	0.38	-27.347	0.021
	173.0	722.10	0.42	-23.260	0.020
	248.0	669.63	0.84	-19.586	0.291
	298.0	639.72	0.32	-17.431	0.013

Table 38: Results of the different groups for iso-butane at 5 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	757.20	1.00	-23.574	0.083
	173.0	686.82	1.82	-19.268	0.123
	248.0	613.36	2.70	-15.197	0.158
	298.0	559.21	3.33	-12.468	0.172
GROMACS(BS)	98.0	774.12	0.10	-23.993	0.003
	173.0	693.84	0.11	-19.394	0.004
	248.0	618.36	0.20	-15.270	0.005
	298.0	563.58	0.29	-12.533	0.008
GROMACS(KL)	98.0	768.61	1.80	-23.872	0.047
	173.0	695.58	0.24	-19.452	0.024
	248.0	618.71	0.37	-15.297	0.012
	298.0	564.01	0.78	-12.553	0.012
LAMMPS(AA)	98.0	759.68	2.56	-23.632	0.067
	173.0	688.71	1.87	-19.299	0.057
	248.0	615.51	2.98	-15.227	0.079
	298.0	561.96	3.51	-12.502	0.103
LAMMPS(KL)	98.0	758.51	2.40	-23.610	0.065
	173.0	687.97	1.85	-19.290	0.059
	248.0	616.33	2.61	-15.239	0.077
	298.0	560.69	4.09	-12.478	0.105
ms2(KL)	98.0	760.46	0.29	-23.649	0.008
	173.0	689.04	0.32	-19.302	0.006
	248.0	614.49	0.44	-15.198	0.009
	298.0	560.30	0.47	-12.461	0.009
ms2(PB)	98.0	759.30	0.13	-23.621	0.004
	173.0	688.48	0.15	-19.295	0.004
	248.0	614.42	0.19	-15.199	0.005
	298.0	562.50	0.28	-12.500	0.007
Tinker(AA)	98.0	760.40	1.00		
	173.0	687.80	1.80		
	248.0	616.10	2.70		
	298.0	560.90	3.50		
TOWHEE(BS)	98.0	761.34	0.45	-23.675	0.024
	173.0	688.85	0.41	-19.304	0.018
	248.0	615.19	0.80	-15.214	0.028
	298.0	561.34	0.59	-12.485	0.021

Table 39: Results of the different groups for iso-butane at 41 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	774.64	1.21	-23.984	0.087
	173.0	710.34	1.60	-19.904	0.122
	248.0	650.01	2.04	-16.265	0.153
	298.0	611.16	2.40	-13.993	0.174
GROMACS(BS)	98.0	784.33	0.06	-24.201	0.002
	173.0	713.67	0.09	-19.962	0.003
	248.0	651.72	0.18	-16.283	0.004
	298.0	612.35	0.20	-14.013	0.005
GROMACS(KL)	98.0	780.97	1.20	-24.148	0.029
	173.0	713.68	0.26	-19.976	0.007
	248.0	652.06	0.56	-16.301	0.006
	298.0	612.39	0.25	-14.022	0.006
LAMMPS(AA)	98.0	772.86	2.23	-23.937	0.065
	173.0	710.82	1.41	-19.912	0.050
	248.0	650.06	2.28	-16.266	0.068
	298.0	610.79	2.82	-13.989	0.074
LAMMPS(KL)	98.0	772.61	2.07	-23.940	0.053
	173.0	709.13	1.43	-19.890	0.049
	248.0	650.40	1.95	-16.270	0.059
	298.0	611.32	2.84	-13.995	0.073
ms2(KL)	98.0	773.40	0.09	-23.953	0.004
	173.0	710.07	0.23	-19.896	0.005
	248.0	649.41	0.34	-16.251	0.004
	298.0	609.98	0.39	-13.970	0.005
ms2(PB)	98.0	773.12	0.11	-23.939	0.003
	173.0	710.06	0.11	-19.899	0.003
	248.0	649.68	0.13	-16.246	0.004
	298.0	610.69	0.19	-13.972	0.004
Tinker(AA)	98.0	774.60	0.90		
	173.0	709.50	2.00		
	248.0	649.90	2.10		
	298.0	611.00	2.60		
TOWHEE(BS)	98.0	774.58	0.77	-23.982	4.946
	173.0	709.87	0.76	-19.888	0.025
	248.0	650.07	0.66	-16.268	0.025
	298.0	610.80	0.51	-13.982	0.021

Table 40: Results of the different groups for iso-butane at 70 MPa from the TraPPE force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0	785.18	1.40	-24.203	0.090
	173.0	724.47	1.62	-20.267	0.125
	248.0	669.88	2.13	-16.823	0.159
	298.0	636.27	2.32	-14.712	0.176
GROMACS(BS)	98.0	792.44	0.04	-24.359	0.002
	173.0	726.88	0.09	-20.296	0.003
	248.0	671.92	0.14	-16.846	0.003
	298.0	636.34	0.15	-14.713	0.004
GROMACS(KL)	98.0	788.74	0.84	-24.299	0.023
	173.0	727.34	0.25	-20.322	0.004
	248.0	671.92	0.26	-16.854	0.006
	298.0	637.34	0.37	-14.729	0.002
LAMMPS(AA)	98.0	782.98	2.04	-24.143	0.054
	173.0	723.84	1.57	-20.255	0.048
	248.0	669.86	1.96	-16.827	0.054
	298.0	635.18	2.30	-14.704	0.063
LAMMPS(KL)	98.0	782.60	1.17	-24.144	0.038
	173.0	724.11	1.31	-20.267	0.046
	248.0	669.97	1.78	-16.821	0.057
	298.0	635.90	2.86	-14.706	0.070
ms2(KL)	98.0	777.39	0.10	-24.135	0.008
	173.0	723.92	0.40	-20.258	0.007
	248.0	669.64	0.36	-16.811	0.004
	298.0	635.52	0.30	-14.687	0.004
ms2(PB)	98.0	782.87	0.13	-24.145	0.003
	173.0	724.57	0.12	-20.263	0.003
	248.0	670.47	0.15	-16.816	0.004
	298.0	635.76	0.15	-14.694	0.004
Tinker(AA)	98.0	783.20	1.10		
	173.0	723.90	1.70		
	248.0	669.50	2.10		
	298.0	636.80	2.20		
TOWHEE(BS)	98.0	783.94	0.40	-24.175	0.020
	173.0	724.18	0.55	-20.263	0.026
	248.0	670.07	0.47	-16.821	0.021
	298.0	636.20	0.40	-14.710	0.016

Table 41: Results of the different groups for iso-butane at 5 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0	703.01	3.62	-20.799	0.173
	248.0	637.54	4.96	-15.543	0.244
	298.0	592.91	6.04	-12.255	0.311
GROMACS(BS)	98.0	772.17	0.07	-26.230	0.003
	173.0	704.59	0.15	-20.722	0.004
	248.0	640.41	0.16	-15.638	0.004
	298.0	593.49	0.24	-12.269	0.007
GROMACS(KL)	98.0	771.26	0.31	-26.206	0.009
	173.0	706.09	0.43	-20.768	0.011
	248.0	640.36	0.48	-15.652	0.010
	298.0	595.30	0.64	-12.312	0.012
Ind.MC(PB)	98.0	767.35	0.12	-26.001	0.007
	173.0	702.77	0.11	-20.621	0.006
	248.0	637.84	0.15	-15.533	0.007
	298.0	591.70	0.17	-12.165	0.008
LAMMPS(AA)	98.0	767.75	1.33	-26.077	0.052
	173.0	702.47	1.81	-20.638	0.057
	248.0	638.58	3.11	-15.555	0.082
	298.0	592.70	2.57	-12.189	0.085
LAMMPS(KL)	98.0	759.92	4.61	-25.877	0.148
	173.0	702.64	3.04	-20.682	0.125
	248.0	638.36	3.69	-15.602	0.167
	298.0	590.72	4.78	-12.212	0.213
ms2(KL)	98.0	760.61	0.80	-25.877	0.023
	173.0	701.21	0.30	-20.607	0.007
	248.0	638.30	0.53	-15.542	0.011
	298.0	591.40	0.52	-12.158	0.011
ms2*(KL)	98.0	769.40	0.08	-26.510	0.005
	173.0	704.12	0.08	-21.348	0.004
	248.0	639.33	0.12	-16.538	0.005
	298.0	593.82	0.12	-13.374	0.005
ms2(PB)	98.0	759.96	0.29	-25.858	0.009
	173.0	702.58	0.16	-20.649	0.005
	248.0	638.05	0.18	-15.551	0.005
	298.0	593.46	0.27	-12.218	0.007
NAMD(FM)	98.0	761.87	3.53	-25.924	0.135
	173.0	702.14	4.02	-20.668	0.180
	248.0	637.90	5.18	-15.588	0.251
	298.0	590.59	6.46	-12.201	0.306
Tinker(AA)	98.0	757.90	0.70		

	173.0	703.00	2.70		
	248.0	639.60	4.20		
	298.0	603.00	4.40		
TOWHEE(BS)	98.0	768.59	0.58	-26.113	0.035
	173.0	703.11	0.62	-20.681	0.034
	248.0	638.34	0.59	-15.589	0.030
	298.0	592.81	0.77	-12.255	0.031

Table 42: Results of the different groups for iso-butane at 41 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0	720.35	3.25	-21.320	0.175
	248.0	666.51	4.21	-16.440	0.235
	298.0	626.77	5.03	-13.417	0.282
GROMACS(BS)	98.0	783.20	0.06	-26.494	0.003
	173.0	721.03	0.13	-21.232	0.004
	248.0	665.83	0.18	-16.499	0.004
	298.0	630.23	0.22	-13.507	0.005
GROMACS(KL)	98.0	782.52	0.47	-26.482	0.014
	173.0	723.85	0.27	-21.299	0.007
	248.0	666.62	0.28	-16.526	0.005
	298.0	630.58	0.37	-13.523	0.005
Ind.MC(PB)	98.0	777.70	0.10	-26.234	0.006
	173.0	720.35	0.08	-21.160	0.005
	248.0	664.65	0.11	-16.420	0.006
	298.0	628.35	0.12	-13.418	0.007
LAMMPS(AA)	98.0	778.71	1.37	-26.338	0.050
	173.0	721.81	1.65	-21.209	0.053
	248.0	663.70	1.89	-16.416	0.063
	298.0	629.77	2.43	-13.435	0.076
LAMMPS(KL)	98.0	771.49	3.73	-26.173	0.118
	173.0	719.09	2.60	-21.195	0.113
	248.0	664.76	2.73	-16.485	0.139
	298.0	629.46	3.49	-13.494	0.169
ms2(KL)	98.0	772.22	0.65	-26.168	0.016
	173.0	720.54	0.42	-21.186	0.008
	248.0	663.77	0.35	-16.415	0.007
	298.0	628.48	0.28	-13.423	0.006
ms2*(KL)	98.0	780.17	0.07	-26.759	0.004
	173.0	721.37	0.08	-21.875	0.004
	248.0	666.03	0.08	-17.420	0.004
	298.0	630.08	0.10	-14.610	0.004

ms2(PB)	98.0	772.57	0.25	-26.196	0.007
	173.0	719.90	0.14	-21.183	0.004
	248.0	665.22	0.16	-16.455	0.004
	298.0	629.10	0.19	-13.443	0.005
NAMD(FM)	98.0	772.86	2.69	-26.200	0.113
	173.0	719.05	3.50	-21.193	0.171
	248.0	664.34	4.26	-16.474	0.231
	298.0	627.85	5.15	-13.465	0.274
Tinker(AA)	98.0	769.10	0.60		
	173.0	716.60	0.90		
	248.0	665.60	2.90		
	298.0	632.80	2.90		
TOWHEE(BS)	98.0	779.97	0.47	-26.400	0.027
	173.0	720.44	0.66	-21.212	0.030
	248.0	664.98	0.64	-16.480	0.032
	298.0	628.84	0.35	-13.478	0.014

Table 43: Results of the different groups for iso-butane at 70 MPa from the OPLSAMBER force field.

Program(Group)	T / K	ρ / kg m^{-3}	$\delta\rho$ / kg m^{-3}	u / kJ mol^{-1}	δu / kJ mol^{-1}
DL_POLY(BS)	98.0				
	173.0	732.72	3.05	-21.576	0.161
	248.0	681.35	4.22	-16.988	0.222
	298.0	649.48	4.57	-14.135	0.269
GROMACS(BS)	98.0	789.47	0.05	-26.616	0.003
	173.0	734.71	0.10	-21.599	0.003
	248.0	683.36	0.13	-17.026	0.003
	298.0	650.81	0.15	-14.162	0.004
GROMACS(KL)	98.0	789.61	0.71	-26.629	0.022
	173.0	734.11	0.29	-21.598	0.007
	248.0	683.31	0.36	-17.040	0.006
	298.0	651.65	0.70	-14.185	0.005
Ind.MC(PB)	98.0	786.37	0.11	-26.435	0.007
	173.0	731.84	0.09	-21.468	0.005
	248.0	681.52	0.10	-16.957	0.006
	298.0	649.25	0.10	-14.091	0.007
LAMMPS(AA)	98.0	787.09	1.19	-26.535	0.051
	173.0	731.79	1.24	-21.505	0.046
	248.0	681.73	1.88	-16.952	0.057
	298.0	649.12	2.07	-14.090	0.061
LAMMPS(KL)	98.0	779.86	3.66	-26.367	0.110
	173.0	729.98	2.46	-21.511	0.107
	248.0	681.04	2.71	-16.999	0.134

	298.0	649.94	3.17	-14.150	0.160
ms2(KL)	98.0	780.69	0.62	-26.368	0.017
	173.0	731.57	0.38	-21.503	0.008
	248.0	681.19	0.27	-16.944	0.005
	298.0	649.35	0.35	-14.077	0.004
ms2*(KL)	98.0	788.61	0.08	-26.954	0.005
	173.0	733.15	0.06	-22.207	0.003
	248.0	682.57	0.08	-17.934	0.004
	298.0	650.77	0.08	-15.273	0.004
ms2(PB)	98.0	781.59	0.28	-26.414	0.008
	173.0	730.58	0.19	-21.495	0.004
	248.0	681.80	0.12	-16.972	0.004
	298.0	648.56	0.14	-14.092	0.004
NAMD(FM)	98.0	782.13	3.09	-26.415	0.119
	173.0	730.17	1.65	-21.506	0.165
	248.0	681.31	2.09	-16.994	0.222
	298.0	649.24	2.44	-14.141	0.261
Tinker(AA)	98.0	777.70	0.90		
	173.0	729.30	0.90		
	248.0	681.60	1.40		
	298.0	656.20	1.60		
TOWHEE(BS)	98.0	779.97	0.47	-26.554	0.038
	173.0	732.49	0.65	-21.553	0.034
	248.0	681.94	0.51	-16.480	0.032
	298.0	649.74	0.77	-14.142	0.037

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