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Thermophysical Properties of the Lennard-Jones Fluid: Database and Data Assessment

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Abstract

Literature data on thermophysical properties of the Lennard-Jones fluid, which were sampled with Molecular Dynamics and Monte Carlo simulations, were reviewed and assessed. The literature data was complemented by simulation data from the present work that was taken in regions in which previously only sparse data was available. Data on homogeneous state points (for given temperature T and density ρ : pressure p , thermal expansion coefficient α , isothermal compressibility β , thermal pressure coefficient γ , internal energy u , isochoric heat capacity c_v , isobaric heat capacity c_p , Grüneisen coefficient Γ , Joule-Thomson coefficient μ_{JT} , speed of sound w , Helmholtz energy a , chemical potential μ , surface tension γ) was considered as well as data on the vapor-liquid equilibrium (for given T : vapor pressure p^s , saturated liquid and vapor densities ρ' and ρ'' , enthalpy of vaporization Δh_v). The entire set of available data, which contains about 35,000 data points, was digitalized and included in a database, which is made available in the electronic supplementary material of this paper. Different consistency tests were applied to assess the accuracy and precision of the data. The data on homogeneous states were evaluated point-wise using data from their respective

vicinity and equations of state. Approximately 5% of all homogeneous bulk data were discarded as outliers. The vapor-liquid equilibrium data were assessed by tests based on the compressibility factor, the Clausius-Clapeyron equation, and by an outlier test. Seven particularly reliable vapor-liquid equilibrium data sets were identified. The mutual agreement of these data sets is approximately $\pm 1\%$ for the vapor pressure, $\pm 0.2\%$ for the saturated liquid density, $\pm 1\%$ for the saturated vapor density, and $\pm 0.75\%$ for the enthalpy of vaporization – excluding the region close to the critical point.

Introduction

The assessment of experimental thermophysical property data is a well established field in chemical engineering,^{1–3} especially for phase equilibrium data.^{4,5} For instance, consistency tests based on thermodynamic limits or balance equations are used to evaluate the quality of data sets or data points of a given thermophysical property. However, such approaches are not common in the analysis of thermophysical property data obtained by computer experiments, like molecular dynamics (MD) or Monte Carlo (MC) simulations. Also, thermophysical data repositories^{6,7} have so far not addressed molecular simulation data of model fluids, like the Lennard-Jones fluid. The present work therefore provides a coherent and consolidated database of thermophysical property data of the Lennard-Jones fluid.

The Lennard-Jones potential^{8,9} is of fundamental importance for the development of theories and methods in soft matter physics,^{10–12} and has been widely used since the early days of computer simulation.^{13–20} It is often taken as a benchmark for the validation of simulation codes and the test of new simulation techniques. Despite its simplicity, the Lennard-Jones model fluid yields a realistic representation of simple fluids.^{21,22} Due to its importance, it is sometimes even referred to as *Lennard-Jonesium*^{23–25} – suggesting that it is viewed as a chemical element.²⁶ The Lennard-Jones potential is defined as the pairwise additive and spherically symmetric potential

$$u_{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r is the distance between two particles. Its parameters ε and σ characterize the size of the particles and the magnitude of their dispersive attraction, respectively. Simulations are usually performed with a truncated potential in combination with a long-range correction.²⁷

To sample thermophysical properties of the Lennard-Jones fluid, computer experiments are carried out. In general, an obtained simulation result of a given observable x^{sim} will not agree with the true model value x^{mod} .²⁸ Like in experiments in the laboratory, also in computer experiments errors occur^{29–33} that can cause deviations between the exact true value x^{mod} and the value observed in the simulation x^{sim} . Both stochastic and systematic errors are usually present to some extent in computer experiments. Techniques to assess statistical errors are well established for computer simulations.^{27,30,34} It is more difficult to assess systematic simulation errors. As in laboratory experiments, round robin studies can be used for doing this, in which the same simulation task is carried out by different groups with different programs. It is known that the results from such studies generally differ by more than the combined statistical uncertainty of the individual data. E.g., the results obtained by repetition usually differ due to varying methods or simulation programs etc.²⁹ Systematic errors may be a consequence of erroneous algorithms,³⁵ user errors, differences due to different simulation methods (for example MD and MC, phase equilibrium simulation methods, techniques for the determination of the chemical potential³⁶ etc.). Systematic errors may furthermore be caused by finite size effects, erroneous evaluation of long range interactions, insufficient equilibration or production periods, compilers, parallelization, and hardware architecture.²⁹ Last but not least, also typographical errors in publications have to be considered as a possible error source. The detection and assessment of outliers in large data sets is a standard task in the field of data science^{37–39} and is widely applied to experimental data,^{40,41} but has to the best of our knowledge not yet been applied to thermophysical property data obtained by computer experiments with model fluids. In the present work, we use the terms *accurate* & *precise* as follows: *accurate* simulation results x^{sim} scatter around the true value x^{mod} without trend; *precise* means here that given simulation results x^{sim} are both accurate and exhibit a low scattering.

This article reviews and assesses molecular simulation data of the Lennard-Jones fluid. Approximately 35,000 data points were taken into account, including new simulation data from this

work that were taken to complement the available data in regions that were only sparsely investigated in the literature. Vapor-liquid equilibrium (VLE) data and data on state points from the homogeneous regions were considered: For the VLE, the vapor pressure, the saturated densities, and the enthalpy of vaporization were investigated; for homogeneous state points, the investigated properties are: the pressure, thermal expansion coefficient, isothermal compressibility, thermal pressure coefficient, internal energy, isochoric heat capacity, isobaric heat capacity, Grüneisen coefficient, Joule-Thomson coefficient, speed of sound, Helmholtz energy, chemical potential, and surface tension. Transport properties were not taken into account.

The data were assessed by consistency tests to provide an indication for their accuracy and precision. The entire database was digitalized and is presented in a consistent form as a spreadsheet in the supplementary material. The database also contains flags that indicate whether a data point was identified as an outlier. All thermophysical property data are reported using reduced units with respect to the Lennard-Jones energy and size parameters ε and σ as well as the Boltzmann constant k_B .²⁷

Molecular simulation data of the Lennard-Jones fluid

Table 1 gives an overview on the thermophysical property data of the Lennard-Jones fluid from the literature. Only data on homogeneous states and vapor-liquid equilibria were considered in this work. Data on the second and third virial coefficients and the so-called characteristic curves^{42,43} were included in the database, but not further assessed regarding their accuracy. The vast majority of studies in the literature report pvT and internal energy data for homogeneous state points, cf. Table 1. The chemical potential and higher order derivatives, like speed of sound, heat capacities, or isothermal compressibility, were less frequently investigated. Wherever statistical uncertainties were reported in the literature, they were also included in the database.

Table 1: Computer experiment data of the Lennard-Jones fluid from the literature. The data are sorted chronologically for each property. The # is the number of data points and T the investigated temperature range.

Authors	Year	#	T
<i>pvT</i> data			
<i>Wood and Parker</i> ¹⁵	1957	13	2.74
<i>Fickett and Wood</i> ⁴⁴	1960	23	1.92 - 177.95
<i>McDonald and Singer</i> ⁴⁵	1967	28	0.72 - 1.24
<i>McDonald and Singer</i> ¹⁹	1967	48	1.45 - 3.53
<i>Verlet and Levesque</i> ⁴⁶	1967	7	1.05 - 2.74
<i>Verlet</i> ¹⁸	1967	39	0.59 - 4.63
<i>Wood</i> ⁴⁷	1968	41	1.06 - 100
<i>Hansen and Verlet</i> ²⁰	1969	25	0.75 - 1.15
<i>Levesque and Verlet</i> ⁴⁸	1969	25	0.72 - 3.67
<i>McDonald and Singer</i> ⁴⁹	1969	28	0.72 - 1.24
<i>Hansen</i> ⁵⁰	1970	9	2.74 - 100
<i>McDonald and Woodcock</i> ⁵¹	1970	6	0.75 - 2.33
<i>Toxvaerd and Praestgaard</i> ⁵²	1970	8	1.35
<i>Weeks et al.</i> ⁵³	1971	5	0.75 - 1.35
<i>McDonald and Singer</i> ⁵⁴	1972	56	0.55 - 1.24
<i>Schofield</i> ⁵⁵	1973	6	0.73 - 1.1
<i>Street et al.</i> ⁵⁶	1974	80	0.75 - 3.05
<i>Adams</i> ⁵⁷	1975	12	2 - 4
<i>Adams</i> ⁵⁸	1976	16	1 - 1.2
<i>Carley</i> ⁵⁹	1977	11	1.35
<i>Adams</i> ⁶⁰	1979	31	1.15 - 1.35
<i>Nicolas et al.</i> ⁶¹	1979	108	0.48 - 6.01
<i>Ree</i> ⁶²	1980	11	0.81 - 2.7
<i>Yao et al.</i> ⁶³	1982	12	1.15 - 1.25
<i>Powles et al.</i> ⁶⁴	1982	37	0.7 - 1.41
<i>Lucas</i> ⁶⁵	1986	10	0.79 - 1.83
<i>Shaw</i> ⁶⁶	1988	265	0.6 - 136.25
<i>Adachi et al.</i> ⁶⁷	1988	328	0.7 - 2.95
<i>Baranyai et al.</i> ⁶⁸	1989	12	0.75 - 1.5
<i>Saager and Fischer</i> ⁶⁹	1990	38	0.57 - 4
<i>Sowers and Sandler</i> ⁷⁰	1991	60	1.35 - 6
<i>Lotfi et al.</i> ⁷¹	1992	19	0.7 - 1.3
<i>Giaquinta et al.</i> ⁷²	1992	12	0.75 - 1.15
<i>Johnson et al.</i> ⁷³	1993	199	0.7 - 6
<i>Kolafa et al.</i> ⁷⁴	1993	43	0.72 - 4.85
<i>Miyano</i> ⁷⁵	1993	112	0.45 - 100
<i>Kolafa and Nezbeda</i> ⁷⁶	1994	13	0.81 - 10
<i>Lustig</i> ⁷⁷	1994	2	1.18

Continued on next page

Authors	Year	#	T
<i>Mecke et al.</i> ⁷⁸	1996	12	1.32 - 1.34
<i>Roccatano et al.</i> ⁷⁹	1998	10	1.4 - 10
<i>Meier</i> ⁸⁰	2002	351	0.7 - 6
<i>Linhart et al.</i> ⁸¹	2005	108	0.7 - 1.2
<i>Morsali et al.</i> ⁸²	2007	13	5.01
<i>Baidakov et al.</i> ⁸³	2008	208	0.35 - 2
<i>Lustig</i> ⁸⁴	2011	8	1.02 - 3
<i>May and Mausbach</i> ⁸⁵	2012	205	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{86,87}	2012	406	1.3 - 2.62
<i>Mairhofer and Sadus</i> ^{88,89}	2013	282	1.36 - 3.05
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Deiters and Neumaier</i> ⁴³	2016	255	0.67 - 22.54
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>Ustinov</i> ^{93,94}	2017	232	0.76 - 1.14
<i>Schultz and Kofke</i> ⁹⁵	2018	404	0.68 - 2272
<i>this work</i>	2019	655	0.7 - 90
Internal energy u			
<i>Wood and Parker</i> ¹⁵	1957	13	2.74
<i>McDonald and Singer</i> ⁴⁵	1967	27	0.72 - 1.24
<i>McDonald and Singer</i> ¹⁹	1967	48	1.45 - 3.53
<i>Verlet</i> ¹⁸	1967	39	0.59 - 4.63
<i>Verlet and Levesque</i> ⁴⁶	1967	7	1.05 - 2.74
<i>Wood</i> ⁴⁷	1968	41	1.06 - 100
<i>Levesque and Verlet</i> ⁴⁸	1969	25	0.72 - 3.67
<i>McDonald and Singer</i> ⁴⁹	1969	28	0.72 - 1.24
<i>Hansen</i> ⁵⁰	1970	9	2.74 - 100
<i>McDonald and Woodcock</i> ⁵¹	1970	6	0.75 - 2.33
<i>Weeks et al.</i> ⁵³	1971	5	0.75 - 1.35
<i>McDonald and Singer</i> ⁵⁴	1972	56	0.55 - 1.24
<i>Street et al.</i> ⁵⁶	1974	80	0.75 - 3.05
<i>Adams</i> ⁵⁷	1975	12	2 - 4
<i>Adams</i> ⁵⁸	1976	16	1 - 1.2
<i>Torrie and Valleau</i> ⁹⁶	1977	7	0.092 - 1.35
<i>Adams</i> ⁶⁰	1979	31	1.15 - 1.35
<i>Nicolas et al.</i> ⁶¹	1979	108	0.48 - 6.01
<i>Ree</i> ⁶²	1980	11	0.81 - 2.7
<i>Yao et al.</i> ⁶³	1982	12	1.15 - 1.25
<i>Lucas</i> ⁶⁵	1986	10	0.79 - 1.83
<i>Shaw</i> ⁶⁶	1988	265	0.59 - 136.25
<i>Baranyai et al.</i> ⁶⁸	1989	18	0.75 - 1.5
<i>Saager and Fischer</i> ⁶⁹	1990	38	0.57 - 4
<i>Sowers and Sandler</i> ⁷⁰	1991	54	1.35 - 6
<i>Continued on next page</i>			

Authors	Year	#	T
<i>Lotfi et al.</i> ⁷¹	1992	19	0.7 - 1.3
<i>Giaquinta et al.</i> ⁷²	1992	12	0.75 - 1.15
<i>Johnson et al.</i> ⁷³	1993	199	0.7 - 6
<i>Kolafa et al.</i> ⁷⁴	1993	43	0.72 - 4.85
<i>Miyano</i> ⁷⁵	1993	112	0.45 - 100
<i>Kolafa and Nezbeda</i> ⁷⁶	1994	13	0.81 - 10
<i>Lustig</i> ⁷⁷	1994	2	1.18
<i>Mecke et al.</i> ⁷⁸	1996	12	1.32 - 1.34
<i>Roccatano et al.</i> ⁷⁹	1998	10	1.4 - 10
<i>Meier</i> ⁸⁰	2002	351	0.7 - 6
<i>Baidakov et al.</i> ⁸³	2008	201	0.35 - 2
<i>May and Mausbach</i> ⁸⁵	2012	218	0.68 - 6.17
<i>Yigzawe and Sadus</i> ^{86,87}	2012	346	1.31 - 2.62
<i>Mairhofer and Sadus</i> ^{88,89}	2013	282	1.36 - 3.05
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Deiters and Neumaier</i> ^{43,97}	2016	255	0.67 - 22.54
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>Ustinov</i> ^{93,94}	2017	232	0.76 - 1.14
<i>Schultz and Kofke</i> ⁹⁵	2018	404	0.68 - 2272
<i>this work</i>	2019	655	0.7 - 90

VLE $p^s, \rho', \rho'', \Delta h_v$

<i>Hansen and Verlet</i> ²⁰ ($p^s, \rho', \rho'', \Delta h_v$)	1969	8	0.75 - 1.15
<i>Lee et al.</i> ⁹⁸ (ρ', ρ'')	1974	10	0.7 - 1.2
<i>Adams</i> ⁵⁸ ($p^s, \rho', \rho'', \Delta h_v$)	1976	44	0.6 - 1.1
<i>Chapela et al.</i> ⁹⁹ (ρ', ρ'')	1977	6	0.7 - 0.84
<i>Adams</i> ⁶⁰ ($p^s, \rho', \rho'', \Delta h_v$)	1979	11	1.15 - 1.30
<i>Panagiotopoulos</i> ¹⁰⁰ ($p^s, \rho', \rho'', \Delta h_v$)	1987	30	0.75 - 1.3
<i>Panagiotopoulos et al.</i> ¹⁰¹ ($p^s, \rho', \rho'', \Delta h_v$)	1988	30	0.75 - 1.3
<i>Nijmeijer et al.</i> ¹⁰² (ρ', ρ'')	1988	2	0.92
<i>Smit and Frenkel</i> ¹⁰³ ($p^s, \rho', \rho'', \Delta h_v$)	1989	20	1.15 - 1.3
<i>Lotfi et al.</i> ⁷¹ (p^s, ρ', ρ'')	1992	52	0.7 - 1.3
<i>Kofke</i> ¹⁰⁴ ($p^s, \rho', \rho'', \Delta h_v$)	1993	80	0.74 - 1.32
<i>Holcomb et al.</i> ¹⁰⁵ (ρ', ρ'')	1993	6	0.72 - 1.13
<i>Agrawal and Kofke</i> ¹⁰⁶ ($p^s, \rho', \rho'', \Delta h_v$)	1995	52	0.68 - 0.74
<i>Hunter and Reinhardt</i> ¹⁰⁷ (ρ', ρ'')	1995	39	1 - 1.35
<i>Sadus and Prausnitz</i> ¹⁰⁸ ($p^s, \rho', \rho'', \Delta h_v$)	1996	30	1 - 1.25
<i>Mecke et al.</i> ¹⁰⁹ (ρ', ρ'')	1997	6	0.7 - 1.1
<i>Plačkov and Sadus</i> ¹¹⁰ ($p^s, \rho', \rho'', \Delta h_v$)	1997	55	0.95 - 1.27
<i>Guo et al.</i> ¹¹¹ (ρ', ρ'')	1997	10	0.75 - 1.25
<i>Guo and Lu</i> ¹¹² (ρ', ρ'')	1997	8	0.75 - 1.15
<i>Martin and Siepmann</i> ¹¹³ (p^s, ρ', ρ'')	1998	18	0.75 - 1.18
<i>Trokhymchuk and Alejandre</i> ¹¹⁴ (p^s, ρ', ρ'')	1999	18	0.72 - 1.27

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Authors	Year	#	T
<i>Anisimov et al.</i> ¹¹⁵ (p^s, ρ', ρ'')	1999	18	0.75 - 1
<i>Potoff and Panagiotopoulos</i> ¹¹⁶ (ρ', ρ'')	2000	36	0.95 - 1.31
<i>Baidakov et al.</i> ¹¹⁷ (p^s, ρ', ρ'')	2000	21	0.72 - 1.23
<i>Okumura and Yonezawa</i> ^{118,119} (p^s, ρ', ρ'')	2000	39	0.7 - 1.3
<i>Shi and Johnson</i> ¹²⁰ (ρ', ρ'')	2001	26	1.15 - 1.27
<i>Chen et al.</i> ²⁴ (ρ', ρ'')	2001	6	0.7 - 0.8
<i>Okumura and Yonezawa</i> ^{121,122} (p^s, ρ', ρ'')	2001	30	1.25 - 1.32
<i>Baidakov et al.</i> ¹²³ ($\rho', \rho'', \text{spinodal}$)	2002	14	0.72 - 1.23
<i>Kioupis et al.</i> ¹²⁴ ($p^s, \rho', \rho'', \Delta h_v$)	2002	40	1.03 - 1.3
<i>Errington</i> ¹²⁵ (p^s, ρ', ρ'')	2003	12	0.7 - 1.3
<i>Errington</i> ^{126,127} (p^s, ρ', ρ'')	2003	39	0.7 - 1.3
<i>Stoll et al.</i> ¹²⁸ ($p^s, \rho', \rho'', \Delta h_v$)	2003	44	0.73 - 1.26
<i>Baidakov et al.</i> ¹²⁹ (p^s, ρ', ρ'')	2007	36	0.5 - 1.2
<i>Betancourt-Cárdenas et al.</i> ¹³⁰ ($p^s, \rho', \rho'', \Delta h_v$)	2008	35	0.7 - 1.27
<i>Janeček</i> ¹³¹ ($p^s, \rho', \rho'', \Delta h_v$)	2009	16	0.72 - 1.25
<i>Galliero et al.</i> ¹³² (ρ', ρ'')	2009	38	0.7 - 1.3
<i>Sadus</i> ¹³³ (p^s)	2012	14	0.7 - 1.29
<i>Mick et al.</i> ²³ ($p^s, \rho', \rho'', \Delta h_v$)	2013	36	0.75 - 1.3
<i>Martinez-Ruiz et al.</i> ¹³⁴ (p^s, ρ', ρ'')	2014	21	0.7 - 1.1
<i>Janeček et al.</i> ¹³⁵ ($p^s, \rho', \rho'', \Delta h_v$)	2017	31	0.7 - 1.25
<i>Janeček et al.</i> ^{135,136} ($p^s, \rho', \rho'', \Delta h_v$)	2017	24	0.8 - 1.25
<i>Werth et al.</i> ¹³⁷ ($p^s, \rho', \rho'', \Delta h_v$)	2017	36	0.72 - 1.24
<i>Stephan and Hasse</i> ¹³⁸ (p^s, ρ', ρ'')	2019	39	0.69 - 1.29
this work ($p^s, \rho', \rho'', \Delta h_v$)	2019	124	0.69 - 1.28

Vapor-liquid surface tension γ

<i>Lee et al.</i> ⁹⁸	1974	5	0.7 - 1.2
<i>Miyazaki et al.</i> ¹³⁹	1976	1	0.7
<i>Chapela et al.</i> ⁹⁹	1977	5	0.7 - 1.27
<i>Nijmeijer et al.</i> ¹⁰²	1988	1	0.92
<i>Holcomb et al.</i> ¹⁰⁵	1993	3	0.72 - 1.13
<i>Mecke et al.</i> ¹⁴⁰	1997	3	0.7 - 1.1
<i>Guo et al.</i> ¹¹¹	1997	5	0.75 - 1.25
<i>Guo and Lu</i> ¹¹²	1997	4	0.75 - 1.15
<i>Trokhymchuk and Alejandre</i> ¹¹⁴	1999	6	0.72 - 1.27
<i>Anisimov et al.</i> ¹¹⁵	1999	6	0.75 - 1
<i>Potoff and Panagiotopoulos</i> ¹¹⁶	2000	18	0.95 - 1.31
<i>Baidakov et al.</i> ¹¹⁷	2000	7	0.72 - 1.23
<i>Chen et al.</i> ²⁴	2001	3	0.7 - 0.8
<i>Baidakov et al.</i> ¹²³	2002	6	0.72 - 1.22
<i>Errington</i> ¹²⁵	2003	4	0.7 - 1.3
<i>Baidakov et al.</i> ¹²⁹	2007	12	0.5 - 1.2
<i>Shen et al.</i> ¹⁴¹	2007	10	0.7 - 1.1
<i>Janeček et al.</i> ¹³¹	2009	4	0.72 - 1.25

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Authors	Year	#	T
<i>Galliero et al.</i> ¹³²	2009	13	0.7 - 1.3
<i>Galliero et al.</i> ¹³²	2009	6	0.7 - 1.2
<i>Werth et al.</i> ¹⁴²	2013	7	0.7 - 1.25
<i>Martinez-Ruiz et al.</i> ¹³⁴	2014	7	0.7 - 1.1
<i>Janeček et al.</i> ¹³⁵	2017	8	0.7 - 1.25
<i>Werth et al.</i> ¹³⁷	2017	9	0.72 - 1.24
<i>Stephan and Hasse</i> ¹³⁸	2019	13	0.69 - 1.29
SLE			
<i>Hansen and Verlet</i> ²⁰	1969	4	0.75 - 2.74
<i>Hansen</i> ⁵⁰	1970	6	2.74 - 100
<i>Agrawal and Kofke</i> ¹⁰⁶	1995	37	0.69 - 274
<i>van der Hoef</i> ¹⁴³	2000	corr. ^(A)	0.1 - 2.0
<i>Barroso and Ferreira</i> ¹⁴⁴	2002	18	0.69 - 4.5
<i>Morris and Song</i> ¹⁴⁵	2002	12	0.72 - 2.65
<i>Errington</i> ¹⁴⁶	2004	2	0.75 - 2
<i>McNeil-Watson and Wilding</i> ¹⁴⁷	2006	34	0.72 - 83
<i>Mastny and Pablo</i> ¹⁴⁸	2007	5	1 - 20
<i>Ahmed and Sadus</i> ^{149,150}	2009	5	0.8 - 2.74
<i>Sousa et al.</i> ¹⁵¹	2012	10	0.75 - 5
<i>Köster et al.</i> ⁹¹	2017	8	1.3 - 30
<i>Schultz and Kofke</i> ⁹⁵	2018	corr. ^(A)	0.68 - 2272
Isochoric heat capacity c_v			
<i>Wood and Parker</i> ¹⁵	1957	11	2.74
<i>McDonald and Singer</i> ⁴⁵	1967	26	0.72 - 1.24
<i>McDonald and Singer</i> ¹⁹	1967	48	1.45 - 3.53
<i>Adams</i> ⁵⁷	1975	12	2 - 4
<i>Adams</i> ⁶⁰	1979	31	1.15 - 1.35
<i>Saager et al.</i> ^{152,153}	1990	12	1.1 - 1.35
<i>Boda et al.</i> ¹⁵⁴	1996	9	1.31 - 2
<i>Roccatano et al.</i> ⁷⁹	1998	10	1.4 - 10
<i>Meier</i> ^{80,155}	2002	327	0.7 - 6
<i>Baidakov et al.</i> ⁸³	2008	208	0.35 - 2
<i>May and Mausbach</i> ^{85,156}	2012	218	0.68 - 6.17
<i>Yigzawe and Sadus</i> ^{86,87}	2012	406	1.3 - 2.62
<i>Mairhofer and Sadus</i> ^{88,89}	2013	282	1.36 - 3.05
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>this work</i>	2019	515	0.7 - 90
Isobaric heat capacity c_p			
<i>Boda et al.</i> ¹⁵⁴	1996	41	0.65 - 1.9

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Authors	Year	#	T
<i>Lustig</i> ⁸⁴	2011	6	1.02 - 3
<i>May and Mausbach</i> ^{85,156}	2012	202	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{86,87}	2012	406	1.3 - 2.62
<i>Mairhofer and Sadus</i> ^{88,89}	2013	282	1.36 - 3.05
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>this work</i>	2019	515	0.7 - 90
Grüneisen coefficient Γ			
<i>Emampour et al.</i> ¹⁵⁷	2011	26	1.2 - 1.8
<i>Mausbach and May</i> ¹⁵⁸	2014	212	0.69 - 6.17
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Mausbach et al.</i> ¹⁵⁹	2016	110	0.72 - 9
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>this work</i>	2019	515	0.7 - 90
Thermal expansion coefficient α			
<i>McDonald and Singer</i> ⁴⁵	1967	20	0.72 - 1.24
<i>Adams</i> ⁵⁷	1975	12	2 - 4
<i>Yigzawe and Sadus</i> ^{86,87}	2012	406	1.3 - 2.62
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>this work</i>	2019	515	0.7 - 90
Isothermal compressibility β			
<i>McDonald and Singer</i> ⁴⁵	1967	22	0.72 - 1.24
<i>Adams</i> ⁵⁷	1975	12	2 - 4
<i>Adams</i> ⁶⁰	1979	31	1.15 - 1.35
<i>Lotfi et al.</i> ⁷¹	1992	19	0.7 - 1.3
<i>Lustig</i> ⁷⁷	1994	2	1.18
<i>Morsali et al.</i> ⁸²	2007	13	3.76
<i>May and Mausbach</i> ^{85,156}	2012	205	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{86,87}	2012	406	1.3 - 2.62
<i>Mairhofer and Sadus</i> ^{88,89}	2013	282	1.36 - 3.05
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>this work</i>	2019	515	0.7 - 90
Thermal pressure coefficient γ			
<i>McDonald and Singer</i> ⁴⁵	1967	20	0.72 - 1.24

Continued on next page

Authors	Year	#	T
<i>Adams</i> ⁵⁷	1975	12	2 - 4
<i>Lustig</i> ⁷⁷	1994	2	1.18
<i>Meier</i> ⁸⁰	2002	326	0.7 - 6
<i>Morsali et al.</i> ⁸²	2007	13	3.76
<i>May and Mausbach</i> ^{85,156}	2012	205	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{86,87}	2012	406	1.3 - 2.62
<i>Mairhofer and Sadus</i> ^{88,89}	2013	282	1.36 - 3.05
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>this work</i>	2019	515	0.7 - 90
Speed of sound w			
<i>Meier</i> ⁸⁰	2002	349	0.7 - 6
<i>Lustig</i> ⁸⁴	2011	8	1.02 - 3
<i>May and Mausbach</i> ^{85,156}	2012	205	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{86,87}	2012	406	1.3 - 2.62
<i>Mairhofer and Sadus</i> ^{88,89}	2013	282	1.36 - 3.05
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>this work</i>	2019	515	0.7 - 90
Joule-Thomson coefficient μ_{JT}			
<i>Lustig</i> ⁸⁴	2011	8	1.02 - 3
<i>May and Mausbach</i> ^{85,156}	2012	205	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{86,87}	2012	406	1.3 - 2.62
<i>Mairhofer and Sadus</i> ^{88,89}	2013	282	1.36 - 3.05
<i>Thol et al.</i> ⁹⁰	2016	197	0.7 - 9
<i>Köster et al.</i> ⁹¹	2017	45	1.01 - 30
<i>Köster et al.</i> ^{91,92}	2017	65	1.01 - 30
<i>this work</i>	2019	515	0.7 - 90
Entropic properties a, μ			
<i>Levesque and Verlet</i> ⁴⁸ (a)	1969	8	1.35
<i>Hansen and Verlet</i> ²⁰ (a)	1969	25	0.75 - 1.15
<i>Weeks et al.</i> ⁵³ (a)	1971	5	0.75 - 1.35
<i>Weeks et al.</i> ¹⁶⁰ (a)	1971	27	0.75 - 1.35
<i>Adams</i> ⁵⁷ (μ)	1975	12	2 - 4
<i>Torrie and Valleau</i> ⁹⁶ (a)	1977	16	0.75 - 2.74
<i>Adams</i> ⁶⁰ (μ)	1979	31	1.15 - 1.35
<i>Yao et al.</i> ⁶³ (μ)	1982	12	1.15 - 1.25
<i>Powles et al.</i> ⁶⁴ (μ)	1982	37	0.7 - 1.41
<i>Panagiotopoulos et al.</i> ¹⁰¹ (μ)	1988	18	0.75 - 1.3
<i>Continued on next page</i>			

Authors	Year	#	T
<i>Baranyai and Evans</i> ⁶⁸ (a)	1989	6	1.15
<i>Lotfi et al.</i> ⁷¹ (μ)	1992	19	0.75 - 1.3
<i>Han</i> ¹⁶¹ (μ)	1992	3	1.2
<i>Kolafa et al.</i> ⁷⁴ (μ)	1993	7	1.2 - 1.45
<i>Lustig</i> ⁷⁷ (μ)	1994	2	1.18
<i>Cuadros et al.</i> ¹⁶² (a)	1996	269	0.7 - 2.6
<i>Hong and Jhon</i> ¹⁶³ (a)	1997	36	0.59 - 2.89
<i>Hong and Jang</i> ¹⁶⁴ (a)	2003	22	0.59 - 2.85
<i>Thol et al.</i> ⁹⁰ (a, μ)	2016	197	0.7 - 9
<i>Köster et al.</i> ^{91,92} (a, μ)	2017	65	1.01 - 30
<i>Ustinov</i> ^{93,94} (μ)	2017	232	0.76 - 1.14
<i>this work</i> (a, μ)	2019	655	0.7 - 90
Virial coefficients B, C			
<i>Bird et al.</i> ¹⁶⁵ (C)	1950	74	0.7 - 400
<i>Hirschfelder et al.</i> ¹⁶⁶ (B, C)	1954	156	0.3 - 400
<i>Barker et al.</i> ¹⁶⁷ (B, C)	1966	66	0.625 - 20
<i>Nicolas et al.</i> ⁶¹ (B)	1979	33	0.625 - 20
<i>Sun and Teja</i> ¹⁶⁸ (B, C)	1996	302	0.39 - 6.1
<i>Shaul et al.</i> ¹⁶⁹ (B, C)	2010	22	0.7 - 2
<i>Wheatley</i> ^{170,171} (B, C)	2013	100	0.1 - 1000
Ideal curves ID, BL, JTI, JI^(B)			
<i>Heyes and Llaguno</i> ¹⁷² (JTI)	1992	16	1.15 - 7.1
<i>Colina and Müller</i> ¹⁷³ (JTI)	1999	24	1.12 - 6.4
<i>Kioupis et al.</i> ¹²⁴ (JTI)	2002	29	1.3 - 6
<i>Vrabec et al.</i> ¹⁷⁴ (JTI)	2005	18	1.2 - 6.3
<i>Yigzawe and Sadus</i> ⁸⁷ (JTI)	2013	9	1.31 - 2.62
<i>Deiters and Neumaier</i> ^{43,97} (ID, BL, JTI, JI)	2016	43	0.01 - 6.4

(A) The authors provided no numerical data, but a correlation that was parametrized to computer experiment data.

(B) ID: Classical ideal curve, BL: Boyle curve, JTI: Joule-Thomson inversion curve, JI: Joule inversion curve.

The simulation method proposed by *Lustig*^{84,175} provides Helmholtz energy derivatives with respect to the density and the inverse temperature simultaneously from a single simulation run. This technique can be combined with Widom's test particle insertion method¹⁷⁶ for the determination of the Helmholtz energy itself. This approach was applied to the Lennard-Jones fluid by *Thol et al.*⁹⁰ and *Köster et al.*^{91,92} in different fluid regions. The simulations of *Thol et al.*⁹⁰ were

restricted to stable fluid states below $T = 9$, while the simulation data of *Köster et al.*^{91,92} focused on the high density region close to the freezing line. These two data sets are complemented in the present work by data on 655 additional homogeneous state points, cf. Figure. 1, that were also sampled with the *Lustig* formalism. The new data was taken in order to get more information on regions in which literature data was comparatively sparse. For the metastable region, only pressure, chemical potential, and internal energy are reported here. The entity of the simulation results of Refs.^{90–92} and from this work is referred to as the *Lustig* formalism (LF) data set in the following. All of them were sampled with the simulation program *ms2*¹⁷⁷ using similar simulation settings. Details on the simulation procedure are given in Appendix .

Results on VLE properties of the Lennard-Jones fluid have been reported many times in the literature, cf. Table 1. 45 VLE data sets were found in the progress of this work. The simulation methods used in these studies can be separated in two types: simulations in which the liquid and the vapor phase are simulated in two separate volumes that are suitably coupled and simulations in which the liquid and the vapor phase coexist in a single volume that also contains the interface. The first are referred to as *indirect methods* and the latter as *direct methods* in the following. Both VLE simulation types provide in general vapor pressure p^s , saturated densities of the liquid and vapor phase ρ' and ρ'' , respectively, and enthalpy of vaporization Δh_v at a given temperature T . However, often only a subset of these properties was reported in the literature, cf. Table 1. Simulation techniques that belong to the indirect type¹⁷⁸ are the Gibbs ensemble method,^{100,101} the Grand equilibrium method,¹⁷⁹ the NpT +test particle method,¹⁸⁰ Gibbs-Duhem integration,¹⁸¹ and the Wang-Landau method.¹⁸² Additional information on interfacial properties can be obtained with the direct method.^{183,184} Data on the surface tension of the Lennard-Jones fluid are also included in the database, cf. Table 1. The Grand equilibrium method was employed in the present work to obtain an extended VLE data set for the Lennard-Jones fluid. Details are given in Appendix .

Data on the triple point^{20,24,95,106,144,148–151,185–188} and the critical point^{18,46,48,60,61,70,71,73,75,78,100,104,107,113,1} of the Lennard-Jones fluid have been reported many times. Numeric values of the critical point are summarized in Table 2. The critical pressure has been less frequently reported than the critical temperature and density. The critical parameters of the LJ fluid reported in the literature scatter

over a large range – especially regarding the temperature. However, 13 critical temperature and density data points (Refs. ^{71,104,119,120,122,191,197,198,200,202}) are in fairly good agreement, even though most of them do not agree within their combined statistical uncertainties. The critical temperature reported by Refs. ^{71,104,119,120,122,191,197,198,200,202} scatters in a range of $T_c = 1.31..1.326$; the critical density in a range of $\rho_c = 0.304..0.318$. The reported critical densities obtained from computer experiment reported by Refs. ^{71,104,119,120,122,191,198,200,202} cluster around two different values: $\rho_c = 0.305$ and 0.316 . Other data points were discarded since they significantly deviate from this entity. The critical pressure reported by Refs. ^{60,119,122,192,197} scatters in the range $p_c = 0.125..0.135$.

In the following, the critical point is presumed to be located at $T_c = 1.321 \pm 0.007$, $\rho_c = 0.316 \pm 0.005$ and $p_c = 0.129 \pm 0.005$. The stated uncertainties were estimated from the standard deviation of the critical parameters reported by Refs. ^{71,104,119,120,122,191,198,200,202} for the critical temperature and density and Refs. ^{60,119,122,192,197} for the critical pressure.

The solid-fluid equilibrium of the Lennard-Jones fluid is used in this study only to delimit the fluid region, as molecular simulation results beyond the freezing line were excluded regarding the assessment. Solid-fluid equilibria have been investigated multiple times, cf. Table 1. The correlation for the freezing line by *Köster et al.*⁹¹ was employed here.

Database of thermophysical properties

All thermophysical property data (approximately 35,000 data points) considered in this work are summarized in a consistent form in an *.xls* spreadsheet in the electronic supplementary material of this work. All data are sorted by thermophysical properties in that spreadsheet. All numerical values are given in a consistent form, i.e. as residual properties with respect to the ideal gas and in the standard 'Lennard-Jones' units. Information on the statistical uncertainties were adopted from publications – wherever such information was reported, which is unfortunately not always the case. The methods for the estimation of statistical uncertainties differ significantly among the publications. Sometimes, statistical uncertainties were reported, but no description on how such were obtained is given. Due to this heterogeneity, statistical uncertainties could unfortunately not

be used for the assessment of data points in this work.

The database furthermore contains notes on pitfalls regarding the conversion of the primary literature data to the format used in the database. Furthermore, known misprints in publications from the literature were corrected, e.g.^{90,92,155} A survey of these misprints is also given. Each data point possesses an additional mark, which indicates whether the data point was found to be an outlier or not, according the assessment described in the following.

Assessment of molecular simulation data

Assessment of data on homogeneous states

Thermophysical property data of the Lennard-Jones fluid reported in the literature (see Table 1) for homogeneous state points were assessed by an equation of state (EOS) consistency test. This consistency test is based on the statistical method proposed by *Rousseeuw and Croux*²⁰⁶ for the detection of outliers that was adopted and extended for the purposes of the present work. The EOS test evaluates each data point individually by comparing it with the most accurate equations of state of the Lennard-Jones fluid available in the literature and computer experiment data in its vicinity. The EOS test is designed in a way to make a binary decision: either a data point is an outlier or not.

The relative deviation δx of a given data point (DP) $x_{\text{DP}}(T, \rho)$ from a given EOS at the same temperature and density was computed as

$$\delta x = \frac{x_{\text{DP}} - x_{\text{EOS}}}{x_{\text{EOS}}}, \quad (2)$$

where x is one of the following homogeneous bulk phase properties: pressure p , internal energy u , speed of the sound w , thermal pressure coefficient γ , Grüneisen coefficient Γ , thermal expansion coefficient α , isothermal compressibility β , Joule-Thomson coefficient μ_{JT} , isochoric heat capacity c_v , isobaric heat capacity c_p , Helmholtz energy divided by the temperature $\tilde{a} = a/T$, or chemical potential μ .

Comprehensive comparisons of EOS for the Lennard-Jones fluid have been carried out recently.^{90,207} Six of the most accurate EOS were used here: *Johnson et al.*,⁷³ *Kolafa and Nezbeda*,⁷⁶ *Lafitte et al.*,¹¹ *Mecke et al.*,^{78,208} *Stephan et al.*,²⁰⁷ and *Thol et al.*⁹⁰ (alphabetically). However, also these EOS have deficiencies, e.g. the EOS of *Thol et al.*⁹⁰ exhibits an unrealistic behavior in the two-phase region, that of *Mecke et al.*^{78,208} shows large deviations in the high density region close to the freezing line, that of *Stephan et al.*²⁰⁷ is less accurate in the high temperature region, the EOS of *Kolafa and Nezbeda*⁷⁶ produces distorted characteristic curves,⁴³ and the one of *Lafitte et al.*¹¹ is less accurate in the low density gas region. The EOS from *Johnson et al.*⁷³ is overall less precise than the ones mentioned before. To take these deficiencies into account in evaluating an individual data point, only the four EOS were considered that yielded the smallest relative deviation δx_j for a given data point. The four best EOS were identified and selected for each data point individually, to prevent that the mentioned deficiencies of the used EOS adulterate the assessment.

To take into account that the precision of molecular simulation results varies in different regions, the deviation of each individual state point was put into relation with the average deviation of the data points in its neighborhood in the $T - \rho$ plane. Each data point j has its own neighborhood with $i = 1..M$ neighbors, where the number of neighbors is $M = 15..20$. The nearest neighbors were determined using the radial distance $\tilde{\delta}R$ between data points in the $T - \rho$ plane, i.e. $\tilde{\delta}R = (\tilde{\delta}T^2 + \tilde{\delta}\rho^2)^{0.5}$. The choice of the radius and, hence, of M depends on the location of the data point in the $T - \rho$ plane, i.e. in a fluid region where data points are sparse or if a data point is close to a phase boundary the radius was chosen large enough, such that at least 15 neighbors were allocated to the neighborhood of each data point. The neighbors of each data point j were taken from the entity of all data points N of a given property, i.e. the neighborhood M contains in general data points from different publications.

To decide whether a data point j is an outlier, a measure P_j is introduced. Following the ideas of Refs.,^{38,39,206,209} P_j was defined as

$$P_j = \frac{|\delta x_j - \text{median}_{i=1}^M(\delta x_{ji})|}{\text{MAD}_j} \quad \text{with } i = 1..M \text{ and } j = 1..N. \quad (3)$$

In the measure P_j , the deviation of a tested data point j and an EOS are compared to the deviations of the data points from its neighborhood and that EOS. Details on the selection of the EOS are given below. The numerator on the right hand side of Eq. (3) is the absolute deviation of the data point j and the median²¹⁰ of the data points in its neighborhood. The denominator is a measure for the mean absolute deviation (MAD) of the data points in the neighborhood of the given data point²¹¹ j

$$\text{MAD}_j = k \cdot \text{median}_{i=1}^M \left(|\delta x_{ij} - \text{median}_{i=1}^M (\delta x_{ij})| \right), \quad (4)$$

where $k = 1.4826$. The selection of that number is related to the assumption that the deviation data δx_{ij} is normally distributed in the set of data points.²¹² The MAD_j quantifies how strong the data points of the neighborhood M scatter on average from their median, i.e. how precise the data in the neighborhood is on average. The MAD is robust, as the median is less affected by outliers than the mean. Hence, this test takes the accuracy of the EOS and the accuracy of the computer experiment data of a certain thermophysical property in a certain fluid region into account. For brevity, it is called EOS test in the following.

The EOS test requires a sufficiently dense neighborhood of data points, to ensure that the accuracy of the reference, i.e. the EOS, remains fairly constant within the neighborhood. Since the data points for $T > 6$ are sparsely distributed in the $T - \rho$ plane, the EOS test was only applied to data at $T \leq 6$.

The measure P_j was computed for the four EOS that were selected as described above, and then compared with a parameter $P_{\max}$

$$P_j \geq P_{\max}. \quad (5)$$

If this decision criterion was fulfilled for at least two of the four EOS, the data point j was identified as an outlier. The parameter $P_{\max}$ introduces an unavoidable subjective attribute into the method^{206,209} and regulates the severity of the EOS test. A fixed number for $P_{\max}$ is used here for all thermophysical properties, EOS, and fluid regions under consideration, which established a consistent framework. The parameter was set to $P_{\max} = 4$. This results in a confirmation rate of approximately 90% of all homogeneous data. Vice versa, 10% of all homogeneous data points

were identified as outliers. This rather conservative choice^{206,209} for $P_{\max}$ was used to prevent a false assessment of data points to be erroneous. A more stringent, but smaller database can be generated easily by increasing $P_{\max}$ and vice versa a larger database, that might however include less precise data, can be generated by decreasing $P_{\max}$. The EOS test enables a robust assessment of the quality of individual data points based on an assessment of the precision of the data points in its neighborhood.

Figure. 2 summarizes the results of the EOS test for the homogeneous state points for $P_{\max} = 4$. About 85% of the pvT data and the data for the internal energy u passed the EOS test. These two thermophysical properties are the most frequently reported: the database contains about ten times more pvT and internal energy data than any other thermophysical property. The relatively low confirmation rate of the pvT and internal energy data is a result from significant differences in the precision among different publications that the EOS test used for the detection of the outliers.

Confirmation rates of 94 - 96% were obtained for data for the isochoric heat capacity c_v , isobaric heat capacity c_p , speed of sound w , thermal pressure coefficient γ , Joule-Thomson coefficient μ_{JT} , and Grüneisen coefficient Γ – which are higher order temperature and density derivatives of the Helmholtz energy. The confirmation rate for the thermal expansion coefficient α and isothermal compressibility β was 92 - 93%. A confirmation rate of 89% was found for the chemical potential μ , which is particularly challenging to determine by molecular simulation. The lowest confirmation rate of 72% was found for the Helmholtz energy $\tilde{a}$, which is mainly due to particularly low confirmation rates for the results from some publications. Details are given in the supplementary material.

Also, the numerical values of all data points and the corresponding result of the EOS test, i.e. whether a data point is confirmed or identified as an outlier with $P_{\max} = 4$, are provided in the supplementary material. Moreover, information on the dependence of the total percentage of confirmed data on the choice of the number for $P_{\max}$ is presented there.

Assessment of vapor-liquid equilibrium data

For the vapor-liquid equilibrium, both bulk and interfacial properties were considered: vapor pressure p^s , saturated liquid and vapor density ρ' and ρ'' , and enthalpy of vaporization Δh_v were considered for the bulk properties and the interfacial tension γ as interfacial property, cf. Table 1.

Bulk VLE data

In contrast to the test on the homogeneous state points, which was assessed for each data point individually entire VLE bulk property data sets from a given publication were assessed and either confirmed or discarded. Furthermore, the EOS test for homogeneous data is designed to identify gross outliers, whereas the assessment of the VLE data additionally aims at determining the most precise data and to give an estimation of that precision. The estimated *precision* indicates the magnitude that a given data set scatters around the presumed *true value*. The true value, i.e. exact and correct, of a given property is approximated here by the mean of the most precise and accurate data sets.

VLE bulk data of the Lennard-Jones fluid were assessed by several independent consistency tests. Two of them were taken from the literature: the compressibility factor test proposed by Nezbeda^{213,214} and the Clausius-Clapeyron test.⁷¹ Furthermore, as a third test, outliers are determined from a direct comparison of the data points as described below in more detail. For brevity, this test is referred to as *deviation* test in the following. Data sets were discarded, if the majority of data points within a data set violate one or more consistency tests. For the following discussion, the *vicinity to the critical point* of the VLE region is defined to be above 95% of the critical temperature. Data points in that region were not included in the consistency tests.

To facilitate the assessment, empirical correlation functions for the vapor pressure p^s , saturated

liquid and vapor density ρ' and ρ'' , and enthalpy of vaporization Δh_v were used:

$$\ln p^s = n_1 T + \frac{n_2}{T} + \frac{n_3}{T^{n_4}}, \quad (6)$$

$$\left(\frac{\rho'}{\rho_c}\right) = 1 + \sum_{i=1}^5 n_i \left(1 - \frac{T}{T_c}\right)^{t_i}, \quad (7)$$

$$\ln \left(\frac{\rho''}{\rho_c}\right) = \sum_{i=1}^5 n_i \left(1 - \frac{T}{T_c}\right)^{t_i}, \quad (8)$$

$$\Delta h_v = \sum_{i=1}^4 n_i (T_c - T)^{t_i}. \quad (9)$$

In an initial step, the VLE data set from this work was used for the parametrization of Eqs. (6) - (9), as it is the most extensive data set. The absolute average deviation from the correlations (6) - (9) and the respective VLE data from this work is: 0.3% for the vapor pressure, 0.06% for the saturated liquid density, 0.5% for the saturated vapor density, and 0.3% for the enthalpy of vaporization. The numerical values of the parameters n_i and t_i are listed in Table 3. The critical values used in Eqs. (6) - (9) are $T_c = 1.321$ and $\rho_c = 0.316$. They are called *base correlations* in the following. It will be shown below, that these correlations match the best available guess for the considered properties within their estimated precision.

In the test proposed by *Nezbeda*,^{213,214} the compressibility factor of the saturated vapor phase $Z'' = p^s / \rho'' T$ is considered. Starting at low temperatures close to the triple point, Z'' must be close to unity. With increasing temperature, Z'' must decrease monotonically until the compressibility factor at the critical point is reached.^{213,214}

This simple criteria can be applied for sorting out outliers: $Z'' > 1$ is not acceptable and the slope dZ''/dT must be negative. More generally, the slope dZ''/dT is sensitive and useful for discriminating data points that deviate from the general trend. Furthermore, the data points were compared to the results for Z'' that was obtained from the base correlations. Data points for which the deviation in Z'' from that correlation is above 1.25% were considered as outliers. The number 1.25% was chosen on the basis of an examination of the scattering of the entire available data. Data sets of which more than 50% of the data points violate at least one of these criteria were discarded. The other data sets are considered as confirmed by the compressibility factor test.

Figure. 3 shows the data sets that were confirmed by the compressibility factor test. These data are in good mutual agreement and in agreement with the base correlation computed from Eqs. (6) and (8). Excellent mutual agreement is found for the data sets from *Agrawal and Kofke*,¹⁰⁶ *Errington*,¹²⁵ *Errington*,^{126,127} *Janeček et al.*,^{135,136} *Lotfi et al.*,⁷¹ *Mick et al.*,²³ *Okumura and Yonezawa*,^{121,122} and from the present work. Taking these data as the reference, and their scattering as a measure for the precision, with which Z'' is known, that precision is estimated to be approximately $\pm 0.5\%$ excluding the vicinity of the critical point. Furthermore, the data sets from *Hansen and Verlet*,²⁰ *Janeček*,¹³¹ *Kofke*,¹⁰⁴ *Martínez-Ruiz et al.*,¹³⁴ *Okumura and Yonezawa*,^{118,119} *Stephan and Hasse*,¹³⁸ *Stoll et al.*,¹²⁸ and *Werth et al.*¹³⁷ also agree well with the data mentioned above, but scatter more. That data were confirmed by the compressibility factor test. The larger scatter of the data of Refs.^{134,137,138} is probably due to the fact that these data were sampled with the direct simulation method. The data sets from Refs.^{118,119,125–127} each contain a single data point that is a clear outlier. These data points are explicitly pointed out in the supplementary information. However, apart from the outlier, these data sets are considered as confirmed by the compressibility factor test. Data sets from Refs.^{58,60,100,101,103,107,108,110,113–115,117,124,129,130} were discarded by the compressibility factor test. Details are given in the supplementary material.

The second consistency test that was employed for the VLE bulk data is based on the Clausius-Clapeyron equation

$$\frac{d \ln p^s}{d(1/T)} = - \frac{T \Delta h_v}{p^s (1/\rho'' - 1/\rho')} . \quad (10)$$

The left hand side (LHS) and right hand side (RHS) of Eq. (10) is considered individually for each data set and compared. The equality of the LHS and RHS within the corresponding statistical uncertainties indicates the thermodynamic consistency by the Clausius-Clapeyron equation. The RHS of Eq. (10) is therefor computed directly from the numerical values of the computer experiments. The statistical uncertainties of the RHS values are determined using the error propagation law. The LHS of Eq. (10) is calculated with an analytical function for the vapor pressure curve. The Clausius-Clapeyron test is applied here in two ways (Test A and Test B). In Test A, the LHS and RHS of a given data set are directly compared. This can only be done in a meaningful way

for those data sets, that enable the parametrization of a correlation of $p^s(T)$ for the LHS in a sufficiently accurate manner. In Test B, the RHS of remaining data sets are compared with the LHS correlations established in Test A. Data points violate the Clausius-Clapeyron test in Test A, if the computed RHS of a given data point does not agree within the statistical uncertainty with the corresponding LHS-value. In the Test B, data points were considered as outliers, if they deviate 2% or more from the two correlations established in Test A. As for the compressibility factor test, data sets for which more than half of the data points violate the Clausius-Clapeyron test were discarded. The remaining data sets were considered as confirmed by the Clausius-Clapeyron test.

The data sets from *Lotfi et al.*⁷¹ and this work were employed in Test A. Correlations for $p^s(T)$ obtained from the other data sets were not found to be sufficiently accurate for carrying out a meaningful test of type A. For the data from this work, the base correlation for $p^s(T)$ from Eq. (6) was used for the comparison. The statistical uncertainty of the LHS was estimated from the error propagation law. *Lotfi et al.*⁷¹ published a correlation of their own p^s -results that was used here for computing the LHS of Eq. (10) for the comparison of the corresponding RHS-values.

Figure. 4 shows the VLE data sets that were confirmed by both the Clausius-Clapeyron test and the compressibility factor test. In the plot, results for the RHS of Eq. (10) that were obtained from the simulation data and are shown as symbols are compared with results for the LHS that were obtained from correlations of the vapor pressure curve and are shown as lines. Two such correlations are shown: one obtained from the data from the present work and one obtained by *Lotfi et al.* from their data.⁷¹ *Lotfi et al.*⁷¹ compared their results for the Lennard-Jones fluid with results for Ne, Ar, and CH₄ and found very good qualitative agreement, i.e. a parabolic shape of $d(\ln p^s)/d(T^{-1})$.

Figure. 4 shows that the two correlations of the LHS of Eq. (10) match well. The differences are far below the uncertainties of the data points for the RHS of Eq. (10). The data from the present work and from *Lotfi et al.*⁷¹ agree well with the correlations. There is one outlier in the data set from the present work. (It was not removed from the data set to ensure a fair comparison with the literature data, for which almost every data set was found to have at least one outlier). The LHS and RHS of Eq. (10) agree within the statistical uncertainties for all but this state point,

which is likely the result of an overly optimistic error estimation. However, the data of *Lotfi et al.*⁷¹ and this work agree very well throughout, but the data of *Lotfi et al.*⁷¹ show a more pronounced scatter and larger error bars than the data from this work.

The RHS data of *Janeček et al.*,^{135,136} *Stoll et al.*,¹²⁸ *Mick et al.*,²³ and *Agrawal and Kofke*¹⁰⁶ are also in excellent agreement with the base correlation of the LHS of Eq. (10). The agreement is also very good for the data sets of *Hansen and Verlet*,²⁰ *Janeček*,¹³¹ *Kofke*,¹⁰⁴ and *Werth et al.*¹³⁷ but their RHS data exhibit considerable scatter, as does the data set of *Lotfi et al.*⁷¹

The data sets from Refs.^{58,60,100,101,103,108,110,124,130} were discarded by the Clausius-Clapeyron test. Details are given in the supplementary material. The results from the Clausius-Clapeyron test reinforce the findings from the compressibility factor test.

As a third assessment, the deviation plots of each VLE bulk property (p^s , ρ' , ρ'' , and Δh_v) from the base correlations were used as follows: First, the data sets with the best mutual agreement were identified, that were also confirmed by the previous two tests. From these data sets, a confidence interval $\pm X\%$ was estimated for each VLE property ($X = p^s$, ρ' , ρ'' , and Δh_v) individually, that is a measure for the precision of the available information. A data point was considered as an outlier, if its relative deviation to the corresponding base correlation exceeds 2.5 times the number of X of one of the four VLE properties. Again, data sets for which more than half of the data points of a given VLE property violate the criteria were discarded. The remaining data sets were considered as confirmed.

Figure. 5 shows the relative deviation of the VLE data (vapor pressure p^s , enthalpy of vaporization Δh_v , and the saturated densities ρ' and ρ'') from the base correlations. Excellent mutual agreement (and also agreement with the base correlations) was found for the data sets from *Errington*,^{126,127} *Errington*,¹²⁵ *Janeček et al.*,^{135,136} *Lotfi et al.*,⁷¹ *Mick et al.*,²³ *Okumura and Yonezawa*,^{121,122} and the data set from the present work. These seven data sets were also confirmed by the other two tests and comprise a total of 86 state points. Interestingly, the precision, i.e. the scatter, of each of the seven best data sets (Refs.^{23,71,121,122,125-127,135,136} and this work) is very similar. Only the saturated vapor density and vapor pressure data of *Errington*^{126,127} were found to be significantly more precise than the other data sets. However, the scatter of the saturated

liquid density data of *Errington*^{126,127} is significantly larger than the scatter of the other selected best data sets (Refs.^{23,71,121,122,125–127,135,136} and this work).

The mutual agreement of these seven selected best bulk VLE data sets is approximately $\pm 1\%$ for the vapor pressure, $\pm 0.2\%$ for the saturated liquid density, $\pm 1\%$ for the saturated vapor density, and $\pm 0.75\%$ for the enthalpy of vaporization – excluding the region close to the critical point. Five of these seven best data sets contain a single or two clear outliers, which are listed in the supplementary material.

The mutual agreement of the seven selected best data sets (Refs.^{23,71,121,122,125–127,135,136} and the data set from the present work) significantly decreases in the region close to the critical point, i.e. $T \gtrsim 1.25$. The mutual agreement in the vicinity of the critical point is better for the vapor pressure and the saturated liquid density than for the enthalpy of vaporization and the saturated vapor density.

The following data sets agree well but scatter strongly (however, within the confidence interval and are thereby considered as confirmed by the deviation test): *Betancourt-Cárdenas et al.*,¹³⁰ *Chen et al.*,²⁴ *Hansen and Verlet*,²⁰ *Martínez-Ruiz et al.*,¹³⁴ *Okumura and Yonezawa*,^{118,119} *Stoll et al.*,¹²⁸ *Stephan and Hasse*,¹³⁸ and *Werth et al.*¹³⁷ The data sets from Refs.^{58,60,98–115,117,123,124,129,131–133,135,197} were discarded because more than 50% of the respective data points exceed the confidence interval of one of the bulk VLE properties.

The seven data sets from Refs.^{23,71,121,122,125–127,135,136} and from the present work were confirmed by all applicable tests and were found to be in excellent mutual agreement and are therefore recommended as a reference. The data sets from Refs.^{20,118,119,128,134,137,138} were also confirmed by all applicable tests, but exhibit a significantly larger scattering compared to these seven most precise data sets. The data sets from Refs.^{24,98,102,105–107,111,112,116,120,123,132} were discarded by a single consistency test, the data sets from Refs.^{104,113–115,117,129} were discarded by two tests and the the data sets from Refs.^{60,100,101,103,124,130} by three tests. Note that, for most data sets only a selection of tests could be applied due to missing properties that were not reported in these publications. For all but one VLE data set, the results of the three applicable tests reinforce each other. The only exception is the data set of *Agrawal and Kofke*:¹⁰⁶ the data set was confirmed

by the compressibility factor test and the Clausius-Clapeyron test, but discarded by the deviation test.

For many of the investigated data sets, the data points do not agree with the seven selected best data sets within the reported statistical uncertainties. Therefore, systematic simulation errors²⁹ are hold responsible for these deviations.

Fitting the combined data of the seven best data sets (Refs. ^{23,71,121,122,125–127,135,136} and the data set from the present work) with the correlations presented in Eqs. (6) - (9) yields a fit that is essentially the same as the one presented in Table 3. For all studied properties, the differences between both fits are well below the differences among the data from the seven data sets. Hence, we simply recommend using the correlations from Table 3.

Interfacial VLE data

As for the bulk VLE properties, the computer experiment data for the surface tension were assessed with respect to their mutual agreement. To facilitate this assessment, a base correlation function was also used for the temperature dependence of the surface tension

$$\gamma = A \left(1 - \frac{T}{T_c} \right)^b, \quad (11)$$

where A and b are parameters. $T_c = 1.321$ was specified for the critical temperature in Eq. (11). In an initial step, the surface tension data from Refs.^{138,142} were used for the parametrization of Eq. (11). The obtained values for the parameters are: $A = 3.03327$ and $b = 1.27748$. The absolute average deviation between correlation (11) and the data used for the parametrization is 1.2%. It will be shown below, that Eq. (11) matches the best available guess for the surface tension within its estimated precision.

The surface tension data was also assessed with the deviation test: First, the data sets with the best mutual agreement were identified. From these data sets, a confidence interval $\pm X\%$ was estimated as measure for the precision that the surface tension is known. For the assessment, a data point was considered as an outlier, if its relative deviation to the base correlation (11) exceeds 2.5 times the number of $\pm X\%$. Again, data sets for which more than half of the data points violate the criterion were discarded. The remaining data sets were considered as confirmed.

Figure 6 shows the surface tension data as a function of the temperature. Overall, the agreement is significantly poorer than for the bulk VLE properties. The best mutual agreement is found for the data sets of *Chen et al.*²⁴, *Janeček et al.*¹³⁵, *Janeček*¹³¹, *Werth et al.*¹⁴², *Werth et al.*¹³⁷, *Lee et al.*⁹⁸, *Martinez-Ruiz et al.*¹³⁴, *Mecke et al.*¹⁴⁰, *Nijmeijer et al.*¹⁰², *Stephan and Hasse*¹³⁸, *Shen et al.*¹⁴¹. These data sets agree approximately within $\pm 4\%$ – excluding the region close to the critical point.

The following data sets agree well, i.e. are considered as confirmed, but exhibit a more pronounced scatter or systematic deviations from the afore mentioned data sets: *Trokhymchuk and Alejandre*¹¹⁴, *Potoff and Panagiotopoulos*¹¹⁶, *Miyazaki et al.*¹³⁹, *Galliero et al.*¹³², *Errington*¹²⁵,

Baidakov et al.,¹²⁹ *Baidakov et al.*¹²³. The data sets of Refs.^{99,105,111,112,115,117} were discarded since more than 50% of the respective data points exceed the confidence interval. Details are given in the supplementary material.

Conclusions

This work reviews and assesses thermophysical property data for the Lennard-Jones fluid. Literature data (approximately 35,000 data points) were digitalized, evaluated, and provided in the supplementary material as a consistent database. For the homogeneous state points, approximately 10% of the data were identified to be gross outliers by an EOS test. The lack of information on the statistical uncertainties in some studies is unfortunate.

Three independent consistency tests were employed for the evaluation of the VLE data: The compressibility factor test considers only the vapor pressure and the saturated vapor density, whereas the Clausius-Clapeyron test also considers the saturated liquid density and the enthalpy of vaporization. The third test evaluates the mutual agreement of data sets for each VLE property individually. The VLE data sets of *Errington*,^{126,127} *Errington*,¹²⁵ *Janeček et al.*,^{135,136} *Lotfi et al.*,⁷¹ *Mick et al.*,²³ *Okumura and Yonezawa*,^{121,122} and this work were confirmed by all tests and found to be the most precise. The precision with which the VLE of the LJ fluid is known is thereby estimated to be $\pm 1\%$ for the vapor pressure, $\pm 0.2\%$ for the saturated liquid density, $\pm 1\%$ for the saturated vapor density, and $\pm 0.75\%$ for the enthalpy of vaporization – excluding the region close to the critical point. Since almost every VLE data set – even the most precise – contain individual outliers, we recommend to use the combination of the above listed data sets as reference. Furthermore, the data sets of *Hansen and Verlet*,²⁰ *Martínez-Ruiz et al.*,¹³⁴ *Okumura and Yonezawa*,^{118,119} *Stephan and Hasse*,¹³⁸ *Stoll et al.*,¹²⁸ and *Werth et al.*¹³⁷ were found to be accurate, but not as precise. The precision of the surface tension is estimated to be $\pm 4\%$, i.e. significantly larger than the VLE bulk properties.

The EOS test presented here can be adopted easily to other applications in thermodynamics. A test based on the ideas described here could for example be used for testing VLE data of a given

mixture based on models of the Gibbs excess energy G^E .

In a follow-up work we will use the consolidated data base that is presented here to investigate the performance of equations of state for the Lennard-Jones fluid. Future work should focus on the region in the direct vicinity of the critical point, where the available VLE data and accordingly the location of the critical point agree less well.

Among the molecular model fluids, the Lennard-Jones fluid has a similar role as water has among real fluids: it is the fluid that has been studied most extensively and most thoroughly. The present work summarizes the present state of these studies. The accuracy with which the properties of the LJ fluid are known is assessed here. It can be assumed that it is a lower limit to the accuracy with which properties of fluids can presently be determined with molecular simulations. That accuracy often exceeds the statistical uncertainties that are reported for individual data points.

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Appendix

Supporting Information

The supplementary material contains the database as an *.xls* spreadsheet of all discussed thermo-physical property data in this work: Each data point is listed with the reference of the original publication, temperature, density, the property itself, eventually the reported statistical uncertainty, and the result of the EOS test. All data are given in standard Lennard-Jones reduced units. In addition, detailed remarks on individual data sets report on conversion pitfalls, likely misprints, etc. The supplementary material also contains the results of all three VLE tests for the discarded VLE data sets. Also, details on the EOS test are given in the supplementary material. The supporting material is available free of charge via the Internet at [<http://pubs.acs.org>].

Molecular simulations in this work

Homogeneous state point simulations

Simulations in the homogeneous state were carried out in the NVT ensemble using Monte Carlo (MC) sampling with an acceptance ratio of 0.5. The simulations contained 1372 particles. The initial conditions were generated as a fcc lattice and subsequently equilibrated for $2.5 \cdot 10^5$ cycles and then sampled for $3 \cdot 10^6$ cycles, where one cycle corresponds to 1372 attempts for a translational move. The cut-off radius was half the edge length of a cubic simulation volume. Statistical uncertainties were estimated by the block averaging method of *Flyvbjerg and Petersen*.³⁴ Numerical values of the simulation results are reported in the supplementary material. Simulations were carried out with the simulation program *ms2*.¹⁷⁷

VLE simulations

The vapor-liquid equilibrium of the Lennard-Jones fluid was obtained with the Grand Equilibrium method of *Vrabec and Hasse*.¹⁷⁹ Two simulations were subsequently carried out to obtain the VLE properties at a given temperature: First, the chemical potential and the molar volume was sampled in a NpT MD liquid phase simulation. Then, the vapor phase was simulated in a

pseudo- μVT ensemble using a MC algorithm. The pressure of the liquid state, was chosen to be approximately 7% above the vapor pressure as estimated by the Lennard-Jones EOS from Ref.²⁰⁷ 2048 particles are initialized on a fcc lattice for the NpT simulations and then equilibrated for $3 \cdot 10^5$ time steps. The time step was set to $\Delta\tau = 0.001$. Velocity scaling was used to specify the temperature. The chemical potential was sampled with Widom’s test particle method,¹⁷⁶ inserting 2500 test particles every time step. The chemical potential and its pressure derivative, i.e. the molar volume, were then used during the second simulation to obtain the saturated vapor phase properties. The pseudo- μVT simulation was carried out such that the specified chemical potential was not constant but a function of the actual pressure of the vapor phase. The vapor phase simulations were started with 1000 particles using MC sampling with an acceptance ratio of 0.5. The system was equilibrated for 10^5 time steps and production was carried out for $5 \cdot 10^5$ time steps. The initial vapor density was also estimated with the Lennard-Jones EOS from Ref.²⁰⁷ As for the homogeneous state point simulations, the cut-off radius was half the edge length of a cubic simulation volume and the statistical uncertainty was estimated by the block averaging method.³⁴ The vapor-liquid equilibrium was sampled at 31 temperatures between $T = 0.69$ and 1.28. Numerical values of the obtained vapor pressure, saturated densities, and enthalpy of vaporization are reported in the supplementary material.

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Table 2: Critical point data for the Lennard-Jones fluid obtained by computer experiment reported in the literature. The numbers in parentheses indicate the reported uncertainties of the last decimal digits.

publication	year	T_c	ρ_c	p_c
<i>Barker et al.</i> ¹⁶⁷	1966	1.291	0.547	0.249
<i>Verlet & Levesque</i> ⁴⁶	1967	1.26	0.316	0.118
<i>Verlet</i> ¹⁸	1967	1.32	0.31	0.12276
<i>Kim et al.</i> ¹⁹⁴	1969	1.35	0.3	0.14
		1.28	0.29	0.13
<i>Levesque & Verlet</i> ⁴⁸	1969	1.36(3)	0.36(3)	0.151776
<i>Sung & Chandler</i> ²⁰⁰	1974	1.348	0.349	0.148
<i>Adams</i> ⁶⁰	1979	1.30(2)	0.33(3)	0.13(2)
<i>Panagiotopoulos</i> ¹⁰⁰	1987	<1.35	0.31(2)	
<i>Meroni et al.</i> ²¹⁵	1990	1.3317	0.332	
<i>Smit</i> ¹⁹⁸	1992	1.316(6)	0.304(6)	
<i>Lotfi et al.</i> ⁷¹	1992	1.31	0.314	
<i>Kofke</i> ¹⁰⁴	1993	1.321(4)	0.306(1)	
		1.324(12)	0.305(2)	
<i>Valleau</i> ^{78,216}	1994	1.328(3)		
<i>Hunter & Reinhardt</i> ¹⁰⁷	1995	1.32		
<i>Mecke et al.</i> ⁷⁸	1996	1.328(3)	0.3107	
<i>Mecke et al.</i> ¹⁰⁹	1997	1.32521		
<i>Caillol</i> ¹⁹¹	1998	1.326(2)	0.316(2)	0.1472(3)
<i>Martin & Siepmann</i> ¹¹³	1998	1.294(9)	0.311(6)	0.1144
		1.311(9)		
<i>Potoff & Panagiotopoulos</i> ¹⁹⁷	1998	1.3120(7)	0.316(1)	0.1279(6)
<i>Potoff & Panagiotopoulos</i> ¹¹⁶	2000	1.311(2)		
		1.3120(7)	0.316(2)	
<i>Okumura & Yonezawa</i> ¹¹⁹	2000	1.313(2)	0.304(2)	0.125(1)
<i>Shi & Johnson</i> ¹²⁰	2001	1.3241(9)	0.3165(7)	
		1.3145(2)	0.316(1)	
<i>Dunikov et al.</i> ¹⁹²	2001	1.350(5)	0.310(5)	0.126(8)
<i>Okumura & Yonezawa</i> ¹²²	2001	1.3207(4)	0.316(1)	0.1288(5)
<i>Pérez-Pellitero et al.</i> ²¹⁷	2006	1.3123(6)	0.3174(6)	
		1.3126(6)	0.3174(6)	
		1.313(1)	0.317(1)	
<i>Betancourt-Cárdenas et al.</i> ¹³⁰	2008	1.302(6)	0.311(2)	0.12(3)
<i>Kulinski</i> ²⁰¹	2013	1.333	0.325	0.122
<i>Heyes & Woodcock</i> ²⁰³	2013	1.3365(5)		0.1405(2)
<i>Heyes</i> ²⁰²	2015	1.316(1)	0.309(6)	
<i>Lishchuk & Fischer</i> ²⁰⁵	2018	1.31766		

Table 3: Parameters of correlations (6) - (9) for the vapor pressure p^s , saturated liquid density ρ' , saturated vapor density ρ'' , and enthalpy of vaporization Δh_v .

	p^s Eq. (6)	ρ' Eq. (7)		ρ'' Eq. (8)		Δh_v Eq. (9)	
	n_i	n_i	t_i	n_i	t_i	n_i	t_i
1	1.156551	1.341700	0.327140	-8.135822	1.651685	6.456728	0.411342
2	-4.431519	2.075332	0.958759	-102.919110	43.469214	2.700099	0.460416
3	-0.423028	-2.123475	1.645654	-3.037979	0.462877	-3.073573	2.350953
4	2.638743	0.328998	17.000001	-44.381841	11.500462	3.149052	5.017010
5		1.386131	2.400858	-34.55892948	5.394370

Figure 1: Overview of 963 state points that were studied with the *Lustig* formalism^{84,175} by different authors. Circles: *Thol et al.*;⁹⁰ triangles: *Köster et al.*;^{91,92} squares: *this work*. Data for the Helmholtz energy and its density and inverse temperature derivatives up to second order are available for the stable state points. For the metastable state points, the derivatives are available up to first order.

Figure 2: Statistics of the EOS test for homogeneous state points for different thermophysical properties: pressure p , internal energy u , isochoric heat capacity c_v , thermal pressure coefficient γ , speed of sound w , isothermal compressibility β , isobaric heat capacity c_p , Joule-Thomson coefficient μ_{JT} , Helmholtz energy divided by temperature $\tilde{a} = a/T$, chemical potential μ , thermal expansion coefficient α , and Grüneisen coefficient Γ . The left ordinate indicates the percentage of confirmed data and the right coordinate the total number of data points available for each thermophysical property.

Figure 3: Compressibility factor test for the vapor-liquid equilibrium data of the Lennard-Jones fluid: saturated vapor phase compressibility factor Z'' as function of the temperature T (top) and the relative deviation of Z'' from the base correlations (6) and (8) (bottom). The black filled star indicates the compressibility factor at the critical point according the base correlation. Error bars are omitted in the bottom plot to avoid visual clutter.

Figure 4: Clausius-Clapeyron test according Eq. (10). Symbols indicate the RHS and the lines the LHS of Eq. (10). The orange shaded area indicates the statistical uncertainty of $\pm 2\%$ computed for the LHS of Eq. (6). The purple line is Eq. (22) from Ref. ⁷¹

Figure 5: Relative deviations of the vapor-liquid equilibrium data for the vapor pressure p^s , saturated liquid density ρ' , saturated vapor density ρ'' , and enthalpy of vaporization Δh_v from correlations (6) - (9) as a function of the temperature T . Error bars were omitted to avoid visual clutter. For clarity, numerical values for out-of-range data points with negative deviation for the vapor pressure, the enthalpy of vaporization, and the saturated vapor density ρ'' are omitted in the respective plot; they lie in the range of $\delta p^s = -0.05.. -0.16$, $\delta \Delta h_v = -0.15.. 0.45$, and $\delta \rho'' = -0.08.. -0.2$.

Figure 6: Surface tension of the LJ fluid as a function of the temperature (top) and the corresponding relative deviation plot (bottom). The black line (top) and baseline (bottom) indicates Eq. (11). Symbols indicate computer experiment data. For clarity, numerical values for out-of-range data points in the vicinity of the critical temperature are omitted in the deviation plot.

TOC graphic

SUPPORTING INFORMATION

Thermophysical Properties of the Lennard-Jones Fluid: Database and Data Assessment

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This supplementary material of the publication *Thermophysical Properties of the Lennard-Jones Fluid: Database and Data Assessment* contains the following:

1. The full database of thermophysical property data of the Lennard-Jones fluid discussed in this work is appended as an `.xls`-spreadsheet, including an indication for each bulk data point whether it was identified as an outlier by the EOS test.
2. Applied conversions for each property in a given publication included in the database to indicate how the values in the database were obtained from those printed in the publication. Also, remarks on individual publications are given regarding possible misprints, conversion pitfalls, outliers etc.
3. Additional information on the EOS test for the assessment of the homogeneous state points.
4. Details on the computation of thermophysical properties with the *Lustig* formalism.
5. Additional information on the compressibility factor test, the Clausius-Clapeyron test, and the deviation test of the VLE bulk data, cf. Fig. S2, S3, and S4, respectively. All available VLE data (both confirmed and discarded) are shown and discussed in detail.
6. Additional information on the surface tension data, cf. Fig. S5.
7. List of clear outliers (eight data point) from the seven best VLE data sets (Refs. ^{23,71,121,122,125–127,135,136} and this work), cf. Table S4.
8. Numerical values of the VLE data set from this work, cf. Table S3.

Database: **.xls-spreadsheet**

The entire database of thermophysical properties considered in this work is provided as an *.xls* spreadsheet in the electronic supplementary material.

List of applied conversions and remarks

For all considered studies in the database, the applied conversions from the numerical values printed in a publication to obtain the numerical values given in the database are given in Table S1. Data are consistently reported as residual properties (with respect to the ideal gas) and in the standard 'Lennard-Jones' units.

In Table S1, the $\hat{}$ indicates the obtained value after the conversion as given in the database. Non-hat symbols were adopted as it stands in the corresponding publication. The asterisk indicates 'Lennard-Jones' units. Non-asterisk values indicate other units systems as applied in a given publication. The tilde $\tilde{a}$ indicates the Helmholtz energy per particle a divided by the temperature, i.e. $\tilde{a} = \frac{a}{T}$. The [Acronym] indicates the string used in the electronic database to uniquely identify a certain publication. The *state point* is the given temperature and density and their respective conversions in case of homogeneous data; and only the temperature in case of VLE data. The column *property* lists the given thermophysical properties and their respective conversions of a given publication.

In cases where multiple results were reported for a given property and state point in a given publication (e.g. simulations performed with varying cut-off, particle number, sampling length etc.), only the numeric value with the largest particle number etc. were included in the database.

For the conversions given in Table S1, the constants $N_{\text{AV}} = 6.02214076 \cdot 10^{23} \text{ mol}^{-1}$ and $k_{\text{B}} = 1.380649 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$ were applied.

For the studies that report data based on the *Lustig* formalism, the Helmholtz energy and the respective derivatives are listed in Table S1. According the thermodynamic relations (see below), other properties were computed from that data and also included in the database.

Table S1: List of conversions from the publications from the literature to the consistent units system (Lennard-Jones units & residual properties with respect to the ideal gas).

Authors & [Acronym]	state point T, ρ	thermophysical properties
<i>Wood and Parker</i> ¹⁵ [WOODPAR]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \left(\frac{v}{v^*}\right)^{-1}$	$\hat{c}_v^* = \frac{3}{2} + C'_v/R$ $\hat{u}_{\text{res}}^* = \hat{T}^* \cdot \frac{E'}{RT}$ $\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot \frac{pv}{RT}$
<i>Hansen</i> ⁵⁰ [HANSEN]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot \left(\frac{\beta p}{\rho}\right)^{\text{ex}}$ $\hat{u}_{\text{res}}^* = \hat{T}^* \cdot (\beta U)^{\text{ex}}$
<i>Levesque and Verlet</i> ⁴⁸ [LEVEVER]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{a}_{\text{res},00}^* = \frac{F_1}{N \cdot k_B \cdot T}$ $\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot Z$ $\hat{u}_{\text{res}}^* = u_i$
<i>Thol et al.</i> ⁹⁰ [THOL]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{a}_{\text{res},00}^* = A_{\text{r},00}$ $\hat{a}_{\text{res},01}^* = A_{\text{r},01}$ $\hat{a}_{\text{res},10}^* = A_{\text{r},10}$ $\hat{a}_{\text{res},11}^* = A_{\text{r},11}$ $\hat{a}_{\text{res},02}^* = A_{\text{r},02}$ $\hat{a}_{\text{res},20}^* = A_{\text{r},20}$
The numeric values provided in the supplementary material in Ref. ⁹⁰ contains some typos. Those are corrected here.		
<i>Verlet</i> ¹⁸ [VERLET]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot \left(\frac{\beta p}{\rho}\right)$ $\hat{u}_{\text{res}}^* = U^i$
<i>Hansen and Verlet</i> ²⁰ [HANSVER]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot \frac{\beta p}{\rho}$ $\hat{a}_{\text{res},00}^* = \frac{F_1}{T^*} - \ln(\hat{\rho}^*) + 1$ $\hat{p}_v^* = p_v^*$ $\Delta \hat{h}_v^* = \mathcal{L}$
<i>McDonald and Singer</i> ⁵⁴	$\hat{T}^* = T^*$	$\hat{p}^* = p^*$

Continued on next page

Authors & [Acronym]	state point T, ρ	thermophysical properties
[MCDSING]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = u_r^*$
<i>Weeks et al.</i> ¹⁶⁰	$\hat{T}^* = T^*$	$\hat{a}_{\text{res},00}^* = -\frac{\beta \Delta A}{N}$
[WEEKCHA1]	$\hat{\rho}^* = \rho^*$	
<i>Adams</i> ⁵⁷	$\hat{T}^* = T^*$	$\hat{\alpha}^* = \alpha^*$
[ADAMS]	$\hat{\rho}^* = \rho^*$	$\hat{\beta}^* = \beta^*$
		$\hat{\gamma}^* = \gamma^*$
		$\hat{p}^* = p^*$
		$\hat{\mu}_{\text{res}}^* = \mu_r^*$
		$\hat{u}_{\text{res}}^* = -u_r^*$
		$\hat{c}_v^* = \frac{3}{2} + c_{v,r}^*$
<i>Ree</i> ⁶²	$\hat{T}^* = T^*$	$\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot \frac{P}{\rho k T}$
[REE]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = \frac{U^e}{kT} \cdot \hat{T}^*$
<i>Panagiotopoulos</i> ¹⁰⁰	$\hat{T}^* = T^*$	$\hat{p}_v^* = P^*$
[PANAGIO]	$\hat{\rho}^* = \rho^*$	$\Delta \hat{h}_v^* = (E_v^* + \frac{\hat{p}_v^*}{\hat{\rho}_v^*} - (E_l^* + \frac{\hat{p}_l^*}{\hat{\rho}_l^*}))$
<i>Shaw</i> ⁶⁶	$\hat{T}^* = T^*$	$\hat{p}^* = p^*$
[SHAW]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = u_r^*$
<i>Panagiotopoulos et al.</i> ¹⁰¹	$\hat{T}^* = T^*$	$\hat{p}_v^* = P$
[PANQUIR]	$\hat{\rho}^* = \rho^*$	$\Delta \hat{h}_v^* = (E^G + \frac{p^G}{\rho^G} - (E^L + \frac{p^L}{\rho^L}))$
<i>Smit and Frenkel</i> ¹⁰³	$\hat{T}^* = T^*$	$\Delta \hat{h}_v^* = (E_v^* + \frac{\hat{p}_v^*}{\hat{\rho}_v^*} - (E_l^* + \frac{\hat{p}_l^*}{\hat{\rho}_l^*}))$
[SMITFRE]	$\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = p_v^*$
<i>Meier</i> ^{80,155}	$\hat{T}^* = T^*$	$\hat{c}_v^* = c_v^*$
[MEIER]	$\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$
		$\hat{u}_{\text{res}}^* = u_r^*$
		$\hat{w}^* = w_o'^*$
		$\hat{\gamma}^* = \gamma^*$

Continued on next page

Authors & [Acronym]	state point T, ρ	thermophysical properties
Two typos in Ref. ⁸⁰ are known ¹⁵⁵ that were corrected in the database: A '0' is missing for the numbers of the reported pressure of two state points ($\hat{\rho}^* = 0.01$ & $\hat{T}^* = 0.900501$ and $\hat{\rho}^* = 0.005$ & $\hat{T}^* = 0.900929$).		
<i>Johnson et al.</i> ⁷³ [JOHNSON]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$ $\hat{u}_{\text{res}}^* = u_r^*$
<i>Hunter and Reinhardt</i> ¹⁰⁷ [HUNTErr]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = p_v^*$
<i>McDonald and Singer</i> ⁴⁵ [MCDSIN1]	$\hat{T}^* = \frac{T \cdot k_B}{\varepsilon}$ $\hat{\rho}^* = \frac{10^{-24} \cdot \sigma^3 \cdot N_{\text{AV}}}{v}$	$\hat{p}^* = \frac{10^{-23} \cdot \sigma^3 \cdot p^*}{\varepsilon}$ $\hat{u}_{\text{res}}^* = -u_r^* \cdot \hat{T}^*$ $\hat{\alpha}^* = \frac{\alpha^* \cdot 10^{-3} \cdot \varepsilon}{k_B}$ $\hat{\beta}^* = \frac{\beta^* \cdot 10^{21} \cdot \varepsilon}{\sigma^3}$ $\hat{\gamma}^* = \frac{\gamma^* \cdot 10^{-24} \cdot \sigma^3}{k_B}$ $\hat{c}_v^* = \frac{3}{2} + c_{v,r}^*$ with $\frac{\varepsilon}{k_B} = 119.76 \text{ K}$, $\sigma = 3.405 \text{ \AA}$
<i>McDonald and Singer</i> ¹⁹ [MCDSIN2]	$\hat{T}^* = \frac{k_B(T+273.15 \text{ K})}{\varepsilon}$ $\hat{\rho}^* = \left(\frac{v}{v^*}\right)^{-1}$	$\hat{p}^* = Z \cdot \hat{\rho}^* \cdot \hat{T}^*$ $\hat{u}_{\text{res}}^* = -\hat{T}^* \cdot u_r^*$ $\hat{c}_v^* = \frac{3}{2} + c_{v,r}^*$ with $\frac{\varepsilon}{k_B} = 119.76 \text{ K}$, $\sigma = 3.405 \text{ \AA}$
<i>Barker et al.</i> ¹⁶⁷ [BARLEOP]	$\hat{T}^* = T^*$	$\hat{B} = \frac{2}{3}\pi \cdot B^*$ $\hat{C} = \left(\frac{2}{3}\pi\right)^2 \cdot C^*$
<i>McDonald and Singer</i> ⁴⁹ [MCDSIN3]	$\hat{T}^* = T \frac{k_B}{\varepsilon}$ $\hat{\rho}^* = \frac{10^{-24} \cdot \sigma^3 \cdot N_{\text{AV}}}{V}$	$\hat{p}^* = \frac{P \cdot 101.325 \cdot \sigma^3 \cdot 10^{-27}}{\varepsilon}$ $\hat{u}_{\text{res}}^* = \frac{-u \cdot 4.184}{N_{\text{AV}} \cdot \varepsilon}$ with $\frac{\varepsilon}{k_B} = 119.8 \text{ K}$, $\sigma = 3.405 \text{ \AA}$
<i>Adams</i> ⁶⁰ [ADAMS2]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{c}_v^* = \frac{3}{2} + c_{v,r}^*$ $\hat{\mu}^* = \tilde{\mu}'$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
		$\hat{p}^* = p^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$ $\hat{\beta}^* = \tilde{\beta}$ $\Delta \hat{h}_v^* = \Delta \tilde{h}$
<i>Sowers and Sandler</i> ⁷⁰ [SOWSAND]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = Z \cdot \hat{\rho}^* \cdot \hat{T}^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
<i>Shi and Johnson</i> ¹²⁰ [SHIJOHN]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	
<i>Morsali et al.</i> ⁸² [MORSALI]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{\beta}^* = \kappa_{\text{MD}}^*$ $\hat{\gamma}^* = \gamma_{\text{MD}}^*$ $\hat{p}^* = p^*$
<i>Kolafa and Nezbeda</i> ⁷⁶ [KOLNEZB]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
<i>Lotfi et al.</i> ⁷¹ [LOTVRAB]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{\beta}^* = \beta^*$ $\hat{p}^* = p^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$ $\Delta \hat{h}_v^* = h''^* - h'^*$ $\hat{\mu}_{\text{res}}^* = (\tilde{\mu} - \ln(\hat{\rho}^*)) \cdot \hat{T}^*$
<i>Miyano</i> ⁷⁵ [MIYANO]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = Z \cdot \hat{\rho}^* \cdot \hat{T}^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^* \cdot \hat{T}^*$
<i>Nicolas et al.</i> ⁶¹ [NICOLAS]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$ $\hat{B} = B \cdot \frac{2\pi}{3}$
<i>Saager and Fischer</i> ⁶⁹ [SAAGFI]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
<i>Kofke</i> ¹⁰⁴	$\hat{T}^* = T^*$	$\hat{p}_v^* = P$
[KOFKE]	$\hat{\rho}^* = \rho^*$	$\Delta \hat{h}_v^* = (u_1 - \frac{\hat{p}_1^*}{\hat{\rho}_1^*} + (-\hat{u}_v + \frac{\hat{p}_v^*}{\hat{\rho}_v^*}))$
<i>Adams</i> ⁵⁸	$\hat{T}^* = T^*$	$\hat{p}^* = p^*$
[ADAMS3]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
		$\hat{\mu}_{\text{res}}^* = \mu_{\text{r}}^*$
		$\Delta \hat{h}_v^* = \Delta h_v^*$
		$\hat{p}_v^* = p_v^*$
<i>Mecke et al.</i> ⁷⁸	$\hat{T}^* = T^*$	$\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
[MECK]	$\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$
<i>Potoff and Panagiotopoulos</i> ¹¹⁶	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[POTPAN2]	$\hat{\rho}^* = \rho^*$	
<i>Kolafa et al.</i> ⁷⁴	$\hat{T}^* = T^*$	$\hat{p}^* = p^*$
[KOLVOR]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
		$\hat{\mu}_{\text{res}}^* = \hat{T}^* \cdot \mu_{\text{r}}^*$
<i>Emampour et al.</i> ¹⁵⁷	$\hat{T}^* = T^*$	$\hat{\Gamma}^* = \Gamma^*$
[EMAM]	$\hat{\rho}^* = \rho^*$	
<i>Agrawal and Kofke</i> ¹⁰⁶	$\hat{T}^* = \frac{1}{T^*}$	$\hat{p}_v^* = 10^{-3} \cdot p^*$
[AGRKOF]	$\hat{\rho}_1^* = \rho_1^*$	$\Delta \hat{h}_v^* = (-u_{\text{g}}^* + \frac{\hat{p}_v^*}{\hat{\rho}_v^*} + u_1^* - \frac{\hat{p}_1^*}{\hat{\rho}_1^*})$
	$\hat{\rho}_v^* = \rho_{\text{g}}^* \cdot 10^{-3}$	
<i>Lustig</i> ⁷⁷	$\hat{T}^* = T^*$	$\hat{p}^* = p^*$
[LUSTIG]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
		$\hat{\beta}^* = \beta^*$
		$\hat{\mu}_{\text{res}}^* = \mu_{\text{r}}^*$
		$\hat{\gamma}^* = \gamma^*$
<i>Boda et al.</i> ¹⁵⁴	$\hat{T}^* = T^*$	$\hat{c}_v^* = \frac{3}{2} + c_{v,\text{r}}^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
[BODA]	$\hat{\rho}^* = \rho^*$	$\hat{c}_p^* = c_{p,r}^* + 1.5$
<i>Weeks et al.</i> ⁵³	$\hat{T}^* = T^*$	$\hat{u}_{\text{res}}^* = -u_r$
[WEECKCHA2]	$\hat{\rho}^* = \rho^*$	$\hat{a}_{\text{res},00}^* = -A_{r,00}$ $\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot \frac{\beta p}{\rho}$
<i>Verlet and Levesque</i> ⁴⁶	$\hat{T}^* = T^*$	$\hat{u}_{\text{res}}^* = u_r^*$
[VERLEV]	$\hat{\rho}^* = \rho^*$	$\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot \frac{\beta p}{\rho}$
<i>Mecke et al.</i> ¹⁰⁹	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[MECKWIN]	$\hat{\rho}^* = \rho^*$	
<i>Toxvaerd and Praestgaard</i> ⁵²	$\hat{T}^* = T^*$	$\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot Z$
[TOXPRA]	$\hat{\rho}^* = \rho^*$	
<i>Street et al.</i> ⁵⁶	$\hat{T}^* = T^*$	$\hat{p}^* = p^*$
[STRRAV]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = u_r^*$
<i>Carley</i> ⁵⁹	$\hat{T}^* = T^*$	$\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot Z$
[CARL]	$\hat{\rho}^* = \rho^*$	
<i>Schofield</i> ⁵⁵	$\hat{T}^* = T^*$	$\hat{p}^* = \rho^* \cdot \hat{T}^* \frac{p_f}{n \cdot k_B \cdot T^*}$
[SCHOF]	$\hat{\rho}^* = \rho^*$	
<i>McDonald and Woodcock</i> ⁵¹	$\hat{T}^* = \frac{T \cdot k_B}{\varepsilon}$	$\hat{p}^* = \hat{\rho}^* \cdot \hat{T}^* \cdot Z$
[MCDWOO]	$\hat{\rho}^* = \frac{\rho \cdot N_{\text{AV}} \cdot \sigma^3 \cdot 10^{-24}}{M}$	$u_{\text{res}}^* = u^* \cdot \hat{T}^*$ $\frac{\varepsilon}{k_B} = 117.2 \text{ K}, \sigma = 3.405 \text{ \AA}$ $M = 39.948 \frac{\text{g}}{\text{mol}}$
<i>Roccatano et al.</i> ⁷⁹	$\hat{T}^* = T^*$	$\hat{c}_v^* = \frac{3}{2} + c_{v,r}^*$
[ROCAMA]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = u_r^*$ $\hat{p}^* = p^*$
<i>Lustig</i> ⁸⁴	$\hat{T}^* = T^*$	$\hat{c}_p^* = c_p^*$
[LUSTIG2]	$\hat{\rho}^* = \rho^*$	$\hat{\mu}_{\text{JT}}^* = \mu_{\text{JT}}^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
		$\hat{p}^* = p^*$ $\hat{w}^* = w^*$
<i>Wood</i> ⁴⁷ [WOOD]	$\hat{T}^* = \theta$ $\hat{\rho}^* = \frac{1}{\tau}$	$\hat{p}^* = Z \cdot \hat{\rho}^* \cdot \hat{T}^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^* \cdot \theta$
<i>Martin and Siepmann</i> ¹¹³ [MARSIE]	$\hat{T}^* = \frac{T \cdot k_{\text{B}}}{\varepsilon}$ $\hat{\rho}^* = \frac{\rho \cdot N_{\text{AV}} \cdot \sigma^3 \cdot 10^{-24}}{M}$	$\hat{p}_v^* = \frac{p_v \cdot \sigma^3 \cdot 10^{-27}}{\varepsilon}$ with $\frac{\varepsilon}{k_{\text{B}}} = 147.9 \text{ K}$, $\sigma = 3.73 \text{ \AA}$, $M = 16.04 \frac{\text{g}}{\text{mol}}$
<i>Fickett and Wood</i> ⁴⁴ [FICWOO]	$\hat{T}^* = \frac{T \cdot k_{\text{B}}}{\varepsilon}$ $\hat{\rho}^* = \frac{N_{\text{AV}} \cdot \sigma^3 \cdot 10^{-24}}{v}$	$\hat{p}^* = \frac{p \cdot \sigma^3 \cdot 10^{-22}}{\varepsilon}$ with $\frac{\varepsilon}{k_{\text{B}}} = 119.3 \text{ K}$, $\sigma = 3.833 \text{ \AA}$
<i>Shaul et al.</i> ¹⁶⁹ [SHASCH]	$\hat{T}^* = T^*$	$\hat{B}^* = B_2 \cdot \sigma^{-3}$ $\hat{C}^* = B_3 \cdot \sigma^{-6}$
<i>Bird et al.</i> ¹⁶⁵ [BIRSPO]	$\hat{T}^* = T^*$	$\hat{C}^* = (\frac{2}{3}\pi)^2 \cdot C^{(0)}$
<i>Hirschfelder et al.</i> ¹⁶⁶ [HIRCUR]	$\hat{T}^* = T^*$	$\hat{B}^* = B^* \cdot \frac{3}{2\pi}$ $\hat{C}^* = C^* \cdot (\frac{3}{2\pi})^2$
<i>Baidakov et al.</i> ¹¹⁷ [BAIDAKO]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = \frac{p_v^*}{10}$ $\hat{\gamma}^* = \gamma^*$
<i>Baidakov et al.</i> ⁸³ [BAIDAKO2]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$ $\hat{c}_v^* = c_v^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
<i>Linhart et al.</i> ⁸¹ [LINHART]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$
<i>Lafitte et al.</i> ¹¹	$\hat{T}^* = T^*$	$\hat{a}_1^* = A_1^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
[LAFITTE]	$\widehat{\rho}^* = \rho^*$	$\widehat{a}_2^* = A_2^*$ $\widehat{a}_3^* = A_3^*$
Data was digitalized from the corresponding plots from Ref. ¹¹		
<i>Lucas</i> ⁶⁵	$\widehat{T}^* = T^*$	$\widehat{p}^* = Z \cdot \widehat{\rho}^* \cdot \widehat{T}^*$
[LUCAS]	$\widehat{\rho}^* = \rho^*$	$\widehat{u}_{\text{res}}^* = \frac{E}{R \cdot T} \cdot \widehat{T}^*$
<i>Betancourt-Cárdenas et al.</i> ¹³⁰	$\widehat{T}^* = T^*$	$\widehat{p}^* = p^*$
[BETANCOU]	$\widehat{\rho}^* = \rho^*$	$\widehat{a}_2 = A_2, \quad \widehat{a}_1 = A_1$ $\Delta \widehat{h}_v^* = u_v^* + \frac{\widehat{p}_v^*}{\widehat{\rho}_v^*} - u_1^* - \frac{\widehat{p}_1^*}{\widehat{\rho}_1^*}$
<i>Janeček et al.</i> ¹³⁵	$\widehat{T}^* = T^*$	$\widehat{p}_v^* = p_v^*$
[JANECEK]	$\widehat{\rho}^* = \rho^*$	$\Delta \widehat{h}_v^* = \Delta h_v^*$ $\widehat{\gamma}^* = \gamma^*$
The VLE data from the <i>inhomogeneous simulations</i> were digitalized from the corresponding plots from Ref. ¹³⁵ In this work the <i>inhomogeneous simulations</i> -data from <i>Janeček et al.</i> ¹³⁵ is referred to as data from Ref. ¹³⁵ and [JANECEK]. For the <i>GEMC</i> results from the same publication see [PRIVJANEC].		
<i>Guo et al.</i> ¹¹¹	$\widehat{T}^* = T^*$	$\widehat{\gamma}^* = \gamma^*$
[GUO]	$\widehat{\rho}^* = \rho^*$	
Surface tension data was digitalized from the corresponding plots from Ref. ¹¹¹		
<i>Lee et al.</i> ⁹⁸	$\widehat{T}^* = \frac{T \cdot k_B}{\varepsilon}$	$\widehat{\gamma}^* = 0.001 \cdot \gamma \sigma^2 \varepsilon^{-1}$
[LEE]	$\widehat{\rho}^* = \rho^*$	with $\frac{\varepsilon}{k_B} = 119.4 \text{ K}, \sigma = 3.4 \text{ Å}$
<i>Werth et al.</i> ¹³⁷	$\widehat{T}^* = T^*$	$\Delta \widehat{h}_v^* = \Delta h_v^*$
[WERTH]	$\widehat{\rho}^* = \rho^*$	$\widehat{p}_v^* = p_v^*$ $\widehat{\gamma}^* = \gamma^*$
<i>Stephan and Hasse</i> ¹³⁸	$\widehat{T}^* = T^*$	$\widehat{p}_v^* = p_v^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
[STEPHAN2]	$\hat{\rho}^* = \rho^*$	
<i>Nijmeijer et al.</i> ¹⁰²	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[NIJMEIJ]	$\hat{\rho}^* = \rho^*$	
<i>Errington</i> ¹²⁵	$\hat{T}^* = T^*$	$\hat{p}_v^* = p_v^*$
[ERRING]	$\hat{\rho}^* = \rho^*$	$\hat{\gamma}^* = \gamma^*$
<i>Baidakov et al.</i> ¹²⁹	$\hat{T}^* = T^*$	$\hat{p}_v^* = p_v^*$
[BAIDAKOV1]	$\hat{\rho}^* = \rho^*$	$\hat{\gamma}^* = \gamma^*$
<i>Janeček</i> ¹³¹	$\hat{T}^* = T^*$	$\Delta \hat{h}_v^* = \Delta h_{v^*}$
[JANECE]	$\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = p_v^*$ $\hat{\gamma}^* = \gamma^*$
<i>Martinez-Ruiz et al.</i> ¹³⁴	$\hat{T}^* = T^*$	$\hat{p}_v^* = p_v^*$
[MARTINEZ]	$\hat{\rho}^* = \rho^*$	$\hat{\gamma}^* = \gamma^*$
<i>Chen et al.</i> ²⁴	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[CHEN]	$\hat{\rho}^* = \rho^*$	
<i>Galliero et al.</i> ¹³²	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[GALLIER]	$\hat{\rho}^* = \rho^*$	
<i>Trokhymchuk and Alexandre</i> ¹¹⁴	$\hat{T}^* = T^*$	$\hat{p}_v^* = p_v^*$
[TROK]	$\hat{\rho}^* = \rho^*$	$\hat{\gamma}^* = \gamma^*$
<i>Anisimov et al.</i> ¹¹⁵	$\hat{T}^* = T^*$	$\hat{p}_v^* = p_v^* \cdot 10^{-3}$
[ANISIMOV]	$\hat{\rho}^* = \rho^*$	$\hat{\gamma}^* = \gamma^*$
<i>Guo and Lu</i> ¹¹²	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[GUOLU]	$\hat{\rho}^* = \rho^*$	
<i>Mausbach et al.</i> ¹⁵⁹	$\hat{T}^* = T^*$	$\hat{\Gamma}^* = \Gamma^*$
[MAUSVRAB]	$\hat{\rho}^* = \rho^*$	
<i>Köster et al.</i> ⁹¹	$\hat{T}^* = T^*$	$\hat{a}_{\text{res},01}^* = A_{\text{r},01}^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
[KOESTER]	$\hat{\rho}^* = \rho^*$	$\hat{a}_{\text{res},11}^* = A_{\text{r},11}^*$ $\hat{a}_{\text{res},10}^* = A_{\text{r},10}^*$ $\hat{a}_{\text{res},20}^* = A_{\text{r},20}^*$ $\hat{a}_{\text{res},02}^* = A_{\text{r},02}^*$
<i>Köster et al.</i> ^{91,92}	$\hat{T}^* = T^*$	$\hat{a}_{\text{res},00}^* = A_{\text{r},00}^*$
[KOESTERPRIVCOM]	$\hat{\rho}^* = \rho^*$	$\hat{a}_{\text{res},01}^* = A_{\text{r},01}^*$ $\hat{a}_{\text{res},10}^* = A_{\text{r},10}^*$ $\hat{a}_{\text{res},11}^* = A_{\text{r},11}^*$ $\hat{a}_{\text{res},02}^* = A_{\text{r},02}^*$ $\hat{a}_{\text{res},20}^* = A_{\text{r},20}^*$

Some of the numerical values from Ref.⁹¹ were not included in the corresponding supplementary material. This data was made available by the authors and is included in the database as [KOESTERPRIVCOM] and referred to as data from Ref.^{91,92}

<i>Yao et al.</i> ⁶³	$\hat{T}^* = T^*$	$\hat{p}^* = p^*$
[YAO]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = -U^*/N$ $\hat{\mu}_{\text{res}}^* = -\mu^* - \ln(\hat{\rho}^*) \cdot T^*$
<i>Baidakov et al.</i> ¹²³	$\hat{T}^* = T^*$	$\hat{\rho}^* = \rho^*$
[BAIDAKOV2]	$\hat{\rho}^* = \rho^*$	$\hat{\gamma}^* = \gamma^*$

Data was digitalized from the corresponding plots from Ref.¹²³

<i>Hong and Jhon</i> ¹⁶³	$\hat{T}^* = T^*$	$\hat{a}_{\text{res},00}^* = -A_{\text{res},00}^*$
[SEUNGMU]	$\hat{\rho}^* = \rho^*$	
<i>Torrie and Valleau</i> ⁹⁶	$\hat{T}^* = T^*$	$\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
[TORVAL]	$\hat{\rho}^* = N/V^*$	$\hat{a}_{\text{res},00}^* = \left(\frac{A_{\text{c}}}{N \cdot \varepsilon}\right) \cdot \frac{1}{T^*} - \ln(\hat{\rho}^*) + 1$
<i>Schultz and Kofke</i> ⁹⁵	$\hat{T}^* = T^*$	$\hat{p}^* = p^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
[SCHULTZKOFKE]	$\hat{\rho}^* = \rho^*$	$\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
<i>van Westen and Gross</i> ¹⁰	$\hat{T}^* = T^*$	$\hat{a}_1^* = A_1^*$
[WESTGROSS]	$\hat{\rho}^* = \rho^*$	$\hat{a}_2^* = A_2^*$ $\hat{a}_3^* = A_3^*$
this work	$\hat{T}^* = T^*$	$\hat{a}_{\text{res},00}^* = \tilde{a}_{\text{res},00}^*$
[STEPHANTHIS]	$\hat{\rho}^* = \rho^*$	$\hat{a}_{\text{res},01}^* = \tilde{a}_{\text{res},01}^*$ $\hat{a}_{\text{res},10}^* = \tilde{a}_{\text{res},10}^*$ $\hat{a}_{\text{res},11}^* = \tilde{a}_{\text{res},11}^*$ $\hat{a}_{\text{res},02}^* = \tilde{a}_{\text{res},02}^*$ $\hat{a}_{\text{res},20}^* = \tilde{a}_{\text{res},20}^*$ $p_v^* = p_v^*$ $\Delta h_v^* = \Delta h_v^*$
<i>Errington</i> ^{126,127}	$\hat{T}^* = T^*$	$\hat{p}_v^* = p_v^*$
[ERRING2]	$\hat{\rho}^* = \rho^*$	
<p>The data listed as [ERRING2] was forwarded by J. Errington.¹²⁷ Please note, that two websites provide numerical values for the LJ VLE.^{215,216} The website can be understood in a way that the numeric values might be those of Ref.,¹²⁶ cf. Ref.¹⁰ The numeric values from^{215,216} are however dissimilar than those from.^{126,127}</p>		
<i>Janeček et al.</i> ^{135,136}	$\hat{T}^* = T^*$	$\Delta \hat{h}_v^* = \Delta h_v^*$
[PRIVJANEC]	$\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = p_v^*$
<p>The numeric values of the VLE data from the <i>GEMC simulations</i> from Ref.¹³⁵ were made available by J. Janeček¹³⁶ and are listed in the database as [PRIVJANEC].</p>		
<i>Okumura and Yonezawa</i> ^{118,119}	$\hat{T}^* = T^*$	$\hat{p}_v^* = p_v^*$
[PRIVOKU]	$\hat{\rho}^* = \rho^*$	
<i>Kioupis et al.</i> ¹²⁴	$\hat{T}^* = T^*$	$\hat{p}_v^* = p_{\text{sat}}$
[KIOUPIS]	$\hat{\rho}^* = \rho$	$\Delta \hat{h}_v^* = H_{\text{vap}} - H_{\text{liq}}$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
<i>Okumura and Yonezawa</i> ^{121,122} [PRIVOKU2]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = p_v^*$
<i>Mick et al.</i> ²³ [MICK]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = p_v^*$ $\Delta \hat{h}_v^* = u_v^* + \frac{p^*}{\hat{\rho}_v^*} - u_l^* - \frac{p^*}{\hat{\rho}_l^*}$
<i>Ustinov</i> ^{93,94} [PRIVUSTINOV]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$ $\hat{\mu}_{\text{res}}^* = \mu^*$
<i>Hong and Jang</i> ¹⁶⁴ [HONG]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{a}_{\text{res},00}^* = -A^{\text{ex}}/Nk_{\text{B}}T$
<i>Giaquinta et al.</i> ⁷² [GIAQUI]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = \frac{\beta P}{\rho} \cdot \hat{\rho}^* \cdot \hat{T}^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$
<i>Cuadros et al.</i> ¹⁶² [CUADROS]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{a}_{\text{res},00}^* = \frac{A_{\text{r},00}}{\hat{T}^*}$
<i>Adachi et al.</i> ⁶⁷ [ADACHI]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$
<i>Baranyai et al.</i> ⁶⁸ [BARANY]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$ $\hat{u}_{\text{res}}^* = u_{\text{r}}^*$ $\hat{a}_{\text{res},00}^* = \frac{A^{\text{ex}}/N}{\hat{T}^*}$
<i>Powles et al.</i> ⁶⁴ [POWLES]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p - 1.09 \cdot (\hat{\rho}^*)^2$ $\hat{\mu}_{\text{res}}^* = \mu_1 - \hat{T}^* \cdot \ln(\hat{\rho}^*)$ $+ \frac{3}{2} \hat{T}^* \cdot \ln(\hat{T}^*) - 1.86 \hat{\rho}^*$
<i>Han</i> ¹⁶¹ [HAN]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{\mu}_{\text{res}}^* = \hat{T}^* \cdot \mu_{\text{r}}^*$
<i>Holcomb et al.</i> ¹⁰⁵ [HOLCOMB]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \hat{\rho}^*$	$\hat{\gamma}^* = \gamma^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
<i>Stoll et al.</i> ¹²⁸ [STOLL]	$\hat{T}^* = \frac{T^*}{4}$ $\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = \frac{1}{4}p_v^*$ $\Delta\hat{h}_v^* = \frac{h_{v,vap}-h_{v,liq}}{4}$
<i>Deiters and Neumaier</i> ^{43,97} [DEINEU]	$\hat{T}^* = \frac{T \cdot k_B}{\varepsilon}$ $\hat{\rho}^* = \frac{10^{-24} \cdot N_{AV} \cdot \sigma^3}{V_M}$	$\hat{p}^* = \frac{p^* \cdot 10^{-24} \cdot \sigma^3}{(\varepsilon/k_B) \cdot k_B}$ $\hat{u}_{res}^* = \frac{u_m}{(\varepsilon/k_B) \cdot k_B \cdot N_{AV}}$ with $\frac{\varepsilon}{k_B} = 119.8 \text{ K}$, $\sigma = 3.405 \text{ \AA}$
<i>Sun and Teja</i> ¹⁶⁸ [SUNTEJA]	$\hat{T}^* = T^*$	$\hat{B}^* = \frac{2}{3}\pi \cdot B_2^*$ $\hat{C}^* = (\frac{2}{3}\pi)^2 \cdot B_3^*$
<i>Sadus and Prausnitz</i> ¹⁰⁸ [SADUS]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = P^*$ $\Delta\hat{h}_v^* = (E_v^* + \frac{\hat{p}_v^*}{\hat{\rho}_v^*} - (E_l^* + \frac{\hat{p}_l^*}{\hat{\rho}_l^*}))$
<i>Yigzawe and Sadus</i> ⁸⁷ [YIGSAD]	$\hat{T}^* = \varphi \cdot 1.312$ $\hat{\rho}^* = \rho^*$	$\hat{p}^* = p^*$
<i>Yigzawe</i> ⁸⁶ [YIGZAWWE]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = p^*$ $\hat{u}^* = u^* - \frac{3}{2}\hat{T}^*$ $\hat{c}_p^* = C_p^*$ $\hat{c}_v^* = C_v^*$ $\hat{\alpha}^* = \alpha_P^*$ $\hat{\beta}^* = \beta_T^*$ $\hat{\gamma}^* = \gamma_V^*$ $\hat{\mu}_{JT}^* = \mu_{JT}^*$ $\hat{w}^* = w_0^*$
<i>Mairhofer and Sadus</i> ^{88,89} [PRIVMAI]	$\hat{T}^* = T^*$ $\hat{\rho}^* = \rho^*$	$\hat{p}_v^* = p^*$ $\hat{u}^* = u^* - \frac{3}{2}\hat{T}^*$ $\hat{c}_p^* = C_p^*$ $\hat{c}_v^* = C_v^*$ $\hat{\beta}^* = \beta_T^*$

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Authors & [Acronym]	state point T, ρ	thermophysical properties
		$\hat{\gamma}^* = \gamma^*$
		$\hat{\mu}_{\text{JT}}^* = \mu_{\text{JT}}^*$
		$\hat{w}^* = w_0^*$
<i>Plačkov and Sadus</i> ¹¹⁰	$\hat{T}^* = T^*$	$\hat{p}_v^* = P^*$
[PLACKOV]	$\hat{\rho}^* = \rho^*$	$\Delta \hat{h}_v^* = (E_v^* + \frac{\hat{p}_v^*}{\rho_v^*} - (E_l^* + \frac{\hat{p}_l^*}{\rho_l^*}))$
<i>Sadus</i> ¹³³	$\hat{T}^* = T^*$	$\hat{p}_v^* = p^*$
[SADUS2]		
<i>Chapela et al.</i> ⁹⁹	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[CHAPELA]		
<i>Shen et al.</i> ¹⁴¹	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[SHEN]		
<i>Werth et al.</i> ¹⁴²	$\hat{T}^* = T^*$	$\hat{\gamma}^* = \gamma^*$
[WERHOR]		
<i>Miyazaki et al.</i> ¹³⁹	$\hat{T}^* = T^*$	$\hat{\gamma}^* = 0.001 \cdot \gamma \sigma^2 \varepsilon^{-1}$
[MIYAZ]		
with $\frac{\varepsilon}{k_B} = 119.8 \text{ K}, \sigma = 3.405 \text{ \AA}$		

Details on the assessment of homogeneous states data

Fig. S1 shows the results of the EOS test on the homogeneous state points as the percentage of the overall confirmed data as a function of the parameter P_{max} . The chosen value of $P_{\text{max}} = 4$ is indicated, which entails approximately 90% confirmed data. For smaller P_{max} values, the EOS test becomes more stringent as more data points are characterized as outliers. For larger P_{max} values, the EOS test becomes more lenient (i.e. more conservative) and less data points are identified as outliers. Evidently, the EOS test converges for large P_{max} values to approximately $N_{\text{conf}} = 98\%$,

which means that these 2% of all homogeneous data are particularly gross outliers.

Details on the calculation of thermophysical properties by the *Lustig*-formalism

The *Lustig* formalism in combination with Widom's test particle insertion method,¹⁷⁶ as implemented in the simulation package *ms2*,¹⁷⁷ provides the Helmholtz energy and its derivatives with respect to the density and the inverse temperature simultaneously from a single simulation run. The Helmholtz energy per particle $a = A/N$ is formally split into an ideal gas contribution (superscript o) and a residual contribution (superscript res), i.e. $a = a^o + a^{\text{res}}$. The following notation is used for the derivatives of the Helmholtz energy $\tilde{a} = a/T$ with respect to inverse temperature and density

$$\tilde{a}_{nm} = \tilde{a}_{nm}^o + \tilde{a}_{nm}^{\text{res}} = (1/T)^n \rho^m \frac{\partial^{n+m}(\tilde{a}^o + \tilde{a}^{\text{res}})}{\partial (1/T)^n \partial \rho}, \quad (1)$$

where only $n, m = 0, 1, 2$ and were considered here. The numerical values of the $\tilde{a}_{nm}$ obtained in the studies of Refs.^{90–92} and from this work are included in the database, as such are the primary simulation data. The relations used for the computation of thermodynamic properties from the sampled $\tilde{a}_{nm}$ values are as follows:

entropic properties

Gibbs energy
$$g = h - Ts = T(1 + \tilde{a}_{00}^o + \tilde{a}_{00}^{\text{res}} + \tilde{a}_{01}^{\text{res}}) \quad (2)$$

thermal properties

pressure
$$p = -\left(\frac{\partial a}{\partial v}\right)_T = \rho T (1 + \tilde{a}_{01}^{\text{res}}) \quad (3)$$

thermal pressure coefficient $\gamma = \left(\frac{\partial p}{\partial T} \right)_\rho = \rho(1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}})$ (4)

isothermal compressibility $\beta = \left(\rho \frac{\partial p}{\partial \rho} \right)_T^{-1} = \frac{1}{\rho T(1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}})}$ (5)

thermal expansion coefficient $\alpha = \beta\gamma = \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial p}{\partial \rho} \right)_T} = \frac{1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}}}{T(1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}})}$ (6)

caloric properties

internal energy $u = a + Ts = T(\tilde{a}_{10}^0 + \tilde{a}_{10}^{\text{res}})$ (7)

$$u_{\text{res}} = a_{\text{res}} + Ts_{\text{res}} = T\tilde{a}_{10}^{\text{res}} \quad (8)$$

enthalpy $h = u + pv = T(1 + \tilde{a}_{10}^0 + \tilde{a}_{10}^{\text{res}} + \tilde{a}_{01}^{\text{res}})$ (9)

isobaric heat capacity $c_p = \left(\frac{\partial h}{\partial T} \right)_p = -(\tilde{a}_{20}^0 + \tilde{a}_{20}^{\text{res}}) + \frac{(1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}})^2}{1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}}}$ (10)

$$\text{isochoric heat capacity} \quad c_v = \left(\frac{\partial u}{\partial T} \right)_v = -(\tilde{a}_{20}^o + \tilde{a}_{20}^{\text{res}}) \quad (11)$$

$$\text{speed of sound} \quad w = \sqrt{\left(\frac{\partial p}{\partial \rho} \right)_s} = \left(T(1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}}) - \frac{(1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}})^2}{\tilde{a}_{20}^o + \tilde{a}_{20}^{\text{res}}} \right)^{0.5} \quad (12)$$

$$\text{Joule-Thomson coefficient} \quad \mu_{\text{JT}} = \left(\frac{\partial T}{\partial p} \right)_h \quad (13)$$

$$= \rho^{-1} \frac{-(\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}} + \tilde{a}_{11}^{\text{res}})}{(1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}})^2 - (\tilde{a}_{20}^o + \tilde{a}_{20}^{\text{res}})(1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}})}$$

$$\text{Grüneisen coefficient} \quad \Gamma = \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho c_v} = \frac{1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}}}{-\tilde{a}_{20}^o - \tilde{a}_{20}^{\text{res}}} \quad (14)$$

Details on the assessment of VLE bulk data

The results of the three VLE tests for all data sets (both confirmed and discarded) are shown in Figs. S2, S3, and S4 for the sake of completeness. Fig. S2 of the supplementary material shows the results of the compressibility factor test for all VLE data, Fig. S3 shows the results of the Clausius-Clapeyron test for all VLE data, and Fig. S4 shows the deviations from all VLE data and the base correlations (6) - (9).

Data sets that were discarded according the criteria for the compressibility factor test (cf. Fig. S2) outlined in the main part of this work are those from *Adams*,⁵⁸ *Adams*,⁶⁰ *Anisimov*

et al.,¹¹⁵ *Baidakov et al.*,¹¹⁷ *Baidakov et al.*,¹²⁹ *Betancourt-Cárdenas et al.*,¹³⁰ *Kioupis et al.*,¹²⁴ *Martin and Siepmann*,¹¹³ *Panagiotopoulos*,¹⁰⁰ *Panagiotopoulos et al.*,¹⁰¹ *Smit and Frenkel*,¹⁰³ and *Trokhymchuk and Alejandre*.¹¹⁴

For the data sets from the literature that report all VLE properties required for the Clausius-Clapeyron test, the RHS of Eq. (10) was computed and shown in Fig. S3 for comparison. Large deviations from the base correlation and the most precise data sets (Refs.^{23,71,135,136} and this work) were found for the data of *Adams*,⁵⁸ *Adams*,⁶⁰ *Kioupis et al.*,¹²⁴ *Betancourt-Cárdenas et al.*,¹³⁰ *Panagiotopoulos*,¹⁰⁰ *Panagiotopoulos et al.*,¹⁰¹ and *Smit and Frenkel*.¹⁰³ According the criteria outlined in the main part of this work, these data sets were discarded.

Fig. S4 shows the deviation plots for each VLE property (p^s , ρ' , ρ'' , and Δh_v) for all VLE data sets considered in this work. The following data sets contain two or more data points with deviations larger than 5%, i.e. are out of the range of Fig. S4: *Adams*,⁵⁸ *Adams*,⁶⁰ *Anisimov et al.*,¹¹⁵ *Baidakov et al.*,¹¹⁷ *Baidakov et al.*,¹²⁹ *Baidakov et al.*,¹²³ *Betancourt-Cárdenas et al.*,¹³⁰ *Guo et al.*,¹¹¹ *Guo and Lu*,¹¹² *Galliero et al.*,¹³² *Hunter and Reinhardt*,¹⁰⁷ *Holcomb et al.*,¹⁰⁵ *Janeček*,¹³¹ *Kioupis et al.*,¹²⁴ *Kofke*,¹⁰⁴ *Lee et al.*,⁹⁸ *Martin and Siepmann*,¹¹³ *Mecke et al.*,¹⁰⁹ *Okumura and Yonezawa*,^{118,119} *Panagiotopoulos*,¹⁰⁰ *Panagiotopoulos et al.*,¹⁰¹ *Potoff and Panagiotopoulos*,¹⁹⁷ *Smit and Frenkel*,¹⁰³ and *Trokhymchuk and Alejandre*.¹¹⁴ These pronounced deviations were found in most cases for the vapor pressure and the saturated vapor density. Deviations of data points that exceed 5% in the saturated liquid density or the enthalpy of vaporization were only found for the data from *Panagiotopoulos*,¹⁰⁰ *Smit and Frenkel*,¹⁰³ *Kofke*,¹⁰⁴ *Kioupis et al.*,¹²⁴ *Hunter and Reinhardt*,¹⁰⁷ *Mecke et al.*,¹⁰⁹ and *Lee et al.*⁹⁸ Data sets exhibiting particularly large deviations from Eqs. (6) - (9) at multiple state points are those from *Anisimov et al.*,¹¹⁵ *Baidakov et al.*,¹¹⁷ *Baidakov et al.*,¹²⁹ *Galliero et al.*,¹³² *Hunter and Reinhardt*,¹⁰⁷ *Kioupis et al.*,¹²⁴ *Lee et al.*,⁹⁸ *Panagiotopoulos*,¹⁰⁰ and *Trokhymchuk and Alejandre*.¹¹⁴ To avoid visual clutter, these out-of-range data points are not shown in Fig. S4. This confirms the findings from the compressibility factor and the Clausius-Clapeyron tests where these data sets could be applied.

The data sets of *Hunter and Reinhardt*,¹⁰⁷ *Potoff and Panagiotopoulos*,¹⁹⁷ *Shi and Johnson*¹²⁰ (only saturated densities reported) show small, but distinct systematic deviations to the base

correlation and the seven most precise data sets.

Details on the assessment of VLE interfacial data

Fig. S5 shows the surface tension of all considered data in this work. The surface tension results reported by *Trokhymchuk and Alejandre*¹¹⁴ and the MC results of *Galliero et al.*¹³² are slightly but noticeably below the mutually best agreeing data sets. The data of *Anisimov et al.*¹¹⁵ show large deviations, which is likely a result of the employed LJ potential version.

The surface tension data of *Potoff and Panagiotopoulos*¹¹⁶ shows distinct deviations from the above mentioned data of best mutual agreement – especially close to the critical point. The same was found for the saturated densities data of *Potoff and Panagiotopoulos*¹¹⁶. This is in line with the relatively low critical temperature reported by Ref..¹¹⁶

Table S4 summarizes the identified outliers in the data sets that were identified to be the best VLE data sets: *Errington*,^{126,127} *Janeček et al.*,^{135,136} *Lotfi et al.*,⁷¹ *Mick et al.*,²³ *Okumura and Yonezawa*,^{121,122} and this work.

Table S3 summarizes the results for the vapor-liquid equilibrium data obtained in this work using the Grand Equilibrium method¹⁷⁹ as implemented in *ms2*.¹⁷⁷

Table S3: Simulation results for the VLE data set obtained in this work. The columns are from left to right: vapor pressure, saturated liquid density, saturated vapor density, and the enthalpy of vaporization. The numbers in parentheses indicate the uncertainties of the last decimal digits.

T	p^s	ρ'	ρ''	Δh_v
0.69	0.001172(24)	0.847111(1)	0.001729(35)	6.766422(34)
0.7	0.001343(25)	0.8427(1)	0.001956(36)	6.762403(39)
0.72	0.001784(28)	0.834385(1)	0.002538(39)	6.652809(43)
0.74	0.002319(29)	0.825751(1)	0.003227(40)	6.641588(48)
0.76	0.002932(32)	0.817195(2)	0.003994(44)	6.528674(58)
0.78	0.003689(40)	0.8083(1)	0.004929(54)	6.513863(71)
0.8	0.004649(44)	0.799470(2)	0.006103(57)	6.395171(72)
0.82	0.005608(44)	0.7903(1)	0.007233(57)	6.278050(94)
0.84	0.006872(44)	0.7812(1)	0.008730(55)	6.25512(12)
0.86	0.008299(53)	0.7718(1)	0.010397(66)	6.13070(14)
0.88	0.009902(63)	0.7623(1)	0.012248(78)	6.10391(17)
0.9	0.011795(39)	0.7527(1)	0.014435(48)	5.97235(16)
0.92	0.013783(67)	0.7427(1)	0.016686(81)	5.84091(21)
0.94	0.016237(79)	0.7328(1)	0.01952(10)	5.80088(26)
0.96	0.018686(63)	0.7224(1)	0.02228(07)	5.66382(30)
0.98	0.021625(75)	0.7120(1)	0.02567(09)	5.51804(44)
1	0.024843(87)	0.7009(1)	0.02938(10)	5.46904(50)
1.02	0.02823(10)	0.6899(1)	0.03329(12)	5.31864(67)
1.04	0.03216(11)	0.6785(1)	0.03795(13)	5.15826(69)
1.06	0.03623(09)	0.6664(1)	0.04277(11)	4.9978(11)
1.08	0.04058(10)	0.6537(2)	0.04799(11)	4.8332(12)

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T	p^s	ρ'	ρ''	Δh_v
1.1	0.04568(12)	0.6409(2)	0.05443(14)	4.7536(16)
1.12	0.05112(13)	0.6275(2)	0.06145(15)	4.5688(18)
1.14	0.05674(16)	0.6133(2)	0.06885(19)	4.3817(24)
1.16	0.06323(20)	0.5985(2)	0.07810(24)	4.1717(33)
1.18	0.06957(21)	0.5820(2)	0.08715(26)	3.9681(39)
1.2	0.07684(25)	0.5639(3)	0.09862(32)	3.7339(59)
1.22	0.08429(33)	0.5446(4)	0.11101(44)	3.3941(87)
1.24	0.09260(36)	0.5235(5)	0.12657(50)	3.122(11)
1.26	0.10129(44)	0.5007(5)	0.14451(62)	2.823(16)
1.28	0.11082(39)	0.4747(8)	0.17041(60)	2.350(21)

Table S4: Identified outliers in the best VLE data sets: *Errington*,^{126,127} *Janeček et al.*,^{135,136} *Lotfi et al.*,⁷¹ *Mick et al.*,²³ *Okumura and Yonezawa*,^{121,122} and this work.

Reference	T	p^s	ρ'	ρ''	Δh_v
<i>Mick et al.</i> ²³	0.75	0.0022(1)	0.8208(2)	0.0030(1)	6.595(3)
	1.25	0.0967(4)	0.514(2)	0.135(2)	3.30(3)
this work ^(a)	1.08	0.040583(62)	0.65371(20)	0.047992(74)	4.8332(12)
<i>Lotfi et al.</i> ⁷¹	0.7	0.00131(6)	0.84266(18)	0.00193(10)	6.758(4)
<i>Errington</i> ¹²⁵	1.3	0.1212(10)	0.4271(13)	0.2096(13)	-
<i>Errington</i> ^{126,127}	1.3	0.1215841(996)	0.4442(51)	0.193072(5552)	-
	1.25	0.0975052(672)	0.5049(12)	0.143990(335)	-

^(a) data point is slightly off the statistical uncertainties regarding the self-consistency Clausius-Clapeyron test (see Fig. S3).

Figure S1: Percentage of overall confirmed data as a function of the parameter $P_{\max}$ for the homogeneous data EOS test. N_{conf} is the confirmation rate of all homogeneous data. The dashed line indicates the value $P_{\max} = 4$ chosen for the identification of outliers as they are specified in the database.

— correlation Eq. (6) & (8)	○ Hunter & Reinhardt ¹⁰⁷	△ Panagiotopoulos ¹⁰⁰
□ Adams ⁶⁰	△ Janecek ¹³¹	▽ Panagiotopoulos et al. ¹⁰¹
○ Adams ⁵⁸	◇ Janecek et al. ^{135,136}	▽ Plackov & Sadus ¹¹⁰
△ Agrawal & Kofke ¹⁰⁶	▽ Kioupis et al. ¹²⁴	◇ Sadus & Prausnitz ¹⁰⁸
▽ Anisimov et al. ¹¹⁵	▷ Kofke ¹⁰⁴	▷ Smit & Frenkel ¹⁰³
◇ Baidakov et al. ¹¹⁷	■ Lotfi et al. ⁷¹	☆ Stephan & Hasse ¹³⁸
▽ Baidakov et al. ¹²⁹	× Martin & Siepmann ¹¹³	+ Stoll et al. ¹²⁸
☆ Betancourt-Cardenas et al. ¹³⁰	× Martinez-Ruiz et al. ¹³⁴	□ this work
× Errington ¹²⁵	+ Mick et al. ²³	× Trokhymchuk & Alejandre ¹¹⁴
× Errington ^{126,127}	○ Okumura & Yonezawa ^{118,119}	× Werth et al. ¹³⁷
□ Hansen & Verlet ²⁰	○ Okumura & Yonezawa ^{121,122}	

Figure S2: Compressibility factor test for the vapor-liquid equilibrium data of the Lennard-Jones fluid according to *Nezbeda*:^{213,214} saturated vapor phase compressibility factor Z'' as function of the temperature T (top) and the relative deviation of Z'' from correlations (6) and (8) (bottom). The dotted line indicates the range of 2.5 times the confidence interval of the most precise data, as discussed in the main part of this work. Error bars are omitted in the bottom plot to avoid visual clutter. For clarity, the out-of-range data points are omitted in both, the top and bottom plot. The black filled star indicates the compressibility factor at the critical point according the base correlation.

Figure S3: Clausius-Clapeyron test according to Eq. (10). Symbols indicate the RHS and the lines the LHS of Eq. (10). The orange line indicates Eq. (6). The purple line is Eq. (22) from Ref.⁷¹ For clarity, the numeric values of the out-of-range data points are omitted in the plot; they lie in the range of $d(\ln p^s)/d(T^{-1}) = -31$ to -0.8 .

Figure S4: Relative deviations of the vapor-liquid equilibrium data for the vapor pressure p^s , saturated liquid density ρ' , saturated vapor density ρ'' , and enthalpy of vaporization Δh_v from correlations (6) - (9) as a function of the temperature T . Error bars were omitted to avoid visual clutter. The dotted lines indicates the range of 2.5 times the confidence interval of the most precise data δx , as discussed in the main part of this work. Error bars are omitted in the plots to avoid visual clutter. For clarity, the out-of-range data points are omitted in the deviation plots.

Figure S5: Surface tension of the LJ fluid as a function of the temperature (top) and the corresponding relative deviation plot (bottom). The black line indicates Eq. (11). Symbols indicate computer experiment data. For clarity, numerical values for out-of-range data points in the vicinity of the critical temperature in the deviation plot are omitted. The dotted lines indicates the range of 2.5 times the confidence interval of the most precise data as discussed in the main part of this work.