Review and Comparison of Equations of State for the Lennard-Jones Fluid

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(Dated: Tuesday 11th August, 2020)

The Lennard-Jones (LJ) potential is widely used for describing simple fluids; it is also a point of departure for developing models of complex fluids. Thermodynamic properties of the LJ fluid have been studied by molecular simulations by many authors and a critical review of the available data, which comprises about 35,000 data points, has been published recently [J. Chem. Inf. Mod. 59 (2019) 4248-4265]. The importance of the LJ fluid has also triggered the development of a large number of equations of state (EOS). In the present work, 20 LJ EOS were critically assessed by comparing their results with consolidated data from computer experiments. A large variety of thermophysical properties was considered: vapor pressure; saturated densities; enthalpy of vaporization; critical properties; thermal, caloric, and entropic properties at homogeneous state points; and second and third virial coefficients. It was found that none of the available LJ EOS meets the following two criteria: (1) it does not yield unphysical artifacts when used for extrapolations, and (2) it describes data from computer experiments within their statistical uncertainty in most fluid regions. Furthermore, a re-parameterization of the monomer term of the PC-SAFT EOS was carried out by fitting it to data of the LJ fluid. The new LJ EOS yields good results for the LJ fluid, but does not outperform the best existing LJ EOS.

Keywords: Lennard-Jones fluid, equation of state, molecular simulation, monomer reference fluid, SAFT

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I. INTRODUCTION

The Lennard-Jones potential^{1,2} has been used extensively as a model of simple fluids with repulsive and dispersive interactions since the early days of computer simulation^{3–10}. It is defined as

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

where ε and σ are the energy and size parameter, respectively. The distance between two particles is denoted by r . It is probably the most frequently investigated monomer model fluid¹¹. The Lennard-Jones potential provides, as already stated by *Nicolas et al.* in 1979¹², "a convenient model for testing liquid theories and for investigating such phenomena as melting, the liquid-vapor surface, nucleation etc.". This has not changed in the past four decades^{13–24}. Furthermore, the Lennard-Jones potential is used as a building block in molecular models of more complex fluids^{25–27}. The Lennard-Jones potential is referred to as LJ potential in the following.

A large number of equations of state (EOS) of the LJ fluid have been proposed in the literature of which Table I gives a survey. To the best of our knowledge, the different LJ EOS from the literature have never been compared systematically. We have therefore compared 20 of the most widely used LJ EOS using a consistent approach and consolidated reference data. The LJ EOS that were included in the present study are marked with abbreviations in Table I. The focus of this work is on the LJ EOS developed in the past 30 years. However, some older yet still frequently used LJ EOS were also included in the comparison^{12,28–30}.

A comprehensive database of thermophysical properties of the LJ fluid determined by computer experiments has recently become available¹¹. There are about 35,000 data points on thermophysical properties of the LJ fluid in the literature, which were critically assessed and screened for outliers in Ref.¹¹. The consolidated database from Ref.¹¹ still contains about 32,000 entries and was used here as basis for the assessment of the LJ EOS.

The following physical properties were considered in the present work:

- vapor-liquid equilibrium (for given T : vapor pressure p^s , saturated liquid and vapor densities ρ' and ρ'' , and enthalpy of vaporization Δh_v).
- the critical point (critical temperature T_c , critical density ρ_c , and critical pressure p_c).
- homogeneous states (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 parameter Γ , Joule-Thomson coefficient μ_{JT} , speed of sound w , Helmholtz energy a , and chemical potential μ) in the different fluid regions such as: gas, liquid, supercritical, etc. (details are given below). Also, second and third thermal virial coefficients B and C were considered.

- the qualitative behavior of $p(\rho)$ isotherms in the metastable and unstable region and the spinodal curve.

LJ EOS can be broadly classified into *empirical* EOS and *theoretically-based* EOS. This is only a crude classification and used here in the following sense³¹: empirical EOS are data-driven and aim at correlating the data well. This is usually accomplished by a flexible mathematical form with a large number of parameters. In contrast, the mathematical form of theoretically-based EOS is derived from theoretical considerations, but usually also use empirical correction terms and simulation data for determining parameters. Theoretically-based EOS usually have a smaller number of adjustable parameters than the empirical EOS. We furthermore use the class *semi-theoretical* for a more distinct differentiation, which comprises EOS that can not be clearly assigned to either of the above two classes. EOS from the semi-theoretical class typically incorporate dominating empirical correction terms, but also contain significant theoretically derived features. Obviously, the border between these three types of EOS is blurred and not unambiguous. In general, most LJ EOS have some physically motivated features and some empirical features, see *Deiters and de Reuck*³¹ for a detailed discussion.

It is widely accepted that both types of EOS have strengths and weaknesses that are often characterized as follows^{31–33}: empirical EOS are strong regarding the accurate description of available data, but weak regarding extrapolations into regions where no data was used for the training of the EOS; for theoretically-based EOS it is the other way around: they are expected to be strong regarding extrapolations, but typically less accurate in the description of existing data. Furthermore, empirical EOS are prone to yield unphysical behavior such as crossing isotherms^{34–36} or several van der Waals loops in the vapor-liquid coexistence region^{32,37,38}.

Lennard-Jones equations of state are often used as a base model for building models of

more complex fluids^{29,39–42}. Among the theoretically-based EOS, those of the SAFT-type are particularly successful and have been widely used for describing complex fluids^{39,42–46}. Most of them were developed starting from an LJ EOS for describing the monomer unit^{40,41,45,47–54}. Different LJ EOS were used in different SAFT EOS. The monomer equations of the following SAFT EOS were included in the present study: the Lennard-Jones extended SAFT^{51,52}, LJ-SAFT^{48,49}, LJ-based SAFT⁵⁴, soft-SAFT^{40,41}, and SAFT-VR Mie^{42,55}; the corresponding LJ EOS considered in the present work are those from Refs.^{12,42,56,57}. Another important SAFT EOS is PC-SAFT^{58,59}. The monomer term of PC-SAFT was not developed to give a good description of the LJ fluid. In the present work, the monomer term of PC-SAFT was reparametrized in order to get good results for the LJ fluid and enable direct comparisons with the monomer terms in other versions of SAFT EOS. The parametrization, which aims at a good description of both the vapor-liquid equilibrium and the homogeneous region, uses elements from multi-criteria optimization. It is briefly described and summarized in the Appendix; details are given in the Supplementary Material. The results that were obtained with the new LJ EOS give insights in strengths and weaknesses of the functional form of the monomer term that is used in PC-SAFT, which is put into relation to the results from other LJ EOS.

The outline of this work is as follows: first, an overview of the LJ EOS from the literature that were considered in this work is given. The second and main part comprises the evaluation and comparison of LJ EOS. Finally, conclusions are drawn.

Throughout the present work, all physical properties are conveniently reduced using the Lennard-Jones potential parameters ε , σ and the molecular mass M , as well as the Boltzmann constant k_B as described in Ref.⁶⁰. The present work is limited to the fluid regions of the Lennard-Jones fluid, i.e. no solid phases are considered. This includes the two-phase regions in which solids occur. The term *two-phase region* refers therefore exclusively to the vapor-liquid coexistence region here.

II. OVERVIEW OF LENNARD-JONES EOS

Table I gives an overview of LJ EOS from the literature. Equations of state that are only defined piecewise are not considered in Table I, since their derivatives can be discontinuous.

TABLE I. Overview of Lennard-Jones equations of state from the literature – sorted chronologically. # indicates the number of parameters of the LJ EOS. LJ EOS indicated with an abbreviation were included in the comparison in the present work.

Authors	Abbr.	EOS-type	Year	#
<i>Levesque and Verlet</i> ⁶¹		BH perturbation theory; pressure explicit	1969	9
<i>Toxvaerd and Praetgaard</i> ⁶²		BH perturbation theory; pressure explicit	1970	8
<i>McDonald and Singer</i> ⁶³		empirical; Helmholtz energy explicit	1972	20
<i>Nicolas et al.</i> ¹²	Ni	empirical (MBWR); pressure explicit	1979	33
<i>Ree</i> ²⁸	Re	empirical; pressure explicit	1980	15
<i>Sys and Malijevski</i> ⁶⁴		empirical + virial; pressure explicit	1980	21
<i>Cotterman et al.</i> ²⁹	Co	BH perturbation theory + virial; Helmholtz energy explicit	1986	15
<i>Adachi et al.</i> ³⁰	Ad	empirical (MBWR); pressure explicit	1988	33
<i>Song and Mason</i> ⁶⁵		modified van der Waals equation + virial; pressure explicit	1989	0
<i>Nezbeda and Aim</i> ⁶⁶		empirical; pressure explicit	1989	5
<i>Sowers and Sandler</i> ⁶⁷		BH perturbation theory; pressure explicit	1991	6
<i>Koutras et al.</i> ⁶⁸	Kou	modified HS equation; pressure explicit	1992	15
<i>Miyano</i> ⁶⁹	Mi	empirical (MBWR); pressure explicit	1993	33
<i>Johnson et al.</i> ⁵⁶	Jo	empirical (MBWR); pressure explicit	1993	33
<i>Kolafa and Nezbeda</i> ⁵⁷	Ko	HS + virial + empirical; Helmholtz energy explicit	1994	32
<i>Mecke et al.</i> ^{70,71}	Me	HS + empirical; Helmholtz energy explicit	1996	38
<i>Sun and Teja</i> ⁷²	Su	empirical (MBWR); pressure explicit	1996	33
<i>Cuadros et al.</i> ⁷³		WCA perturbation theory; Helmholtz energy explicit	1996	5
<i>Amadei et al.</i> ⁷⁴		quasi Gaussian entropy theory; Helmholtz energy explicit	1999	43
<i>Hess</i> ⁷⁵	He	WCA reference + virial; pressure explicit	1999	0
<i>Boltachev and Baidakov</i> ⁷⁶	Bo	empirical + virial; pressure explicit	2003	39
<i>Paricaud</i> ⁷⁷	Pa	BH perturbation theory; Helmholtz energy explicit	2006	34
<i>Betancourt-Cardenas et al.</i> ⁷⁸		BH perturbation theory; Helmholtz energy explicit	2008	10
<i>Quiñones-Cisneros et al.</i> ⁷⁹	Qui	empirical; pressure explicit	2009	16
<i>May and Mausbach</i> ^{80,81}	Ma	empirical (MBWR); pressure explicit	2012	33
<i>Lafitte et al.</i> ⁴²	La	BH perturbation theory; Helmholtz energy explicit	2013	62
<i>Thol et al.</i> ³⁷	Th	empirical; Helmholtz energy explicit	2016	67
<i>van Westen and Gross</i> ⁸²	vWe	BH perturbation theory; Helmholtz energy explicit	2017	43
<i>Gottschalk</i> ⁸³	Go	empirical + virial	2019	167
this work	th	BH perturbation theory; Helmholtz energy explicit	2020	18

The 20 LJ EOS for which an abbreviation is given in Table I were considered for the comparison in the present work. As only some of the LJ EOS are available in executable form or as source code, such a comparison requires programming and validation of the considered EOS. Besides the 20 LJ EOS studied here, two more LJ EOS^{73,78} were implemented in the course of this work, but the results reported in the respective publications could not be reproduced using the given equations and numerical values of the parameters. Hence, they were not considered for the comparison in this work.

Furthermore, in the course of the present work, misprints were identified in Refs.⁸² and⁷⁹. The corrections are reported in the Supplementary Material. Using these corrections, our implementations of the LJ EOS from Refs.^{79,82} yield results that are consistent with data reported in the respective publications.

All LJ EOS listed in Table I are either formulated explicitly in the pressure or the Helmholtz energy. The number of parameters that were adjusted to obtain a good fit of data from computer experiments varies between 0 and 177. The LJ EOS that were considered in the present work are classified here as follows: theoretically-based: Refs.^{29,42,77,82} and the LJ EOS from the present work; semi-theoretical: Refs.^{57,68,70,71,75,76}; and empirical: Refs.^{12,28,30,37,56,69,72,79–81,83}.

The most popular LJ EOS are those of *Johnson et al.*⁵⁶, *Nicolas et al.*¹², *Kolafa and Nezbeda*⁵⁷, *Cotterman et al.*²⁹, *Lafitte et al.*⁴², *Ree*²⁸, and *Mecke et al.*^{70,71} (sorted by their number of citations; for more information, see the Supplementary Material).

The first LJ EOS were published soon after molecular simulations became feasible by ‘computing machines’^{3–6}. The oldest LJ EOS considered in the present work is that of *Nicolas et al.*¹² from 1979, which is a modified Benedict-Webb-Rubin (MBWR) type EOS^{84,85}. That LJ EOS has been re-parametrized several times, e.g. from *Adachi et al.*³⁰, *Miyano*⁶⁹, *Johnson et al.*⁵⁶, *Sun and Teja*⁷², and *May and Mausbach*^{80,81}, of which the parametrization of *Johnson et al.*⁵⁶ is by far the most frequently used. The oldest LJ EOS of the ‘theoretically-based’ type considered here is that of *Cotterman et al.*²⁹ from 1986. Both *Kolafa and Nezbeda*⁵⁷ and *Mecke et al.*^{70,71} proposed semi-theoretical LJ EOS in the 90s that became popular. Several theoretically-based LJ EOS have been developed in the recent years, e.g. those of *Paricaud*⁷⁷, *Lafitte et al.*⁴², and *van Westen and Gross*⁸². But also new empirical LJ EOS have become available recently, e.g. those of *Thol et al.*³⁷ and *Gottschalk*⁸³. Further semi-theoretical LJ EOS that are considered in the present work are

those of *Boltachev and Baidakov*⁷⁶, *Quiñones-Cisneros et al.*⁷⁹, *Koutras et al.*⁶⁸, and *Hess*⁷⁵; and the empirical LJ EOS of *Ree*²⁸.

Theoretically-based LJ EOS are usually either built on the perturbation theory of *Barker and Henderson*^{86,87} (BH) or that of *Weeks-Chandler-Andersen*⁸⁸ (WCA). The LJ EOS of *Song and Mason*⁶⁵ is of the WCA type, those of *Cotterman et al.*²⁹, *Paricaud*⁷⁷, *Lafitte et al.*⁴², *van Westen and Gross*⁸², and the PC-SAFT monomer are of the BH type. *Van Westen and Gross*⁸² also proposed a WCA type LJ EOS and found it equally precise as their BH type LJ EOS. Only the latter is employed here for comparison. Perturbation theory is expected to be a good approximation for state points for which the influence of the attractive forces is not particularly strong, i.e. high temperatures^{86,89}.

The theoretically-based LJ EOS apply different formulations for the hard sphere reference term, e.g. the LJ EOS of *Cotterman et al.*²⁹, *Paricaud*⁷⁷, *van Westen and Gross*⁸², and *Lafitte et al.*⁴² use the hard sphere equation of *Carnahan and Starling*⁹⁰, whereas the PC-SAFT monomer uses that of *Boublik*⁹¹ and *Mansoori et al.*⁹². Also the semi-theoretical LJ EOS of *Mecke et al.*^{70,71} employs the *Carnahan and Starling*⁹⁰ equation for the description of the hard sphere Helmholtz energy. The semi-theoretical LJ EOS of *Kolafa and Nezbeda*⁵⁷ employs a slightly modified version of the *Carnahan and Starling*⁹⁰ equation. The LJ EOS of *Koutras et al.*⁶⁸ is based on an empirically modified version of the *Carnahan and Starling*⁹⁰ equation.

The BH type LJ EOS of *Cotterman et al.*²⁹, *Paricaud*⁷⁷, *Lafitte et al.*⁴², and *van Westen and Gross*⁸² as well as the PC-SAFT monomer use slightly differing formulations for the temperature-dependent diameter for the modeling of the softness of the repulsive interactions^{86,89}. The PC-SAFT monomer model, which was re-parametrized in the present work, uses a simplified version of the temperature-dependent diameter, cf. Eq. (24) in the Appendix.

The theoretically-based LJ EOS of *Cotterman et al.*²⁹, *Paricaud*⁷⁷, and the PC-SAFT monomer model are developed up to the second order perturbation term. The LJ EOS of *Lafitte et al.*⁴² and *van Westen and Gross*⁸² are formulated up to third and fourth order perturbation terms, respectively.

Also the perturbation terms are designed differently in the considered theoretically-based LJ EOS: the LJ EOS of *Cotterman et al.*²⁹ and the PC-SAFT monomer model are simplified and developed in a series expansion in the packing fraction, whereas the LJ EOS

*Paricaud*⁷⁷, *Lafitte et al.*⁴², and *van Westen and Gross*⁸² use an analytic function for the radial distribution function of the hard sphere system.

All LJ EOS considered here were fitted to computer experiment data (except that of *Hess*⁷⁵, which has no adjustable parameter). However, the data that was used generally differs. Furthermore, in many cases the training data set, the objective functions, and weights were not disclosed in the publications. Most LJ EOS were parametrized using pvT data – often in combination with internal energy data. In some cases also data on the thermal virial coefficients were used for the parametrization – mainly for empirical LJ EOS. The LJ EOS of *Thol et al.*³⁷, which is explicit in the Helmholtz energy a , was parametrized directly using computer experiment data of a and its density and inverse temperature derivatives. Most theoretically-based LJ EOS^{29,42,82} are directly parametrized using computer experiment data of the perturbation term. The data type used for the parametrization of each LJ EOS is summarized in the Supplementary Material.

In some publications in which new LJ EOS are proposed (cf. Table I), an estimated range of validity of the LJ EOS is reported (which is usually given for the density and temperature). Since this range of validity is mostly based only on estimates and in some cases only described ambiguously, we compare all LJ EOS to the same computer experiment database¹¹, disregarding the eventual statements on the range of validity to ensure a fair comparison. We find that the reported range of validity of many LJ EOS is either far too optimistic or pessimistic. Information on the reported range of validity of each LJ EOS is given in the Supplementary Material.

III. EVALUATION OF LJ EOS

Table VII in the Appendix summarizes the reference database adopted from Ref.¹¹, which contains approximately 35,000 data points. These data are also available electronically in the Supplementary Material, such that the tests of the different LJ EOS that were carried out in the present work can easily be reproduced and the approach can be extended to the evaluation of new LJ EOS. Data points that were identified as outliers in Ref.¹¹ were discarded for the comparison in the present work. The reference data was not differentiated here regarding the source of the data points. However, also that information can be retrieved from the electronic Supplementary Material. Moreover, the reference data was produced

over the last decades by a large number of different source codes and will in general differ in system size, simulation time, cut-off radius, time step, the employed long-rang correction scheme etc. Hence, finite-size effects may have been treated differently for the production of that large entity of reference data. See Ref.¹¹ for a detailed discussion of the reference data and the algorithm used for the identification of gross outliers.

As the results from computer simulations are subject to both systematic and statistical errors^{11,93,94}, the true value of a given property of the LJ fluid at a given state point is only known with some uncertainty. That uncertainty depends on the property that is investigated as well as on the state point. Furthermore, the uncertainty can only be estimated and, depending on the way this estimate is carried out, different numbers for the uncertainty are obtained. We do not re-enter into the discussion of the quality of the reference data and simply refer to Ref.¹¹. The goal of any description of properties of the LJ fluid by an EOS must be to describe the primary data within their uncertainty. Ideally, this should be fulfilled for all properties of interest in the entire fluid region.

The systematic approach for the comparison of the LJ EOS that was applied in the present work is briefly described in the following. The performance of each LJ EOS i was examined for different thermophysical properties j and fluid regions k regarding data points l from computer experiments.

The relative deviation δY_{ijkl} of a result Y_{ijkl} from an LJ EOS i from the corresponding computer experiment $Y_{\text{ref},jkl}$ for a given property j in a given fluid region k is defined as

$$\delta Y_{ijkl} = \frac{Y_{ijkl} - Y_{\text{ref},jkl}}{Y_{\text{ref},jkl}} . \quad (2)$$

The complete set of numeric values Y_{ijkl} computed for each data point l from the database¹¹ for each LJ EOS i is provided in the electronic Supplementary Material together with the corresponding reference value $Y_{\text{ref},jkl}$. Where available, also the statistical uncertainties from the computer experiment data are given.

The absolute average deviation AAD_{ijk} of a given LJ EOS i for a thermophysical property j in a fluid region k is defined as

$$\text{AAD}_{ijk} = 1/N_{jk} \sum_{l=1}^{N_{jk}} |\delta Y_{ijkl}| , \quad (3)$$

where N_{jk} is the number of reference data points for the respective property j in the fluid

region k . Hence, the AAD_{ijk} quantifies the performance of an LJ EOS for a certain property j in a certain fluid region k . The overall performance of an LJ EOS i for a given property j was evaluated using

$$\text{AAD}_{ij} = 1/N_{\text{tot}} \sum_{l=1}^{N_{\text{tot}}} |\delta Y_{ijl}|, \quad (4)$$

where N_{tot} is the number of data points available for a given property j . For clarity and simplicity we sometimes refer to AAD_{ij} for a given property j simply as $\text{AAD}_{j,\text{total}}$ in the following text, when it is clear which LJ EOS i is meant.

The classification into different fluid regions k is only used for homogeneous state data points specified as $Y = Y(T, \rho)$. Fig. 1 shows the eight fluid regions that were used in the present work for the classification of $Y = Y(T, \rho)$ data. Table II summarizes the conditions for each region. The binodal was adopted from an analytic correlation of *Stephan et al.*¹¹, and the freezing line from *Köster et al.*²¹. The line separating data in the high density liquid and high density supercritical region was chosen as 95% of the density of the freezing line reported by *Köster et al.*²¹. Since only very few computer experiment data has been reported for the unstable region^{11,69,95} obtained from specialized techniques and the location of the spinodal is only known with large uncertainty (see below), the metastable and unstable region were combined for the comparison to a single region enclosed by the binodal. An eighth characteristic region was defined at extreme temperatures $T > 6$, i.e. the supercritical and high density supercritical region end at $T = 6$. All data points from the database¹¹ of the type $Y = Y(T, \rho)$ were assigned to one of these eight regions. The allocation of each data point is reported in the electronic Supplementary Material. Data points that are specified as $Y = Y(T)$, namely VLE properties, virial coefficients, and spinodal data, belong to individual fluid regions.

For each LJ EOS i , the obtained AAD_{ijk} for each property j and each region k and AAD_{ij} are reported in Tables III - V and are discussed in the following sections.

TABLE II. Definition of characteristic fluid regions, cf. Fig. 1. The correlations for the bubble line $\rho'(T)$, the dew line $\rho''(T)$, and the freezing line $\rho'''(T)$ were adopted from Refs.^{11,21}. The employed critical parameters are $T_c = 1.321$ and $\rho_c = 0.316$.

	Name	Abbr.	$T_{\min}$	$T_{\max}$	$\rho_{\min}$	$\rho_{\max}$	comment
	gas	G	≥ 0.66	< 1.321	-	$< \rho''$	(a)
	liquid	L	≥ 0.66	< 1.321	$> \rho'$	$< 0.95\rho'''$	(a)
	high density liquid	HD-L	≥ 0.66	< 1.321	$\geq 0.95\rho''$	$< \rho'''$	
	critical	C	≥ 1.3	< 1.45	> 0.21	< 0.44	
	metastable & unstable	MU	≥ 0.66	< 1.321	$> \rho''$	$< \rho'$	(a)
	supercritical	Su	≥ 1.321	≤ 6	-	$< 0.95\rho'''$	(a)
	high density supercritical	HD-Su	≥ 1.321	≤ 6	$\geq 0.95\rho'''$	$< \rho'''$	
	extreme temperature	Ex-T	> 6	-	-	-	

(a) excluding critical region C

FIG. 1. Definition of characteristic fluid regions (colored) of the LJ fluid used for the evaluation and comparison of LJ EOS in the present work: metastable/ unstable (MU), gas (G), liquid (L), critical (C), supercritical (Su), high density liquid (HD-L), high density supercritical (HD-Su), and extreme temperature (Ex-T). Details on the boundaries of the regions are given in Table II. Solid states and the melting region were not considered in the present study.

1. Vapor-Liquid Equilibrium

The vapor-liquid equilibrium of the LJ fluid has been investigated numerous times^{10,11,18,78,96–135}. Seven of these 45 data sets were found to be significantly more precise and accurate than the remaining¹¹. Only these seven best data sets were used here for the comparison, cf. Table VII in the Appendix. However, also these seven data sets contain eight clear outliers¹¹ that were discarded for the present investigation. The mutual agreement of these seven data sets was 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 point¹¹. Furthermore, empirical correlations of these seven best datasets for p^s , Δh_v , ρ' , and ρ'' have been proposed in Ref.¹¹. The relative deviations of the VLE properties are shown in Fig. 2 (vapor pressure p^s and the enthalpy of vaporization Δh_v) and in Fig. 3 (saturated liquid and vapor density ρ' and ρ'' , respectively). The baselines are the empirical correlations from Ref.¹¹, other lines are the LJ EOS, and symbols indicate reference data from the computer experiments. Table III lists the $\text{AAD}_{j,\text{total}}$ as defined by Eq. (4) obtained from the reference VLE data up to $T = 1.29$ and each of the 20 considered LJ EOS for $j = \rho'$, ρ'' , p^s , Δh_v . The VLE computed from each of the considered LJ EOS are reported in the electronic Supplementary Material.

FIG. 2. Comparison of results from 20 LJ EOS with reference data: relative deviation of the vapor pressure (top) and enthalpy of vaporization (bottom). The base line indicates the respective correlation of computer experiment data of *Stephan et al.*¹¹. The other lines are results from the LJ EOS; symbols are data from computer experiment.

The LJ EOS of *Thol et al.*³⁷, *Mecke et al.*^{70,71}, *Kolafa and Nezbeda*⁵⁷, *Gottschalk*⁸³, and from the present work show the best agreement with the VLE simulation results. Nevertheless, the LJ EOS of *Thol et al.*³⁷, *Mecke et al.*^{70,71}, *Gottschalk*⁸³, and the LJ EOS from the present work exhibit minor systematic deviations from the simulation results in the saturated liquid density at $T > 1$. Only the LJ EOS of *Kolafa and Nezbeda*⁵⁷ captures this trend correctly.

FIG. 3. Comparison of results from 20 LJ EOS with reference data: relative deviation of the saturated densities: liquid density (top) and vapor density (bottom). The base line indicates the correlation of computer experiment data of *Stephan et al.*¹¹. The other lines are results from the LJ EOS; symbols are data from computer experiment.

The LJ EOS of *Johnson et al.*⁵⁶, *May and Mausbach*^{80,81}, *Sun & Teja*⁷², *Lafitte et al.*⁴², and *van Westen and Gross*⁸² also give a good description of the VLE properties of the LJ fluid. However, the LJ EOS of *Lafitte et al.*⁴², *van Westen and Gross*⁸², and *Johnson et al.*⁵⁶ exhibit distinct systematic deviations from the reference data of the vapor pressure and the saturated densities. The LJ EOS of *May and Mausbach*^{80,81} exhibits noticeable deviations regarding the saturated liquid density at $T > 1$.

Particularly large deviations from the computer experiment VLE data are found for the LJ EOS of *Nicolas et al.*¹², *Miyano*⁶⁹, *Boltachev and Baidakov*⁷⁶, *Adachi et al.*³⁰, *Cotterman et al.*²⁹, *Paricaud*⁷⁷, *Hess*⁷⁵, *Koutras et al.*⁶⁸, *Ree*²⁸, and *Quiñones-Cisneros et al.*⁷⁹.

All considered LJ EOS are fully analytic and thereby exhibit classical scaling behavior, e.g. quadratic convergence of the saturated densities near the critical point^{136–138}. This, and the fact that the investigated LJ EOS have significantly differing critical temperatures (see following section), leads to the diverging deviations of the VLE properties in Figs. 2 and 3 in the vicinity of the critical point. Also the scattering of the computer experiment VLE data significantly increases in the vicinity of the critical point and, accordingly, only very few consistent data points are available in that region¹¹.

For each VLE property j , the lowest absolute average deviation AAD_{ij} among the considered LJ EOS i in Table III is in good agreement with the stated mutual agreement of the best computer experiment data, which indicates that the lowest absolute average deviation values are in fact good guesses for the accuracy of the reference data.

TABLE III. Comparison of results from 20 LJ EOS i with reference data, cf. Table VII: absolute average deviations AAD_{ijk} given as percentage values (cf. Eq. 4) for the vapor-liquid equilibrium region k with the properties $j =$ vapor pressure p^s , saturated liquid and vapor densities ρ' and ρ'' , enthalpy of vaporization Δh_v , and the corresponding spinodal properties – excluding the region in the vicinity of the critical point ($T > 1.29$). # indicates the number of data points available. The EOS of *Gottschalk*⁸³ and *Thol et al.*³⁷ yield unphysical results in the two-phase region and were therefore not applied for the computation of the spinodal (see Supplementary Material for details). The lines 'total' states the mean AAD_i for all binodal and spinodal VLE data, respectively.

	#	Cotterman et al. ²⁹	Particaud ⁷⁷	Lafitte et al. ⁴²	van Westen & Gross ⁸²	this work	Kourtas et al. ⁶⁸	Kolafa & Nezbeda ⁵⁷	Mecke et al. ^{70,71}	Hess ⁷⁵	Bolachev and Baidakov ⁷⁶	Gottschalk ⁸³	Quinones-Cisneros et al. ⁷⁹	Nicolas et al. ¹²	Adachi et al. ³⁰	Miyano ⁶⁹	Johnson et al. ⁵⁶	Sun & Teja ⁷²	May & Mautsbaach ^{80,81}	Ree ²⁸	Thol et al. ³⁷
<i>binodal</i>																					
ρ'	72	0.6	1.4	0.7	1.3	0.1	0.5	0.1	0.2	4.6	1.2	0.3	0.6	2.5	6.9	0.5	0.3	0.3	0.6	3.3	0.1
ρ''	72	6.3	5.7	1.8	2.4	0.9	10.8	1.1	1.0	47.1	10.0	0.6	8.4	8.2	13.5	4.6	2.0	1.1	1.5	7.8	1.0
p^s	72	6.6	1.9	2.7	3.0	0.5	5.6	0.5	0.5	40.7	7.9	0.5	6.7	4.6	10.9	3.8	1.6	0.9	0.9	3.2	0.5
Δh_v	53	4.0	4.3	1.3	1.4	0.5	10.5	0.6	0.5	40.3	6.2	0.4	10.4	5.3	8.9	1.1	0.6	0.7	0.9	6.1	0.5
total	269	4.4	3.3	1.6	2.1	0.5	6.6	0.6	0.5	32.6	6.3	0.5	6.2	5.2	10.1	2.6	1.2	0.8	1.0	5.0	0.5
<i>spinodal</i>																					
ρ' spin	3	2.3	3.3	1.0	0.7	0.9	4.3	0.5	0.7	2.3	0.7	-	2.3	3.3	3.4	2.5	1.1	1.7	2.2	2.2	-
ρ'' spin	9	8.6	17.0	12.1	12.4	9.0	14.7	4.8	4.0	11.8	5.6	-	9.3	10.6	8.3	7.0	5.7	9.6	6.3	24.1	-
p^s spin	7	6.2	20.6	16.8	16.3	10.8	23.0	5.2	4.2	6.3	5.7	-	15.0	12.8	11.8	7.6	6.4	11.7	7.2	30.4	-
total	19	6.7	16.1	12.1	12.0	8.4	16.1	4.3	3.5	8.3	4.9	-	10.3	10.3	8.8	6.5	5.2	9.1	6.0	23.0	-

2. Critical Point

Critical data derived from computer experiment data of the LJ fluid have been reported several times in the literature^{8,28,61,67,78,99,100,104,108,113,116,118,119,121,139–152}. They were summarized and assessed in Ref.¹¹. The critical data of the LJ fluid were thereby estimated to be $T_c = 1.321 \pm 0.007$ and $\rho_c = 0.316 \pm 0.005$ and $p_c = 0.129 \pm 0.005$ ¹¹. These values are referred to as ‘computer experiment’ critical data in the following. They were obtained from a large number of critical data for the LJ fluid reported in the literature and cross-evaluation with the most reliable VLE data available in the vicinity of the critical point¹¹. The given uncertainties were estimated from the mutual agreement of the reported data. The uncertainties for example account for differences in the extrapolation to infinite systems, different cut-off radius, etc.

The numeric values of the critical data computed from the LJ EOS are reported in the Supplementary Material. Fig. 4 shows the comparison of the critical data obtained from the LJ EOS and the computer experiment values with their uncertainties. The critical data from the LJ EOS scatter in a large range compared to the uncertainty of the critical data from the computer experiments. Six LJ EOS (Refs. ^{12,68,69,75,77,82}) have particularly large deviations from the computer experiment critical point. Many LJ EOS show fair agreement with the critical density from the computer experiments, but a significant overestimation of the critical temperature and pressure is found in most cases, which is due to the scaling behavior of the EOS^{136–138}. The critical pressure obtained from the vast majority of LJ EOS lies within a narrow band in the $p - T$ diagram. The width of that band is similar to the estimated uncertainty of the critical pressure from the computer experiments $\delta p_c = \pm 0.005$. Hence, the deviation of the critical point computed from the LJ EOS is mainly a result of the mismatching critical temperature – as expected from the scaling behavior.

The critical parameters obtained from the LJ EOS of *Johnson et al.*⁵⁶, *Lafitte et al.*⁴², *May and Mausbach*^{80,81}, and *Thol et al.*³⁷ are in excellent agreement with the computer experiment, which is surprising considering the fact that they are analytic EOS and therefore should not be accurate in the vicinity of the critical point. *Lafitte et al.*⁴² assume that the applied third order perturbation term is responsible for the relatively low critical temperature of their LJ EOS. However, the LJ EOS of *van Westen and Gross*⁸² significantly overestimates the critical temperature of the computer experiment, but also includes higher

FIG. 4. Critical point of the LJ fluid. Top: critical pressure over temperature. Bottom: critical density over temperature. Each combination of a star & abbreviation indicates the critical parameters from an LJ EOS. The abbreviations are the same as those in Table I. The blue shaded area indicates the critical parameters from computer experiments and their uncertainties¹¹. The solid lines indicate the correlations of the respective VLE properties from Stephan et al.¹¹. The numeric values of the critical parameters obtained from the LJ EOS are reported in the Supplementary Material.

order perturbation terms. Despite its good results for the critical data, the LJ EOS of Thol et al.³⁷ has a relatively poor performance for state points in the vicinity of the critical point, even crossing isotherms are observed (see next section). This poor performance is probably also related to the presence of a second spurious critical point at $T_c = 1.30351$, $\rho_c = 0.31027$, $p_c = 0.12124$ obtained from the LJ EOS of Thol et al.³⁷, see also Refs.^{83,153}.

The critical parameters obtained from the LJ EOS of Cotterman et al.²⁹, Kolafa and Nezbeda⁵⁷, Mecke et al.^{70,71}, Quiñones-Cisneros et al.⁷⁹, Gottschalk⁸³, and the LJ EOS from the present work are generally in reasonable agreement with critical data from the computer simulations, but they overestimate the critical temperature T_c by about 0.01 ... 0.02. The

LJ EOS of *Paricaud*⁷⁷, *Hess*⁷⁵, and *Ree*²⁸ overestimate the critical temperature by about 0.06 .. 0.09.

3. Isotherms in the Two-Phase Region and Spinodal

Equations of state should exhibit only a single van der Waals loop in the two-phase region. Multiple oscillations of isotherms are prohibitive for calculating interfacial properties, e.g. with density gradient theory^{154–158}. Furthermore, isotherms in the two-phase region can show artificial undulations around the general course of the van der Waals loop, which have a smaller amplitude than that of the van der Waals loop. Another problem that can occur are crossing isotherms (multiplicity).

In this section, the behavior of the LJ EOS is characterized regarding the behavior of isotherms in the two-phase region in the $p - \rho$ diagram and the spinodal. The results from the quantitative comparison of the LJ EOS with computer experiment data of the type $Y = Y(T, \rho)$ for state points between the binodals with LJ EOS are discussed in the subsequent section.

The isotherms in the $p - \rho$ diagram of all 20 considered LJ EOS were examined in the temperature range $T = 0.5 \dots 1.32$ regarding the following features in the two-phase region: the number of zero crossings of $dp/d\rho = 0$ and $d^2p/d\rho^2 = 0$; the results are summarized in Fig. 5. The numeric values of four isotherms in the two-phase region are reported in the electronic Supplementary Material.

Most theoretically-based LJ EOS show none of the problems mentioned above in the two-phase region, whereas most empirical and semi-theoretical LJ EOS show at least some artifacts in the two-phase region. The LJ EOS of *Gottschalk*⁸³ and *Thol et al.*³⁷ exhibit multiple minima and maxima in a wide temperature range, cf. Fig. 5. The LJ EOS of *Thol et al.*³⁷ exhibits artificial oscillations up to extreme negative and positive pressures (details are given in the Supplementary Material), which results in a crossing of isotherms^{34–36} not only in the two-phase region but also the supercritical region. For both the LJ EOS of *Gottschalk*⁸³ and *Thol et al.*³⁷ for some temperatures above the triple point temperature, two subcritical isotherms may cross each other (in the two-phase region) as well as a subcritical and a supercritical isotherm may cross (above the critical temperature). For the LJ EOS of *Boltachev and Baidakov*⁷⁶, supercritical isotherms above $T \gtrsim 2$ exhibit a maximum and

FIG. 5. Number of zero crossings of the first and second derivative of the p – ρ isotherms ($dp/d\rho = 0$ and $d^2p/d\rho^2 = 0$) in the two-phase region as a function of the temperature for all 20 considered LJ EOS. The top panel indicates the number of $dp/d\rho = 0$ at a given temperature; the bottom panel indicates the number of $d^2p/d\rho^2 = 0$. The desired values are: two for the upper panel and one for the lower panel and are indicated in green. The abbreviations for the LJ EOS are the same as in Table I.

minimum that also yields a crossing of isotherms. For $T \gtrsim 2.6$, supercritical isotherms of the LJ EOS of *Boltachev and Baidakov*⁷⁶ may even cross the vapor-liquid phase boundary.

The LJ EOS of Refs. ^{56,70,71,80,81} exhibit multiple extrema only in the vicinity or below the triple point temperature. For the LJ EOS of *Boltachev and Baidakov*⁷⁶, isotherms exhibit

a second (unphysical) maximum in the homogeneous high density region, which yields large deviations from reference data in that region (see following section).

Several LJ EOS also exhibit undulations of the isotherms between the binodals in the $p - \rho$ diagram. This leads to the fact that the isotherms in the $p - \rho$ diagram of the LJ EOS of *Johnson et al.*⁵⁶, *May and Mausbach*^{80,81}, *Nicolas et al.*¹², *Mecke et al.*^{70,71}, *Boltachev and Baidakov*⁷⁶, *Kolafa and Nezbeda*⁵⁷, and *Adachi et al.*³⁰ exhibit a single van der Waals loop, but multiple turning points. The isotherms of the LJ EOS of *Miyano*⁶⁹, *Lafitte et al.*⁴², *Koutras et al.*⁶⁸, and the LJ EOS from the present work exhibit such turning points only below the triple point temperature, cf. Fig. 5 - bottom.

For most of the investigated LJ EOS, the undulations of the isotherms in the two-phase region decrease with increasing temperature and vanish upon approaching the critical point (see the Supplementary Material). The only exception is the LJ EOS of *Thol et al.*³⁷, which exhibits large oscillations up to the critical temperature.

LJ EOS with isotherms with a single and smooth van der Waals loop in the entire considered temperature range (cf. Fig. 5) are those of *Cotterman et al.*²⁹, *Paricaud*⁷⁷, *Quiñones-Cisneros et al.*⁷⁹, *Hess*⁷⁵, *Ree*²⁸, and *van Westen and Gross*⁸². The isotherms of the LJ EOS of *Sun and Teja*⁷², *Lafitte et al.*⁴², and the LJ EOS from the present work exhibit very small undulations between the binodals above the triple point – without producing a second turning point in the isotherms (see electronic Supplementary Material).

Recently, *Alsaiifi*¹⁵³ carried out a study on the behavior of six empirical and semi-theoretical LJ EOS^{12,37,56,57,70,71,80,81} regarding possible artificial phenomena. The findings for these six LJ EOS are in line with the results from the present work.

Data derived from computer experiments for the spinodal of the LJ fluid have been reported by *Baidakov et al.*¹²² and *Linhart et al.*¹⁵⁹. This data was compared with the spinodals computed from the 20 LJ EOS that were considered here. The bottom section of Table III reports the obtained absolute average deviations. In the assessment of the deviations, it must be considered that only few reference data points are available that are also subject to strong scattering (see Supplementary Material).

The LJ EOS of *Mecke et al.*^{70,71}, *Kolafa and Nezbeda*⁵⁷, *Boltachev and Baidakov*⁷⁶, and *Johnson et al.*⁵⁶ yield the best agreement with the spinodal reference data. Due to the artificial oscillatory behavior of the isotherms from the LJ EOS of *Gottschalk*⁸³ and *Thol et al.*³⁷, no unique spinodal can be obtained from those LJ EOS. We computed the spinodal

for the first maximum and minimum and report the results in the electronic Supplementary Material for completeness.

4. Homogeneous Fluid States

In the present section, the performance of the LJ EOS for describing thermodynamic properties of homogeneous fluid state points is discussed, which are calculated as $Y = Y(T, \rho)$. The considered states are grouped in the fluid regions k shown in Fig. 1. The reference data of each property j of that type (cf. Table VII in the Appendix) was compared with the corresponding results of each of the LJ EOS i . The obtained numbers for AAD_{ijk} and AAD_{ij} , cf. Eq. (3) and (4), are reported in Tables IV - V. Since several LJ EOS have extremely large deviations from the reference data (many orders of magnitude) in the extreme temperature region $k = \text{Ex-T}$, which would lead to a meaningless total AAD_{ij} , the Ex-T results were not comprised in the AAD_{ij} calculation but are reported separately in Table V instead.

TABLE IV. Comparison of results from 20 LJ EOS i with reference data, cf. Table VII (outliers identified in the data set¹¹ were discarded): absolute average deviations AAD_{ijk} given in percentages (cf. Eq. 3) for different thermodynamic properties j for homogeneous state points in different regions k . The last line ‘total’ of each section gives the mean AAD_{ik} (cf. Eq. 4). # is the number of data points.

pvT data		#	Cotterman et al. ²⁹	Paricaud ⁷⁷	Lafitte et al. ⁴²	van Westen & Gross ⁸²	this work	Koutas et al. ⁶⁸	Kolafa & Nezbeda ⁵⁷	Mecke et al. ^{70,71}	Hess ⁷⁵	Boltachev and Baidakov ⁷⁶	Gottschalk ⁸³	Quinones-Cisneros et al. ⁷⁹	Nicolas et al. ¹²	Adachi et al. ³⁰	Miyano ⁶⁹	Johnson et al. ⁵⁶	Sun & Teja ⁷²	May & Mausbach ^{80,81}	Ree ²⁸	Thol et al. ³⁷
G	169	1.2	1.0	1.0	0.9	0.8	0.1	2.4	0.1	0.1	0.8	0.1	0.1	1.0	0.6	0.9	0.6	0.2	0.2	0.1	1.2	0.1
L	537	15.2	9.5	6.4	6.4	8.1	2.8	11.6	3.4	3.0	65.8	16.4	2.9	5.0	8.6	21.0	8.2	3.6	5.0	5.1	16.9	2.9
HD-L	233	32.0	5.6	18.6	10.6	10.6	3.9	6.8	3.4	3.1	87.7	40.8	3.2	3.5	6.8	7.3	6.9	3.1	5.0	6.2	5.4	3.2
MU	495	14.9	23.5	13.9	20.7	20.7	7.8	21.7	7.1	6.1	89.5	14.5	167.3	15.4	28.7	35.8	11.1	7.5	8.1	14.4	51.9	528.7
C	225	4.6	6.5	5.0	4.0	4.0	2.1	3.1	2.1	2.1	27.4	4.1	2.1	2.3	4.5	13.5	3.7	3.7	4.2	3.1	9.0	2.3
Su	1715	2.7	2.1	2.0	2.3	2.3	1.5	10.5	0.5	0.5	4.2	3·10 ³	0.5	1.1	1.9	3.6	1.3	0.7	1.5	0.6	1.9	0.5
HD-Su	152	4.4	9.6	10.4	12.8	12.8	5.6	20.4	0.2	0.2	4.3	3·10 ⁴	0.1	3.9	0.3	1.1	0.2	0.2	1.2	0.2	1.3	0.2
total	3526	8.4	7.0	5.9	6.8	6.8	2.9	11.6	2.1	1.9	32.4	3·10 ³	24.5	4.1	7.1	11.4	4.2	2.4	3.3	3.7	11.8	75.3
2 nd and 3 rd virial coefficient																						
B	359	12.6	0.6	5.4	4.1	4.1	13.2	56.8	0.4	1.0	0.0	0.6	0.0	146.7	9.3	1.4	0.6	1.4	3.4	1.4	41.9	1.1
C	393	317.5	299.0	115.4	100.0	110.8	159.3	159.3	53.2	46.6	50.0	22.6	25.9	170.9	253.4	254.2	74.5	123.8	134.0	103.9	338.7	7.7
total	752	171.9	156.5	62.9	54.2	64.2	64.2	110.4	28.0	24.8	26.1	12.1	13.5	159.4	136.9	133.5	39.2	65.4	71.6	55.0	197.0	4.6

continued on next page

#	Cotterman et al. ²⁹	Particaud ⁷⁷	Laftite et al. ⁴²	van Westen & Gross ⁸²	this work	Koutras et al. ⁶⁸	Kolafa & Nezbeda ⁵⁷	Mecke et al. ^{70,71}	Hess ⁷⁵	Botlachev and Baidakov ⁷⁶	Gottschalk ⁸³	Quinones-Cisneros et al. ⁷⁹	Nicolas et al. ¹²	Adachi et al. ³⁰	Miyano ⁶⁹	Johnson et al. ⁵⁶	Sun & Teja ⁷²	May & Mausbach ^{50,81}	Rec ²⁸	Thol et al. ³⁷	
Internal energy u^{res}																					
G	174	13.3	5.1	9.7	6.7	1.5	2·10 ⁴	0.5	0.4	0.8	0.3	0.3	29.7	5.3	2.5	1.2	0.9	3.6	1.1	18.7	0.3
L	438	4.5	0.8	0.4	0.4	0.3	623.3	0.1	0.1	24.1	6.7	0.1	6.2	0.2	5.2	0.2	0.1	0.2	0.5	0.8	0.1
HD-L	212	3.3	1.1	0.6	0.5	0.5	2·10 ³	0.3	0.3	33.6	15.8	0.3	14.2	0.4	8.1	0.5	0.4	0.4	0.9	0.3	0.3
MU	307	6.6	4.6	6.3	5.0	2.5	2·10 ⁴	0.6	0.6	21.6	3.6	0.3	18.3	3.5	7.2	1.9	1.3	3.1	2.1	11.7	0.5
C	185	4.9	4.6	3.9	5.1	1.6	484.4	1.0	1.1	10.0	1.9	0.8	12.9	2.7	1.2	2.0	0.9	1.9	1.2	10.8	1.0
Su	1492	5.4	2.8	2.2	2.3	6.8	4·10 ³	0.3	0.3	4.6	1·10 ⁴	0.3	7.7	1.1	3.6	1.1	0.7	1.3	0.6	3.0	0.2
HD-Su	139	10.2	13.3	20.6	22.3	36.0	2·10 ³	0.9	0.7	9.0	2·10 ⁵	0.5	9.4	1.8	13.9	0.8	2.2	4.8	3.0	1.2	0.3
total	2947	5.9	3.3	3.7	3.5	5.7	5·10 ³	0.4	0.3	11.7	2·10 ⁴	0.3	10.8	1.5	4.8	1.1	0.8	1.6	0.9	4.7	0.3
Isochoric heat capacity c_v																					
G	151	2.4	4.7	6.0	5.0	4.4	1·10 ⁴	1.1	0.9	2.5	2.0	0.5	4.2	3.4	2.5	3.3	1.7	4.1	2.3	10.5	0.4
L	205	3.9	3.3	4.3	1.8	5.3	1·10 ⁴	0.4	0.4	121.8	208.1	2.4	99.0	2.5	41.2	1.8	2.5	1.6	6.8	3.5	0.4
HD-L	57	9.5	2.9	5.3	1.6	9.6	3·10 ⁴	0.7	0.7	212.5	730.5	4.9	235.1	1.8	51.3	1.1	10.2	3.1	28.8	0.9	0.5
MU	113	10.7	9.8	11.6	9.4	10.1	4·10 ⁴	4.6	3.7	103.5	65.5	10.6	135.9	6.7	32.6	7.0	7.9	8.4	15.6	16.2	16.6
C	152	18.1	20.3	18.4	20.2	17.5	3·10 ³	10.1	8.1	9.6	30.7	3.2	16.0	14.5	7.7	19.1	9.1	19.6	14.8	30.5	42.9
Su	1160	3.9	2.9	1.7	2.0	4.2	3·10 ³	0.4	0.3	12.6	2·10 ³	0.5	9.7	1.6	6.6	2.0	1.2	2.3	2.0	5.6	0.4
HD-Su	53	4.8	4.8	1.0	1.1	16.4	2·10 ³	0.6	0.3	20.6	2·10 ⁴	0.5	6.0	1.3	14.9	0.7	2.9	2.7	3.5	0.7	0.3
total	1891	5.5	5.0	4.4	4.1	6.3	7·10 ³	1.5	1.2	35.1	2·10 ³	1.7	33.7	3.2	13.3	3.7	2.7	4.2	5.3	8.1	4.8
Isobaric heat capacity c_p																					
G	92	1.9	4.7	5.3	4.3	2.4	8·10 ³	0.5	0.4	0.9	0.8	0.2	5.4	3.3	2.6	1.3	1.1	2.9	1.3	9.8	0.3
L	156	4.7	2.9	3.5	2.9	3.7	6·10 ³	1.4	1.5	77.0	187.8	2.5	51.1	3.5	22.8	2.4	2.6	2.4	4.8	2.2	1.4
HD-L	45	7.1	4.6	4.1	2.5	8.1	1·10 ⁴	0.7	0.8	130.8	2·10 ³	2.8	112.6	2.1	35.0	1.4	6.2	2.7	18.7	2.0	0.9
MU	6	15.8	95.9	29.4	14.0	27.2	2·10 ⁴	29.2	30.7	77.6	26.5	30.5	48.8	109.4	23.7	22.3	26.9	23.1	24.2	45.8	68.7
C	101	26.4	332.9	28.5	82.2	26.6	432.4	29.9	30.6	977.1	30.7	25.2	29.0	1·10 ³	36.4	101.1	35.8	28.2	27.5	839.4	30.2
Su	934	4.4	3.8	3.0	2.9	3.7	1·10 ³	2.0	2.0	14.6	4·10 ³	2.0	6.3	3.3	5.5	2.7	2.3	2.7	2.5	5.3	2.0
HD-Su	43	6.6	4.5	5.1	3.2	10.9	2·10 ³	1.2	0.9	15.2	4·10 ⁴	1.0	4.9	1.4	11.9	1.6	2.6	2.6	3.1	1.6	0.6
total	1377	6.1	28.3	5.3	8.8	5.8	3·10 ³	4.0	4.0	95.4	4·10 ³	3.8	16.6	81.1	10.8	9.8	4.9	4.6	5.1	66.4	4.1
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#	Helmholtz energy	$\bar{\mu}^{\text{res}}$	Cotterman et al. ²⁹	Particaud ¹⁷	Lafitte et al. ⁴²	van Westen & Gross ⁸²	this work	Koutras et al. ⁶⁸	Kolafa & Nezbeda ⁵⁷	Mecke et al. ^{70,71}	Hess ⁷⁵	Boltachev and Baidakov ⁷⁶	Gottschalk ⁸³	Quinones-Cisneros et al. ⁷⁹	Nicolas et al. ¹²	Adachi et al. ³⁰	Miyano ⁶⁹	Johnson et al. ⁵⁶	Sun & Teja ⁷²	May & Mausbach ^{80,81}	Rec ²⁸	Thol et al. ³⁷
G	95	11.4	2.2	5.1	3.0	0.2	4·10 ⁴	0.1	0.1	0.5	0.1	0.1	18.7	1.9	1.8	0.8	0.7	0.8	0.4	2.8	0.1	
L	136	2.4	0.3	1.4	1.3	0.3	2·10 ³	0.3	0.3	15.2	1.9	0.3	1.4	1.9	3.6	1.8	0.5	0.4	0.3	1.4	0.3	
HD-L	49	2.6	0.9	1.7	1.7	0.8	2·10 ³	0.8	0.8	23.0	5.4	0.8	3.1	2.2	4.1	2.0	0.8	1.0	0.8	1.5	0.8	
MU	155	5.2	1.6	2.8	2.2	0.3	7·10 ³	0.2	0.2	12.9	1.6	0.2	6.8	1.8	2.6	1.3	0.7	0.7	0.5	2.4	0.8	
C	34	2.1	2.1	2.3	2.8	0.3	4·10 ³	0.1	0.1	7.1	0.2	0.1	0.8	0.5	4.4	3.4	0.9	0.2	0.2	1.0	0.1	
Su	224	8.3	1.6	3.4	3.3	4.2	5·10 ⁴	0.7	0.6	7.8	1·10 ³	0.6	15.1	5.2	8.7	6.6	1.9	2.0	0.5	10.6	0.5	
HD-Su	25	5.2	6.5	6.5	8.8	4.1	3·10 ³	2.1	2.1	15.9	2·10 ⁴	2.2	3.7	4.9	8.9	4.4	1.6	3.1	2.1	3.3	2.1	
total	718	6.1	1.6	3.0	2.7	1.7	2·10⁴	0.5	0.4	10.6	1·10³	0.4	9.3	3.0	5.0	3.2	1.1	1.2	0.5	4.7	0.5	
Chemical potential μ^{res}																						
G	105	10.0	3.0	5.0	3.2	0.2	2·10 ⁴	0.2	0.2	1.1	0.1	0.0	13.9	2.3	2.4	1.3	0.7	0.8	0.4	3.6	0.1	
L	205	4.2	3.4	8.0	9.3	1.5	3·10 ³	1.5	1.4	59.3	71.7	1.7	3.5	7.0	12.4	5.3	2.2	6.9	2.0	3.3	1.4	
HD-L	103	14.6	3.5	25.3	25.6	6.6	3·10 ³	2.9	2.6	116.5	194.3	2.9	4.7	11.3	7.0	7.7	3.3	12.7	5.7	3.3	2.7	
MU	153	3.8	2.9	2.9	2.5	0.7	4·10 ³	0.3	0.3	13.2	1.5	0.2	5.3	2.6	3.0	1.2	0.8	1.1	1.0	5.4	0.4	
C	39	0.6	1.3	2.2	2.4	0.4	2·10 ³	0.3	0.1	10.1	0.7	0.1	0.4	1.2	5.3	2.9	0.9	0.7	0.3	2.1	0.2	
Su	206	7.0	2.8	3.5	4.1	3.8	3·10 ⁴	0.3	0.3	9.3	4·10 ³	0.3	10.3	5.0	9.3	4.9	1.5	2.8	0.5	7.8	0.2	
HD-Su	26	6.2	12.0	11.8	14.9	7.4	3·10 ²	0.3	0.4	6.1	4·10 ⁴	0.3	5.3	5.3	2.0	0.6	0.5	1.7	0.3	1.1	0.4	
total	837	6.7	3.3	7.6	7.9	2.5	1·10⁴	0.9	0.8	34.4	2·10³	0.9	6.8	5.2	7.4	4.0	1.6	4.3	1.6	4.7	0.8	

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#	Cotterman et al. ²⁹	Particaud ⁷⁷	Laftite et al. ⁴²	van Westen & Gross ⁸²	this work	Koutras et al. ⁶⁸	Kolafa & Nezbeda ⁵⁷	Mecke et al. ^{70,71}	Hess ⁷⁵	Botlachev and Baidakov ⁷⁶	Gottschalk ⁸³	Quñones-Cisneros et al. ⁷⁹	Nicolas et al. ¹²	Adachi et al. ³⁰	Miyano ⁶⁹	Johnson et al. ⁵⁶	Sun & Teja ⁷²	May & Mausbach ^{80,81}	Ree ²⁸	Thol et al. ³⁷	
Thermal expansion coefficient α																					
G	86	2.5	4.0	4.0	3.1	1.1	8.1	0.3	0.3	0.8	0.3	0.2	5.7	3.0	2.5	0.5	0.9	1.9	0.8	6.9	0.3
L	126	8.2	4.2	6.2	4.5	3.0	8.8	2.2	2.3	22.0	251.3	2.3	2.5	4.5	9.3	3.3	2.6	2.7	4.0	2.2	2.2
HD-L	44	16.1	5.4	13.4	9.5	8.5	3.5	1.3	1.4	32.1	926.2	3.1	2.2	3.7	12.1	1.7	2.8	1.3	18.0	3.9	1.7
MU	7	25.1	30.6	30.6	32.8	32.6	20.3	34.5	36.6	92.6	38.1	37.9	37.0	39.0	42.4	39.4	38.3	33.8	25.5	34.5	34.0
C	84	28.3	346.1	31.0	95.6	29.6	164.2	33.6	34.6	866.0	33.2	28.2	30.5	1·10 ³	40.6	122.2	39.4	29.9	29.1	976.6	35.8
Su	525	5.2	5.4	5.3	4.8	3.8	8.8	3.1	3.0	12.9	46.8	3.0	4.1	4.9	6.6	3.7	3.1	4.1	3.2	7.5	3.1
HD-Su	28	11.5	5.8	18.0	17.9	3.2	26.0	1.8	1.4	11.0	218.5	1.4	6.9	1.2	3.0	2.8	1.8	3.2	1.4	2.6	1.1
total	900	8.4	37.1	8.7	14.0	6.3	23.6	5.7	5.8	94.2	118.0	5.2	6.8	130.0	10.2	14.6	6.4	6.2	6.3	97.0	5.9
Isothermal compressibility β																					
G	92	2.0	2.7	2.1	2.0	0.4	4.8	0.2	0.2	2.6	0.3	0.2	1.9	1.8	2.0	1.1	0.6	0.7	0.4	3.4	0.3
L	159	4.9	4.7	5.4	5.5	2.8	7.2	2.6	2.5	13.8	204.8	2.4	2.6	5.6	7.5	4.4	2.6	4.5	3.9	4.5	2.3
HD-L	46	8.0	3.6	11.7	11.5	5.4	6.7	0.8	0.7	16.2	322.1	1.6	1.3	2.5	5.9	1.0	1.3	2.0	12.4	4.7	1.0
MU	23	12.6	13.1	11.5	14.0	11.3	15.9	12.7	12.0	50.3	12.8	11.8	11.0	14.5	27.6	14.4	12.0	11.4	11.9	14.5	18.2
C	108	42.1	379.9	40.2	84.5	36.0	137.6	38.1	41.2	869.5	37.9	44.2	46.1	1·10 ³	44.6	107.6	42.3	35.6	33.8	779.9	44.8
Su	935	5.7	5.3	5.0	5.1	4.0	12.0	2.6	2.6	10.5	482.8	2.5	3.3	4.6	5.3	3.3	2.6	3.8	2.6	5.6	2.6
HD-Su	43	11.5	14.2	18.8	20.7	9.5	18.9	1.0	1.0	6.1	91.0	0.7	9.1	1.0	0.5	1.3	1.0	0.7	1.0	2.5	1.1
total	1406	8.5	34.2	8.3	11.9	6.4	20.7	5.2	5.4	77.1	360.7	5.6	6.7	92.4	8.6	11.3	5.6	6.1	5.4	64.8	5.8
Thermal pressure coefficient γ																					
G	113	0.8	1.8	2.0	1.6	0.8	3.8	0.2	0.2	0.4	0.3	0.1	4.1	1.5	0.7	1.0	0.4	1.3	0.5	4.4	0.1
L	177	5.0	1.9	1.6	3.0	1.2	9.0	0.6	0.5	8.1	67.3	0.8	0.9	1.5	3.7	1.1	0.7	2.3	1.9	4.2	0.5
HD-L	52	8.9	3.6	2.3	2.0	3.7	4.5	0.6	0.6	12.6	234.8	2.1	1.0	1.3	5.5	1.3	1.5	2.5	6.6	1.1	0.6
MU	50	4.0	5.3	5.3	5.7	4.0	9.6	2.0	1.7	9.9	3.9	1.3	6.1	3.8	4.0	3.7	2.2	4.7	4.3	9.5	3.9
C	131	6.8	4.6	3.2	3.4	1.9	11.1	1.6	1.4	14.1	3.3	0.7	3.2	1.6	5.3	3.2	1.1	3.2	1.2	4.9	2.8
Su	1111	3.4	2.3	1.1	1.8	2.7	16.4	0.4	0.4	3.8	8·10 ³	0.4	1.6	0.9	1.4	1.2	0.6	1.3	0.6	1.8	0.4
HD-Su	54	7.3	14.2	2.3	5.7	14.1	49.8	1.2	0.5	5.1	1·10 ⁵	0.9	5.7	0.9	3.0	1.7	1.5	2.7	0.9	0.6	0.4
total	1688	3.9	2.9	1.6	2.3	2.8	14.8	0.6	0.5	5.3	9·10 ³	0.5	2.1	1.1	2.2	1.5	0.7	1.7	1.0	2.6	0.7

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#	Speed of sound w	Cotterman et al. ²⁹	Particaud ⁷⁷	Lafitte et al. ⁴²	van Westen & Gross ⁸²	this work	Koutras et al. ⁶⁸	Kolafa & Nezbeda ⁵⁷	Mecke et al. ^{70,71}	Hess ⁷⁵	Botlachev and Baidakov ⁷⁶	Gottschalk ⁸³	Quinones-Cisneros et al. ⁷⁹	Nicolas et al. ¹²	Adachi et al. ³⁰	Miyano ⁶⁹	Johnson et al. ⁵⁶	Sun & Teja ⁷²	May & Mausbach ^{80,81}	Ree ²⁸	Thol et al. ³⁷
G	117	0.4	0.5	0.8	0.6	0.6	28.8	0.1	0.1	0.1	0.2	0.1	1.4	0.2	0.6	0.1	0.3	0.3	0.2	0.8	0.1
L	182	2.5	1.5	1.3	2.8	1.3	32.6	0.4	0.3	15.7	52.2	0.7	11.8	1.4	6.9	1.1	0.6	1.9	2.0	4.2	0.3
HD-L	50	1.8	2.1	2.5	4.4	0.7	22.8	0.2	0.1	15.9	72.0	0.8	11.5	0.3	6.2	0.5	1.5	1.0	6.3	1.8	0.1
MU	49	2.9	3.1	3.2	3.7	2.9	36.8	1.4	1.1	4.8	6.0	1.3	6.1	1.8	3.8	1.7	1.8	2.6	5.9	5.8	1.5
C	131	17.5	12.8	13.9	12.4	9.3	69.3	5.5	4.5	8.4	23.0	1.8	9.4	7.3	10.0	10.1	6.2	14.5	8.0	17.4	8.9
Su	1111	2.6	2.3	2.0	2.3	2.4	30.3	0.4	0.4	3.5	84.8	0.4	3.0	0.8	1.4	0.9	0.6	1.8	0.7	2.3	0.4
HD-Su	43	4.1	8.7	8.1	9.7	5.7	12.2	0.3	0.1	4.5	100.0	0.1	4.5	0.3	1.3	0.3	0.4	0.6	0.5	0.8	0.2
total	1683	3.6	3.1	3.0	3.3	2.7	33.0	0.8	0.7	5.4	68.3	0.5	4.7	1.3	2.8	1.6	1.1	2.7	1.7	3.6	1.1
Joule-Thomson coefficient μ_{JT}																					
G	100	8.2	5.3	6.2	4.3	1.2	100.2	0.6	0.5	3.4	0.9	0.4	13.9	4.5	3.5	2.3	1.0	2.3	1.1	10.1	0.5
L	138	11.5	8.5	7.6	5.8	5.0	99.0	3.3	3.2	50.7	49.0	3.8	27.6	9.1	25.2	6.7	4.5	4.4	6.4	3.2	2.8
HD-L	45	13.9	6.0	9.3	6.0	9.2	97.7	1.1	1.2	55.8	140.1	3.2	42.0	3.2	28.5	1.8	8.0	3.2	26.1	3.5	1.3
MU	7	15.0	9.2	12.2	8.7	4.4	165.6	4.5	1.8	21.2	6.4	1.0	14.5	11.7	11.5	9.0	5.5	7.2	3.2	12.7	90.3
C	126	8.1	9.3	7.6	5.7	5.9	161.1	5.5	5.0	11.9	6.8	4.6	5.7	7.5	14.9	6.8	5.8	7.2	5.2	14.7	7.0
Su	898	11.2	6.1	7.1	5.8	7.1	236.8	4.5	4.6	10.5	163.5	4.6	7.9	7.9	11.9	6.6	5.0	6.2	5.3	7.3	4.5
HD-Su	44	8.9	4.4	9.0	6.8	12.0	101.2	1.6	1.2	14.7	100.0	1.4	6.3	1.6	11.7	2.2	2.9	3.1	3.6	2.3	0.9
total	1358	10.8	6.5	7.3	5.7	6.5	196.3	4.0	3.9	15.9	121.7	4.0	11.3	7.4	13.5	6.0	4.7	5.6	5.7	7.5	4.5
Grüneisen coefficient Γ																					
G	90	0.9	1.5	2.9	2.3	2.6	101.0	0.5	0.3	1.3	0.8	0.1	3.3	1.0	1.1	1.2	0.8	1.5	1.0	4.6	0.1
L	154	7.9	3.2	4.9	2.2	4.5	99.7	0.7	0.6	51.2	127.6	2.4	44.8	3.3	27.5	1.7	2.4	2.3	6.6	6.6	0.5
HD-L	43	11.8	3.4	5.4	1.1	6.0	98.3	0.4	0.4	55.7	114.5	1.9	48.1	1.1	25.9	0.9	4.1	2.3	13.5	1.3	0.4
MU	15	16.6	11.4	12.1	10.7	10.6	100.6	5.4	3.8	41.6	50.9	9.3	49.1	6.2	26.4	6.8	14.0	11.6	45.1	20.0	7.0
C	39	24.7	24.6	20.8	22.3	15.9	96.3	8.0	6.0	10.5	47.2	1.3	15.9	13.8	7.2	18.7	7.3	22.5	13.0	40.3	4.4
Su	419	2.9	4.5	1.8	2.5	9.3	100.2	0.4	0.3	11.3	448.3	0.5	7.7	1.4	6.6	1.3	1.4	2.3	2.1	4.5	0.3
HD-Su	36	5.6	14.2	2.8	5.0	39.4	101.9	0.9	0.4	17.0	404.5	0.4	12.8	1.0	10.1	1.3	3.2	3.2	3.0	0.4	0.3
total	796	5.6	5.4	3.9	3.6	9.2	100.0	0.9	0.7	21.1	288.5	1.1	18.0	2.4	11.6	2.3	2.3	3.4	4.8	6.6	0.7

For all considered LJ EOS, the thermodynamic properties were computed from their relations to the reduced Helmholtz energy $\tilde{a} = a/T$ and its derivatives with respect to the density and the inverse temperature using the following notation:

$$\tilde{a}_{nm} = \tilde{a}_{nm}^{\text{id}} + \tilde{a}_{nm}^{\text{res}} = (1/T)^n \rho^m \frac{\partial^{n+m}(\tilde{a}^{\text{id}} + \tilde{a}^{\text{res}})}{\partial(1/T)^n \partial \rho^m}, \quad (5)$$

where 'id' and 'res' indicate the ideal gas contribution and the residual contribution to the Helmholtz energy, respectively. Only, data for $n, m = 0, 1, 2$ were considered here. This formalism was also applied to pressure-explicit LJ EOS, cf. Table I. As the Lennard-Jones fluid is a monoatomic gas, its ideal gas heat capacity is a priori known. The following thermodynamic properties were studied here^{32,37}:

thermal properties

pressure
$$p = -\left(\frac{\partial a}{\partial v}\right)_T = \rho T (1 + \tilde{a}_{01}^{\text{res}}) \quad (6)$$

caloric properties

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

isobaric heat capacity
$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = -(\tilde{a}_{20}^{\text{id}} + \tilde{a}_{20}^{\text{res}}) + \frac{(1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}})^2}{1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}}} \quad (8)$$

isochoric heat capacity
$$c_v = \left(\frac{\partial u}{\partial T}\right)_\rho = -(\tilde{a}_{20}^{\text{id}} + \tilde{a}_{20}^{\text{res}}) \quad (9)$$

entropic properties

residual chemical potential
$$\mu^{\text{res}} = h^{\text{res}} - T s^{\text{res}} = T(1 + \tilde{a}_{00}^{\text{res}} + \tilde{a}_{01}^{\text{res}}) \quad (10)$$

2nd-order thermodynamic derivatives

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

isothermal compressibility
$$\beta = \left(\rho \frac{\partial p}{\partial \rho}\right)_T^{-1} = \frac{1}{\rho T(1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}})} \quad (12)$$

thermal expansion coefficient

$$\alpha = \beta\gamma = \frac{\left(\frac{\partial p}{\partial T}\right)_\rho}{\rho\left(\frac{\partial p}{\partial \rho}\right)_T} = \frac{1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}}}{T(1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}})} \quad (13)$$

speed of sound

$$w = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s} = \left(T\left((1 + 2\tilde{a}_{01}^{\text{res}} + \tilde{a}_{02}^{\text{res}}) - \frac{(1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}})^2}{\tilde{a}_{20}^{\text{id}} + \tilde{a}_{20}^{\text{res}}}\right)\right)^{0.5}} \quad (14)$$

Joule-Thomson coefficient

$$\mu_{\text{JT}} = \left(\frac{\partial T}{\partial p}\right)_h \quad (15)$$

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

Grüneisen parameter

$$\Gamma = \frac{\left(\frac{\partial p}{\partial T}\right)_\rho}{\rho c_v} = \frac{1 + \tilde{a}_{01}^{\text{res}} - \tilde{a}_{11}^{\text{res}}}{-\tilde{a}_{20}^{\text{id}} - \tilde{a}_{20}^{\text{res}}} \quad (16)$$

Thermal Properties

The AAD_{ijk} computed according to Eq. (3) for the pressure data $j = p$ is given in Table IV for all considered LJ EOS i and all regions k , except for the extreme temperature region $k = \text{Ex-T}$, for which the corresponding results are presented in Table V. Table IV furthermore reports the absolute average deviations from the (exact) values for the second and third virial coefficient $k = B, C$, which were taken from the literature¹¹ (Refs. ^{12,72,139,160–162} for second virial coefficient data and Refs. ^{72,139,160–163} for third virial coefficient data).

The overall best description of the pvT data is found for the LJ EOS of *Gottschalk*⁸³, *Thol et al.*³⁷, *Mecke et al.*^{70,71}, and *Kolafa and Nezbeda*⁵⁷. However, the LJ EOS of *Thol et al.*³⁷ and *Gottschalk*⁸³ exhibit extreme deviations in the metastable/ unstable region (see above). The LJ EOS from the present work describes the pvT data in the gas, liquid, and critical region as good as the best LJ EOS in those regions. In the HD liquid, and metastable/ unstable region, the LJ EOS from the present work has slightly larger mean deviations than the best LJ EOS in those regions.

Also the LJ EOS of *Johnson et al.*⁵⁶ gives a good description of the pvT data (cf. Table IV); however, it is somewhat less precise than the three aforementioned LJ EOS. The LJ

EOS of *Sun and Teja*⁷², *May and Mausbach*^{80,81}, *Quiñones-Cisneros et al.*⁷⁹, and *Miyano*⁶⁹ are in turn slightly less precise than the LJ EOS of *Johnson et al.*⁵⁶. The theoretically-based LJ EOS of *Cotterman et al.*²⁹, *Lafitte et al.*⁴², *Paricaud*⁷⁷, and *van Westen and Gross*⁸² overall yield an absolute average deviation two to three times larger than the most precise LJ EOS, cf. Table IV. In general no fluid region is represented significantly better or worse than the others by the theoretically-based LJ EOS. The performance of the LJ EOS from *Cotterman et al.*²⁹, *Lafitte et al.*⁴², *Paricaud*⁷⁷, and *van Westen and Gross*⁸² regarding the pvT behavior is overall similar. Also the LJ EOS of *Nicolas et al.*¹² has a similar performance regarding the pvT data as the theoretically-based LJ EOS from Refs.^{29,42,77,82}, which is surprising considering the fact that the LJ EOS of *Nicolas et al.*¹² is one of the oldest LJ EOS considered here. The LJ EOS from the present work performs significantly better than the other theoretically-based LJ EOS, which is likely due to the parametrization procedure (see Supplementary Material). The LJ EOS of *Koutras et al.*⁶⁸, *Hess*⁷⁵, *Ree*²⁸, *Boltachev and Baidakov*⁷⁶, and *Adachi et al.*³⁰ exhibit large deviations in all fluid regions ($AAD_{i,j=p} > 10\%$).

The isotherms obtained from the LJ EOS of *Boltachev and Baidakov*⁷⁶ exhibit an artificial maximum in the supercritical region, which results in gross deviations in the HD liquid, supercritical and HD supercritical region. This also holds for properties discussed in the following. The LJ EOS of *Boltachev and Baidakov*⁷⁶ is therefore discarded from the following discussions.

For the second and third virial coefficients B and C , the obtained absolute average deviations are reported in the bottom section of Table IV. The second virial coefficient B is exactly described by the LJ EOS of *Gottschalk*⁸³ and *Hess*⁷⁵, which comprise the corresponding expression in their mathematical form. Good results are also obtained for the LJ EOS of *Paricaud*⁷⁷, *Kolafa and Nezbeda*⁵⁷, *Mecke et al.*^{70,71}, *Boltachev and Baidakov*⁷⁶, *Miyano*⁶⁹, and *Thol et al.*³⁷. The third virial coefficient C is described best by the LJ EOS of *Thol et al.*³⁷. Also the LJ EOS of *Gottschalk*⁸³ yields an excellent description of C in a wide temperature range, but a wrong limit at low temperatures yields an overall large absolute average deviation. A detailed discussion on the performance of LJ EOS on the virial coefficients and their relation to the characteristic curves can be found in a follow-up work¹⁶⁴.

Caloric Properties

Also the absolute average deviations AAD_{ijk} for the residual internal energy $j = u^{\text{res}}$ (for brevity, the addition 'residual' is omitted in the following) in the different fluid regions k are reported in Table IV for all studied LJ EOS i . As for the pvT data, the LJ EOS of *Mecke et al.*^{70,71}, *Gottschalk*⁸³, *Thol et al.*³⁷, and *Kolafa and Nezbeda*⁵⁷ give the best descriptions of the internal energy data. The LJ EOS from the present work performs well in most fluid regions, i.e. only slightly exceeds the absolute average deviations from the best LJ EOS, but becomes unreliable in the supercritical and HD supercritical region. This is likely due to the simplifications of the temperature-dependent diameter, cf. Eq. (24), and hence an inadequate description of the soft repulsive interactions¹⁶⁵ of the PC-SAFT monomer equation in that fluid region (details are given in the Supplementary Material).

The LJ EOS of *Johnson et al.*⁵⁶, *May and Mausbach*^{80,81}, *Nicolas et al.*¹², *Sun and Teja*⁷², and *Miyano*⁶⁹ exhibit total deviations $AAD_{i,j=u^{\text{res}}}$ for the internal energy of about 1...2%, cf. Table IV, and are thereby less precise than the aforementioned LJ EOS^{37,57,70,71,83} – in agreement with what was observed for the pvT data.

The $AAD_{i,j=u^{\text{res}}}$ obtained for the theoretically-based LJ EOS of *Cotterman et al.*²⁹, *Lafitte et al.*⁴², *Paricaud*⁷⁷, *van Westen and Gross*⁸², and the LJ EOS from the present work is about an order of magnitude larger than for the most precise LJ EOS (Refs. ^{37,57,70,71,83}). The deviations of the theoretically-based LJ EOS are particularly large in the gas and high density supercritical region. Nevertheless, the theoretically-based LJ EOS of *Lafitte et al.*⁴², *Paricaud*⁷⁷, *van Westen and Gross*⁸², and from the present work show a good performance in the liquid and HD liquid region, where the deviations are not significantly higher than those of the empirical LJ EOS, cf. Table IV.

The empirical LJ EOS of *Ree*²⁸ and *Adachi et al.*³⁰ perform not better than the considered theoretically-based LJ EOS for the internal energy. The LJ EOS of *Koutras et al.*⁶⁸, *Hess*⁷⁵, *Quiñones-Cisneros et al.*⁷⁹, and *Boltachev and Baidakov*⁷⁶ exhibit mean deviations $AAD_{i,j=u^{\text{res}}} > 10\%$.

Interestingly, most LJ EOS show a better performance for the internal energy u^{res} than for the pressure p , i.e. $AAD_{i,j=p} > AAD_{i,j=u^{\text{res}}}$. This does not hold for the LJ EOS from the present work, which is based on the PC-SAFT monomer equation. The mean deviation for the internal energy data $AAD_{i,j=u^{\text{res}}}$ is more than three times larger than the corresponding value for the pvT data $AAD_{i,j=p}$, which is likely due to the mathematical form of the under-

lying model, namely on the chosen simplification for describing the temperature-dependent diameter and the perturbation terms (see Supplementary Material for details). These simplifications have also been attributed to shortcomings of PC-SAFT regarding its description of the soft repulsion, see *Boshkova and Deiters*¹⁶⁵. The simplifications in describing the soft repulsion in the PC-SAFT EOS may also explain its poorer performance for caloric properties at supercritical states that was reported in the literature^{166–169}.

The absolute average deviations AAD_{ijk} of the isochoric and isobaric heat capacity $j = c_v$ and $j = c_p$, respectively, found for the different LJ EOS i in the different fluid regions k are also reported in Table IV. The four LJ EOS of *Thol et al.*³⁷, *Gottschalk*⁸³, *Mecke et al.*^{70,71}, and *Kolafa and Nezbeda*⁵⁷ give the best description of the computer experiment data for the heat capacities, which is in line with the findings for the internal energy u^{res} and the pvT data. The LJ EOS of *Thol et al.*³⁷ has large deviations in the critical and metastable/unstable region, but performs slightly better than the LJ EOS of *Mecke et al.*^{70,71} and *Kolafa and Nezbeda*⁵⁷ in the gas and in both the high density liquid and high density supercritical region. While the LJ EOS of *Gottschalk*⁸³ gives a slightly better description of the pvT data than that of *Thol et al.*³⁷, this is reversed for the caloric properties in most fluid regions except the critical and metastable/unstable region.

For the isochoric and isobaric heat capacity, the LJ EOS of *Johnson et al.*⁵⁶ and *Sun and Teja*⁷² have slightly increased absolute average deviations in most fluid regions compared to the four best LJ EOS. The theoretically-based LJ EOS of *Cotterman et al.*²⁹, *Lafitte et al.*⁴², *Paricaud*⁷⁷, *van Westen and Gross*⁸², and the LJ EOS from the present work are less precise than the best empirical ones for the isochoric and isobaric heat capacity, but the difference is only about a factor of two to four instead an order of magnitude as found for the internal energy data.

The LJ EOS of *Nicolas et al.*¹² and *Paricaud*⁷⁷ exhibit large relative deviations of the isobaric heat capacity data in the critical region, which is due to the significantly overestimated critical temperature of these LJ EOS. The large deviations found for both isochoric and isobaric heat capacity data for the LJ EOS of *Thol et al.*³⁷ in the critical and metastable/unstable region are probably a result of the multiple van der Waals loops and the crossing of the isotherms in the critical region. However, it should be noted that the critical temperature of the LJ EOS of *Thol et al.*³⁷ is in excellent agreement with the presumed true value (see above).

The LJ EOS of *Koutras et al.*⁶⁸, *Hess*⁷⁵, *Ree*²⁸, *Adachi et al.*³⁰, *Boltachev and Baidakov*⁷⁶, and *Quiñones-Cisneros et al.*⁷⁹ exhibit for both $j = c_v$ and $j = c_p$ mean deviations $\text{AAD}_{ij} \gtrsim 10\%$.

Entropic Properties

The results obtained for performance of the considered LJ EOS i on entropic properties $j =$ (residual reduced Helmholtz energy $\tilde{a}^{\text{res}} = a^{\text{res}}/T$ and chemical potential μ^{res} – mentioning ‘residual’ is again omitted for brevity in the following) in the different fluid regions k are also given in Table IV. The LJ EOS of *Thol et al.*³⁷, *Gottschalk*⁸³, *Mecke et al.*^{70,71}, and *Kolafa and Nezbeda*⁵⁷ give a generally similar precise description of the entropic properties, cf. Table IV. The relative deviation of the LJ EOS of *Johnson et al.*⁵⁶ is approximately twice as large as those of the four best LJ EOS^{37,57,70,71,83} for both the Helmholtz energy and the chemical potential. The absolute average deviation for the entropic properties obtained for the theoretically-based LJ EOS of *Cotterman et al.*²⁹, *Lafitte et al.*⁴², *Paricaud*⁷⁷, and *van Westen and Gross*⁸², and the LJ EOS from the present work significantly exceed those from the most precise LJ EOS. Large deviations for the entropic properties are found for all theoretically-based LJ EOS in the high density supercritical region. Furthermore, high deviations are found for the LJ EOS of *Cotterman et al.*²⁹ and *Lafitte et al.*⁴² in the gas region for both the Helmholtz energy and the chemical potential. The LJ EOS of *Boltachev and Baidakov*⁷⁶, *Koutras et al.*⁶⁸, and *Hess*⁷⁵ exhibit $\text{AAD}_{ij} > 10\%$ for both considered entropic properties $j = \tilde{a}^{\text{res}}$ and $j = \mu^{\text{res}}$.

Overall, the results for the entropic properties support the findings from the caloric and thermal properties discussed above. This also indicates that the reference data¹¹ for these properties have overall a similar quality and outliers were equally well detected.

Second Order Derivatives of the Helmholtz energy

The Helmholtz energy is considered here as a function of the inverse temperature and the density, cf. Eq. (5); accordingly the second derivatives are $\tilde{a}_{20}$, $\tilde{a}_{11}$, and $\tilde{a}_{02}$. Six more thermodynamic properties were studied here that contain at least one of these derivatives: the thermal pressure coefficient γ , the isothermal compressibility β , the thermal expansion coefficient α , the speed of sound w , the Joule-Thomson coefficient μ_{JT} , and the Grüneisen parameter Γ , cf. Eqs. (11) - (16). The AAD_{ijk} results for the LJ EOS i for $j = \alpha, \beta, \gamma, w, \mu_{\text{JT}}, \Gamma$ in the different fluid regions k are given in Table IV.

The thermal pressure coefficient γ , isothermal compressibility β , and thermal expan-

sion coefficient α is best and overall equally well described by the LJ EOS of *Kolafa and Nezbeda*⁵⁷, *Mecke et al.*^{70,71}, *Gottschalk*⁸³, and *Thol et al.*³⁷ – as it was also found for the thermal, caloric, and entropic properties discussed above.

The LJ EOS of *Johnson et al.*⁵⁶, *May and Mausbach*^{80,81}, and *Sun and Teja*⁷² exhibit slightly larger mean deviations for α , β , and γ than the aforementioned LJ EOS, cf. Table IV. Also the LJ EOS of *Lafitte et al.*⁴², *Cotterman et al.*²⁹, *Quiñones-Cisneros et al.*⁷⁹, and the LJ EOS from the present work give a reasonably precise description of the α , β , and γ computer experiment data. Mean deviations $\text{AAD}_{ij} > 10\%$ for either $j = \alpha$, β , or γ were obtained for the LJ EOS of *Miyano*⁶⁹, *Adachi et al.*³⁰, *Ree*²⁸, *Nicolas et al.*¹², *Hess*⁷⁵, *Paricaud*⁷⁷, *van Westen and Gross*⁸², *Koutras et al.*⁶⁸, and *Boltachev and Baidakov*⁷⁶. For the latter two LJ EOS mean deviations $\text{AAD}_{ij} > 10\%$ are found for all three properties $j = \alpha$, β , and γ , cf. Table IV.

All five theoretically-based LJ EOS (*Cotterman et al.*²⁹, *Lafitte et al.*⁴², *Paricaud*⁷⁷, and *van Westen and Gross*⁸², and the LJ EOS from the present work) exhibit high relative deviations for α , β , and γ in the high density supercritical and high density liquid region compared to other fluid regions. Furthermore, the theoretically-based LJ EOS of *Lafitte et al.*⁴² and *Paricaud*⁷⁷ are considerably less precise in the gas region for $j = \alpha$, β , and γ than the other theoretically-based LJ EOS, cf. Table IV.

The LJ EOS of *Nicolas et al.*¹², *Hess*⁷⁵, *Ree*²⁸, and *Paricaud*⁷⁷ exhibit large relative deviations for the α and β computer experiment data in the critical region, similar to the findings for the heat capacity. This is attributed to the significantly overestimated critical temperature by these LJ EOS (see above).

The findings for $j = w$, μ_{JT} , and Γ are in line with the findings for the properties discussed above: the three LJ EOS of *Kolafa and Nezbeda*⁵⁷, *Mecke et al.*^{70,71}, *Gottschalk*⁸³, and *Thol et al.*³⁷ give similarly precise descriptions, followed by that of *Johnson et al.*⁵⁶. The theoretically-based LJ EOS are significantly less precise.

Distinct performance features for w , μ_{JT} , and Γ are: the LJ EOS of *Thol et al.*³⁷ exhibits large deviations in the metastable/ unstable region for the Joule-Thomson coefficient and the LJ EOS from the present work is significantly less precise than other LJ EOS for the Grüneisen parameter in the supercritical and high density supercritical region. The latter is again attributed to the simplified temperature-dependent diameter (see Appendix).

Extreme Temperature Region

The performance of the investigated LJ EOS i in the extreme temperature region, i.e. $T > 6$, is summarized in Table V by reporting the corresponding absolute average deviations AAD_{ijk} with $k = \text{Ex-T}$ for all considered homogeneous state properties j . Since the reference data in the extreme temperature region covers a large range of states¹¹, high absolute average deviations obtained for a given LJ EOS are in some cases a result of a poor performance in only a sub-region of states, cf. the electronic Supplementary Material.

The LJ EOS of *Quiñones-Cisneros et al.*⁷⁹, *Boltachev and Baidakov*⁷⁶, and *Koutras et al.*⁶⁸ give an erratic description of the extreme temperature region. The empirical LJ EOS of *Thol et al.*³⁷ and *Ree*²⁸ give an astonishingly accurate description of thermodynamic properties at extreme temperatures considering the fact that they were parametrized exclusively using data at moderate temperatures. On the contrary, the theoretically-based LJ EOS exhibit large deviations for most properties. This is surprising, considering the fact that the studied theoretically-based LJ EOS are based on perturbation theory, which is expected to perform well at high temperatures, where the attractive forces, i.e. the perturbation contribution, plays a minor role. The assumption that theoretically-based EOS are in general expected to show a better performance upon extrapolation than empirical EOS should not be taken for granted.

The LJ EOS of *Mecke et al.*^{70,71} and *Gottschalk*⁸³, which are generally precise (see above), exhibit large deviations for the pressure and internal energy at extreme temperatures – the LJ EOS of *Mecke et al.*^{70,71} also for other properties. A detailed examination of the data (see the electronic Supplementary Material) shows that these large deviations mainly stem from the region $T > 50$ and $\rho > 2$ (for the LJ EOS of *Gottschalk*⁸³, very few reference data points entail these large deviations, which probably lie beyond the freezing line). The LJ EOS of *Johnson et al.*⁵⁶, *Sun and Teja*⁷², *May and Mausbach*^{80,81}, *Nicolas et al.*¹², *Adachi et al.*³⁰, *Hess*⁷⁵, and *Kolafa and Nezbeda*⁵⁷ give a reasonable description of the extreme temperature region – except the internal energy data in some cases.

TABLE V. Comparison of results from 20 LJ EOS i with reference data, cf. Table VII (outliers identified in the data set¹¹ were discarded); absolute average deviations $\text{AAD}_{i,j,k}$ given in percentages (cf. Eq. 3) for different thermodynamic properties j for homogeneous state points in the extreme temperature ($k = \text{Ex-T}$) region. The last line 'total' gives the mean AAD_i for all extreme temperature data. # is the number of data points.

	#	Cotterman et al. ²⁹	Paricaud ⁷⁷	Laflitte et al. ⁴²	van Westen & Gross ⁸²	this work	Koutas et al. ⁶⁸	Kolaja & Nezbeda ⁵⁷	Mecke et al. ^{70,71}	Hess ⁷⁵	Boltachev and Baidakov ⁷⁶	Gottschalk ⁸³	Quinones-Cisneros et al. ⁷⁹	Nicolas et al. ¹²	Adachi et al. ³⁰	Miyano ⁶⁹	Johnson et al. ⁵⁶	Sun & Teja ⁷²	May & Mautsba ^{80,81}	Rec ²⁸	Thol et al. ³⁷
pvT	643	$2 \cdot 10^3$	173.8	$2 \cdot 10^5$	$1 \cdot 10^4$	$1 \cdot 10^3$	$1 \cdot 10^7$	37.6	$1 \cdot 10^7$	38.9	$1 \cdot 10^7$	$3 \cdot 10^4$	$3 \cdot 10^{297}$	14.2	14.2	183.9	15.3	12.1	14.3	7.5	9.2
u^{res}	626	$2 \cdot 10^3$	165.6	$2 \cdot 10^5$	$9 \cdot 10^3$	307.3	$9 \cdot 10^5$	30.5	$5 \cdot 10^6$	39.2	$3 \cdot 10^6$	$3 \cdot 10^4$	$2 \cdot 10^{298}$	118.5	110.0	44.3	90.1	71.2	87.8	28.7	7.7
c_v	298	17.3	8.0	1.7	2.4	23.5	$7 \cdot 10^4$	2.3	516.3	3.0	$1 \cdot 10^5$	1.4	$2 \cdot 10^{294}$	6.3	13.0	1.3	11.4	8.4	11.2	0.2	0.4
c_p	273	8.2	7.3	4.5	5.6	23.8	$2 \cdot 10^5$	4.0	449.9	6.3	$4 \cdot 10^5$	2.3	$7 \cdot 10^{143}$	3.8	6.2	6.6	5.7	4.7	5.5	0.5	0.8
$\bar{a}^{\text{res}}$	236	10.9	7.3	4.0	5.7	58.0	$2 \cdot 10^5$	1.3	97.9	2.6	$3 \cdot 10^5$	0.5	$9 \cdot 10^{294}$	9.0	10.3	4.0	8.7	5.8	7.3	1.9	0.9
μ^{res}	236	14.5	16.2	8.7	13.6	182.3	$2 \cdot 10^7$	2.9	384.1	4.4	$7 \cdot 10^5$	0.4	$6 \cdot 10^{297}$	9.1	10.2	9.3	9.6	6.2	7.9	1.5	1.6
α	262	36.4	19.1	17.5	20.4	6.9	972.3	9.1	63.2	13.7	47.1	3.3	199.0	9.4	13.6	23.6	6.4	10.9	7.1	0.9	3.0
β	273	17.7	19.6	13.5	18.1	34.5	334.3	10.5	64.6	9.4	90.5	1.3	58.3	4.7	5.1	97.0	7.4	3.9	5.7	0.8	4.1
γ	294	30.9	7.7	7.6	7.8	303.3	$6 \cdot 10^7$	6.8	$2 \cdot 10^3$	8.2	$1 \cdot 10^6$	2.2	$2 \cdot 10^{301}$	13.8	18.2	20.1	14.1	12.6	13.0	0.5	1.3
w	294	9.4	12.3	6.9	10.3	117.5	$1 \cdot 10^5$	3.4	63.4	3.6	$1 \cdot 10^4$	0.4	$1 \cdot 10^{71}$	7.0	10.5	10.9	9.6	6.2	8.5	0.3	1.6
μ_{JT}	273	14.9	12.5	9.9	18.6	14.6	104.2	7.8	105.5	11.7	304.0	3.1	57.3	7.1	8.7	20.6	8.5	8.4	7.7	3.1	1.7
Γ	299	44.7	9.1	10.0	23.0	605.7	$4 \cdot 10^3$	7.0	69.7	5.7	$5 \cdot 10^3$	1.4	72.8	23.4	40.6	21.3	33.0	25.1	31.4	0.2	1.5
total	4007	679.7	61.8	$6 \cdot 10^4$	$3 \cdot 10^3$	357.1	$7 \cdot 10^6$	14.6	$3 \cdot 10^6$	17.1	$3 \cdot 10^6$	$9 \cdot 10^3$	$2 \cdot 10^{300}$	27.3	29.0	51.2	24.6	19.5	23.4	6.3	3.8

IV. OVERVIEW OF THE PERFORMANCE OF THE LJ EOS

To enable a systematic comparison of the performance of the considered LJ EOS, we define the performance index PI_{ij} of a given LJ EOS i for a given property j by setting its absolute average deviation in a given region k AAD_{ijk} in relation to the lowest absolute average deviation obtained from all considered LJ EOS for that property and region $AAD_{i=\text{best},jk}$ and summing up the result over all regions:

$$PI_{ij} = 1/N_{\text{reg}} \sum_{k=1}^{N_{\text{reg}}} \frac{AAD_{ijk}}{AAD_{i=\text{best},jk}}, \quad (17)$$

where N_{reg} indicates the number of fluid regions. Here, $N_{\text{reg}} = 7$, as the extreme temperature region was excluded. The $AAD_{i=\text{best},jk}$ is the smallest value in a row in Table III and IV for a given property, i.e.

$$AAD_{i=\text{best},jk} = \min_i (AAD_{ijk}). \quad (18)$$

The formalism of Eq. (17) and (18) implies that all fluid regions are equally important and sufficiently densely occupied by reference data points to enable a reasonable evaluation. In fact, out of about 100 considered property-region pairs jk , only four have less than 20 data points, cf. Table IV and V. The value $AAD_{i=\text{best},jk}$ describes how accurate a given property can be currently described in a given fluid region by the considered LJ EOS.

Low values of the performance index PI_{ij} are desired. A $PI_{ij} = 1$ would imply that the LJ EOS i is the best for a given property j in all studied fluid regions. High values of PI_{ij} imply that the LJ EOS is bad compared to the best competitors. Furthermore, the $AAD_{i=\text{best},jk}$ can be considered as an upper limit for the uncertainty, i.e. the scattering of the reference data $Y_{\text{ref},jkl}$. The ratios of the number of reference data points available for a given property j in the different fluid regions k does not influence the PI_{ij} value. Eq. (17) was applied to all properties discussed in Table IV $j = (p, u^{\text{res}}, c_v, c_p, \tilde{a}^{\text{res}}, \mu^{\text{res}}, \alpha, \beta, \gamma, w, \mu_{\text{JT}}, \Gamma)$ as well as the VLE properties discussed in Table III $j = (\rho', \rho'', p^s, \Delta h_v)$. Since the VLE properties stem all from the same region, no summation has to be carried out in the evaluation of Eq. (17).

Following the differential approach for the extreme temperature region $k = \text{Ex-T}$, i.e. separating the extreme temperature region deviations from the respective $AAD_{j,\text{total}}$ (cf. Table IV) and reporting the Ex-T data collectively in Table V, this region was not comprised

in the calculation of the PI_{ij} values in Eq. (17). Instead, a separate performance index was defined for the comparison of the Ex-T region performance of the LJ EOS on the homogeneous state properties k :

$$PI_i^{\text{ex-T}} = 1/N_{\text{prop}} \sum_{j=1}^{N_{\text{prop}}} \frac{AAD_{ij,k=\text{ex-T}}}{AAD_{i=\text{best},j,k=\text{ex-T}}}, \quad (19)$$

where $N_{\text{prop}} = 12$ indicates the number of properties ($j = p, u^{\text{res}}, c_v, c_p, \tilde{a}^{\text{res}}, \mu^{\text{res}}, \alpha, \beta, \gamma, w, \mu_{\text{JT}}, \Gamma$) for which data are available in that region and the denominator $AAD_{i=\text{best},j,k=\text{ex-T}}$ indicates the absolute average deviation of the best performing LJ EOS for a given property j in the region $k = \text{Ex-T}$ (smallest value in a line in Table V).

Table VI summarizes the performance of the investigated LJ EOS regarding the VLE and homogeneous state properties by reporting the PI_{ij} and $PI_i^{\text{ex-T}}$ values according to Eqs. (17) and (19), respectively. Additionally, it summarizes the maximum number of points with $dp/d\rho = 0$ and $d^2p/d\rho^2 = 0$ found in $p - \rho$ isotherms for $0.66 < T < 1.321$ in the two-phase region (cf. Fig. 5).

The LJ EOS of *Kolafa and Nezbeda*⁵⁷, *Mecke et al.*^{70,71}, *Gottschalk*⁸³, and *Thol et al.*³⁷ yield an overall similar performance. However, their performance on individual properties differs significantly: the LJ EOS of *Mecke et al.*^{70,71} and *Gottschalk*⁸³ exhibit large deviations in the extreme-temperature region; the LJ EOS of *Thol et al.*³⁷ and *Gottschalk*⁸³ exhibit multiple van der Waals loops, which yields large PI_{ij} values for the pvT data. Overall, the LJ EOS of *Kolafa and Nezbeda*⁵⁷ is found to give the most favorable and robust performance of those four most precise LJ EOS, i.e. for the majority of properties its performance index values are in the range $1.2 < PI_{ij} < 1.9$.

The LJ EOS of *Johnson et al.*⁵⁶ and the LJ EOS from the present work (re-parametrized PC-SAFT monomer) also give a good description of the LJ fluid.

In the group of the MBWR type LJ EOS^{12,30,56,69,72,80,81} (cf. Table I) that of *Johnson et al.*⁵⁶ yields overall the best performance: comparing the PI_{ij} values among the MBWR type LJ EOS yields: the LJ EOS of *Johnson et al.*⁵⁶ has eight lowest performance index values, that of *May and Mausbach*^{80,81} has four lowest values, and both those of *Miyano*⁶⁹ and *Sun and Teja*⁷² have two lowest values.

Comparing the LJ EOS of *Johnson et al.*⁵⁶ and *Kolafa and Nezbeda*⁵⁷ (two of the most popular ones; see Supplementary Material), the latter has better performance index values

for all properties that were considered here. This is surprising, considering the fact that the LJ EOS of *Johnson et al.*⁵⁶ has approximately four times more citations. This also holds comparing their performance on practically all considered properties in the individual fluid regions, cf. Table III - V.

The theoretically-based LJ EOS yield PI_{ij} values between about two and ten for the majority of studied properties j . Surprisingly, they show a poor performance when used for extrapolations into the extreme temperature region, where they perform worse than some empirical and semi-theoretical LJ EOS. However, the theoretically-based LJ EOS show a good performance in the two-phase region, throughout, i.e. no undulations of the isotherms at most temperatures. Among the studied theoretically-based LJ EOS, the one from the present work shows the best performance as measured by the PI_{ij} values: for 11 properties it has the best PI_{ij} value in that group, which is probably due to the parametrization procedure that considers both bulk and VLE properties. However, for the caloric properties, it performs only poorly, which is attributed here to the unfavorable choice of the temperature-dependent diameter term taking a dominant role at high densities and temperatures. This supports the findings of *Boshkova and Deiters*¹⁶⁵. The other four theoretically-based LJ EOS (Refs. ^{29,42,77,82}) show overall a similar good performance – with strengths and weaknesses in different properties.

TABLE VI. Summary of the performance of all 20 considered LJ EOS using the performance index PI, cf. Eq. (17) and (19). The columns ' $\#_{dp/d\rho=0}$ ' and ' $\#_{d^2p/d\rho^2=0}$ ' indicate the highest number of maxima and minima and the highest number of turning points observed for $p-\rho$ isotherms in the two-phase region, respectively, cf. Fig. 5.

EOS	Abbr.	Δh_v	ρ_l	ρ_v	$\#_{dp/d\rho=0}$	$\#_{d^2p/d\rho^2=0}$	L_{ad}	n_{res}	c_p	c_v	d_p	q_{res}	m_{res}	α	β	γ	w	L_{JT}	L	$Ex-T$
<i>Cotterman et al.</i> ²⁹	Co	15.6	9.4	4.5	10.3	2	1	12.5	32.3	10.8	5.3	34.1	46.3	6.1	7.2	10.3	12.3	9.3	16.9	88.7
<i>Paricaud</i> ⁷⁷	Pa	4.6	10.3	10.1	9.2	2	1	17.3	15.6	9.0	8.2	10.6	22.9	6.6	8.8	11.1	17.7	5.5	18.5	24.9
<i>Lafitte et al.</i> ⁴²	La	6.4	3.0	4.9	3.0	2	1	18.1	20.2	7.9	6.2	18.5	33.2	7.5	10.0	5.9	17.9	7.3	16.4	4·10 ³
<i>van Westen and Gross</i> ⁸²	vWe	7.1	3.4	9.0	3.9	2	1	20.7	19.0	5.7	4.9	15.1	29.0	6.7	10.6	7.3	22.7	5.2	13.9	2·10 ²
<i>this work</i>	th	1.2	1.2	1.1	1.5	2	1	8.4	22.5	18.5	6.8	3.0	8.6	2.8	4.7	9.2	12.0	4.9	36.5	4·10 ²
<i>Koutras et al.</i> ⁶⁸	Kou	13.3	25.0	3.6	17.5	2	1	37.0	2·10 ⁴	2·10 ⁴	9·10 ³	1·10 ⁵	9·10 ⁴	11.2	11.7	35.8	1·10 ²	1·10 ²	5·10 ²	1·10 ⁷
<i>Kolafa and Nezbeda</i> ⁵⁷	Ko	1.1	1.4	1.2	1.7	2	3	1.2	1.6	1.9	1.5	1.3	2.2	1.3	1.2	1.7	1.9	1.7	3.4	10.1
<i>Mecke et al.</i> ^{70,71}	Me	1.1	1.3	1.5	1.6	2	5	1.1	1.4	1.5	1.4	1.2	1.7	1.3	1.2	1.3	1.3	1.2	2.2	2·10 ⁵
<i>Hess</i> ⁷⁵	He	96.9	95.9	32.6	76.1	2	1	20.3	99.5	1·10 ²	46.8	39.2	56.1	12.6	12.5	13.1	36.6	17.0	56.4	11.8
<i>Boltachev and Baidakov</i> ⁷⁶	Bo	18.8	14.7	8.6	16.2	2	3	3·10 ⁴	1·10 ⁵	1·10 ⁴	1·10 ⁴	2·10 ³	2·10 ⁴	1·10 ²	1·10 ²	4·10 ⁴	3·10 ²	44.0	5·10 ²	7·10 ⁵
<i>Gottschalk</i> ⁸³	Go	1.0	1.0	2.0	1.0	4	3	4.8	1.2	3.6	1.8	1.1	1.1	1.4	1.3	1.6	2.1	1.4	2.5	6·10 ²
<i>Quiñones-Cisneros et al.</i> ⁷⁹	Qui	15.9	24.8	3.9	13.6	2	1	8.8	58.7	1·10 ²	34.3	48.9	61.3	5.9	4.8	9.5	32.1	15.1	53.9	4·10 ³⁰⁰
<i>Nicolas et al.</i> ¹²	Ni	11.0	12.7	18.0	13.2	2	3	4.3	7.1	5.0	10.4	9.1	17.2	10.3	7.7	4.0	3.2	4.8	7.1	22.2
<i>Adachi et al.</i> ³⁰	Ad	25.9	21.1	49.5	21.9	2	3	7.9	30.8	45.1	14.9	18.9	29.7	4.9	4.0	6.4	16.0	10.6	30.7	33.7
<i>Miyano</i> ⁶⁹	Mi	9.1	2.7	3.5	7.4	2	1	3.4	3.7	4.6	2.7	11.8	15.4	2.2	2.4	3.9	3.2	3.4	7.8	34.3
<i>Johnson et al.</i> ⁵⁶	Jo	3.9	1.5	2.4	3.3	2	3	1.8	3.1	7.5	3.5	4.4	6.5	1.9	1.6	2.2	4.3	3.2	8.1	28.3
<i>Sun and Teja</i> ⁷²	Su	2.2	1.8	2.4	1.7	2	1	3.5	7.3	6.7	3.7	3.7	9.0	2.6	1.9	5.4	5.8	3.3	11.4	21.7
<i>May and Mausbach</i> ^{80,81}	Ma	2.2	2.1	4.4	2.4	3	4	1.8	5.3	16.2	6.5	2.1	3.8	3.4	3.7	4.0	11.9	5.5	15.5	26.3
<i>Rec</i> ²⁸	Re	7.7	14.5	23.7	12.6	2	1	8.2	22.1	10.1	12.4	13.3	27.2	11.2	8.0	9.7	10.2	6.8	22.7	1.8
<i>Thol et al.</i> ³⁷	Th	1.2	1.1	1.0	1.7	4	5	13.4	1.2	3.3	1.6	1.6	1.8	1.2	1.5	1.7	1.8	13.4	1.5	3.0

V. CONCLUSIONS

In the present work Lennard-Jones equations of state were reviewed and evaluated by comparing their results to an extensive consolidated database of molecular simulation results¹¹. Different types of LJ EOS are considered; they are classified here as: empirical EOS, semi-theoretical EOS, and theoretically-based EOS. In total, 20 LJ EOS were considered in the present work. The performance of these LJ EOS was investigated and compared for a large number of properties. The numeric values computed from each LJ EOS for each reference data point are reported in the electronic Supplementary Material, which makes the employed test procedure fully transparent and reproducible and enables an extension of the present study to new LJ EOS that may be developed in future work.

Despite the simplicity of the Lennard-Jones fluid and the underlying intermolecular potential and the fact that for more than 50 years LJ EOS have been proposed, no LJ EOS gives a satisfactory description of the LJ fluid, in a sense that it a) represent the available reference data well for most of the properties, i.e. the deviations between the results of the EOS and the computer simulation data are of the same order of magnitude as the uncertainties of the simulation data, b) it shows no unphysical behavior in the two-phase region, and c) it is well-behaved when used for extrapolations to regions in which extreme conditions prevail. Some LJ EOS meet the criterion a) well, namely the LJ EOS of *Mecke et al.*^{70,71}, *Gottschalk*⁸³, and *Thol et al.*³⁷, but they fail to meet the other criteria in one or several ways. Only the LJ EOS of *Kolafa and Nezbeda*⁵⁷ is found to meet all criteria reasonably well, but is, regarding criterion a) slightly less precise than the three aforementioned LJ EOS. The four LJ EOS of *Kolafa and Nezbeda*⁵⁷, *Mecke et al.*^{70,71}, *Gottschalk*⁸³, and *Thol et al.*³⁷ were found to give an overall similarly good description of the Lennard-Jones fluid. However, their performance was found to differ significantly in different fluid regions and thermodynamic properties. The LJ EOS of *Kolafa and Nezbeda*⁵⁷ is found to be the most robust LJ EOS, cf. Table VI. The LJ EOS of *Thol et al.*³⁷ and *Gottschalk*⁸³ exhibit multiple van der Waals loops and the LJ EOS of *Mecke et al.*^{70,71} exhibit large deviations at extreme temperature and density.

The LJ EOS of *Johnson et al.*⁵⁶ has been used extensively in the literature, but is found to be significantly less precise than either of the four aforementioned. Nevertheless, among the MBWR type LJ EOS^{12,30,56,69,72,80,81}, that of *Johnson et al.*⁵⁶ is found to be the best.

The four overall most precise LJ EOS^{37,57,70,71,83} are empirical or semi-theoretical LJ EOS; the theoretically-based LJ EOS are found to be overall significantly less precise (for most properties they are about an order of magnitude less precise than the best LJ EOS). Very surprisingly, the theoretically-based LJ EOS are found to give a less precise performance upon extrapolating to extreme temperatures and densities compared to the best empirical LJ EOS. This is particularly striking since the considered LJ EOS are based on *Barker and Henderson's* perturbation theory, which is expected to perform well at high temperatures, where the attractive forces play a minor role. Hence, the systematic deviations are probably due to the modeling of the soft repulsion in the theory around the hard sphere reference system.

The theoretically-based LJ EOS of *Cotterman et al.*²⁹, *Paricaud*⁷⁷, *Lafitte et al.*⁴², and *van Westen and Gross*⁸² are found to give a good representation of most thermodynamic properties, but are overall significantly less precise than the best empirical and semi-theoretical LJ EOS. Despite the large differences of the year of publication which varies between 1986 and 2017 and differences of the underlying models, the performance of the four theoretically-based LJ EOS of Refs.^{29,42,77,82} is overall similar.

SAFT type EOS have become very popular in the last 30 years and many variants of these EOS exist. Several of them use monomer terms that were developed to match data of the Lennard-Jones fluid, i.e. the monomer terms are LJ EOS. Four of them were included in the present study^{12,42,56,57}. However, the monomer term of PC-SAFT – a particularly important version of SAFT – could not be included directly in the present study, as it was not developed to describe the Lennard-Jones fluid. Therefore, in the present work, the PC-SAFT monomer term was re-parameterized using data of the LJ fluid. The resulting LJ EOS is found to be more precise for most properties and fluid regions than the theoretically-based LJ EOS of Refs.^{29,42,77,82}, which is probably due to the employed parametrization strategy that takes both VLE and homogeneous data into account. However, the present work reveals also shortcomings of the PC-SAFT monomer term: it exhibits important systematic deviations in the supercritical region – especially for caloric properties. This is attributed to the simplified form of the temperature-dependent diameter, which is used for the modeling of the soft repulsive interactions in the PC-SAFT monomer term.

The comparison and evaluation of LJ EOS employed in the present work is based on a systematic strategy: an extensive and consolidated database is used as reference data that

comprises a broad variety of properties; each EOS is tested on that reference data; the fluid region is divided into characteristic sub-regions, e.g. in the $T - \rho$ space; each property is studied in each region separately before the results are combined to achieve an overall assessment. This strategy could also be useful for testing other pure component EOS and be applied as a benchmark test for new Lennard-Jones equations of state.

APPENDIX A – LENNARD-JONES REFERENCE DATABASE

Table VII gives an overview of the consolidated database of computer experiment data on the LJ fluid used in the present work for the evaluation of the LJ EOS. Table VII also reports the number of data points available in a given reference and the number of outliers identified therein¹¹. The latter were discarded in the present work for the evaluation of the LJ EOS. The numeric values computed from each LJ EOS for each reference data point are reported in the electronic Supplementary Material.

TABLE VII: Computer experiment data of the LJ fluid used as reference. The database is adapted from Ref.¹¹. The data is sorted for each property chronologically. The column # reports number of data points and, in brackets, is the number of outliers therein. The column T reports the temperature range in which data are available.

Authors	Year	#	T
VLE $p^s, \rho', \rho'', \Delta h_v$			
<i>Lotfi et al.</i> ¹⁰⁴ ($p^s, \rho', \rho'', \Delta h_v$)	1992	48(4)	0.7 - 1.5
<i>Okumura and Yonezawa</i> ¹²¹ (p^s, ρ', ρ'')	2001	15(0)	1.25 - 1.29
<i>Errington</i> ¹²⁴ (p^s, ρ', ρ'')	2003	9(0)	0.7 - 1.1
<i>Errington</i> ¹²⁵ (p^s, ρ', ρ'')	2003	36(3)	0.7 - 1.2
<i>Mick et al.</i> ¹³¹ ($p^s, \rho', \rho'', \Delta h_v$)	2013	32(8)	0.75 - 1.3
<i>Janeček et al.</i> ¹³³ ($p^s, \rho', \rho'', \Delta h_v$)	2017	24(0)	0.8 - 1.25
<i>Stephan et al.</i> ¹¹ ($p^s, \rho', \rho'', \Delta h_v$)	2019	124(4)	0.69 - 1.28
pvT			
<i>Wood and Parker</i> ⁵	1957	13(8)	2.74
<i>Fickett and Wood</i> ¹⁸¹	1960	23(6)	1.92 - 177.95
<i>McDonald and Singer</i> ¹⁸²	1967	28(17)	0.72 - 1.24
<i>McDonald and Singer</i> ⁹	1967	48(9)	1.45 - 3.53
<i>Verlet and Levesque</i> ¹⁴⁷	1967	7(5)	1.05 - 2.74
<i>Verlet</i> ⁸	1967	39(9)	0.59 - 4.63
<i>Wood</i> ¹⁸³	1968	41(17)	1.06 - 100
<i>Hansen and Verlet</i> ¹⁰	1969	25(5)	0.75 - 1.15
<i>Levesque and Verlet</i> ⁶¹	1969	25(7)	0.72 - 3.67
<i>McDonald and Singer</i> ¹⁸⁴	1969	28(15)	0.72 - 1.24
<i>Hansen</i> ¹⁸⁵	1970	9(1)	2.74 - 100
<i>McDonald and Woodcock</i> ¹⁸⁶	1970	6(3)	0.75 - 2.33
<i>Toxvaerd and Praestgaard</i> ⁶²	1970	8(2)	1.35
<i>Weeks et al.</i> ⁸⁸	1971	5(1)	0.75 - 1.35
<i>McDonald and Singer</i> ⁶³	1972	56(19)	0.55 - 1.24

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Authors	Year	#	T
<i>Schofield</i> ¹⁸⁷	1973	6(6)	0.73 - 1.10
<i>Street et al.</i> ¹⁸⁸	1974	80(45)	0.75 - 3.05
<i>Adams</i> ¹⁸⁹	1975	12(8)	2 - 4
<i>Adams</i> ⁹⁷	1976	16(7)	1.0 - 1.2
<i>Carley</i> ¹⁹⁰	1977	11(3)	1.35
<i>Adams</i> ⁹⁹	1979	31(11)	1.15 - 1.35
<i>Nicolas et al.</i> ¹²	1979	108(13)	0.48 - 6.01
<i>Ree</i> ²⁸	1980	11(1)	0.81 - 2.7
<i>Yao et al.</i> ¹⁹¹	1982	12(1)	1.15 - 1.25
<i>Powles et al.</i> ⁹⁵	1982	37(9)	0.7 - 1.41
<i>Lucas</i> ¹⁹²	1986	10(2)	0.79 - 1.83
<i>Shaw</i> ¹⁹³	1988	265(44)	0.6 - 136.25
<i>Adachi et al.</i> ³⁰	1988	328(250)	0.7 - 2.95
<i>Baranyai et al.</i> ¹⁹⁴	1989	12(0)	0.75 - 1.5
<i>Saager and Fischer</i> ¹⁹⁵	1990	38(1)	0.57 - 4
<i>Sowers and Sandler</i> ⁶⁷	1991	60(6)	1.35 - 6
<i>Lotfi et al.</i> ¹⁰⁴	1992	19(7)	0.7 - 1.3
<i>Giaquinta et al.</i> ¹⁹⁶	1992	12(0)	0.75 - 1.15
<i>Johnson et al.</i> ⁵⁶	1993	199(6)	0.7 - 6
<i>Kolafa et al.</i> ¹⁹⁷	1993	43(2)	0.72 - 4.85
<i>Miyano</i> ⁶⁹	1993	112(13)	0.45 - 100
<i>Kolafa and Nezbeda</i> ⁵⁷	1994	13(0)	0.81 - 10
<i>Lustig</i> ¹⁹⁸	1994	2(0)	1.18
<i>Mecke et al.</i> ⁷⁰	1996	12(0)	1.32 - 1.34
<i>Roccatano et al.</i> ¹⁹⁹	1998	10(3)	1.4 - 10.0
<i>Meier</i> ²⁰⁰	2002	351(4)	0.7 - 6
<i>Linhart et al.</i> ¹⁵⁹	2005	108(18)	0.7 - 1.2
<i>Morsali et al.</i> ²⁰¹	2007	13(0)	5.01
<i>Baidakov et al.</i> ²⁰²	2008	208(5)	0.35 - 2
<i>Lustig</i> ²⁰³	2011	8(0)	1.02 - 3.0
<i>May and Mausbach</i> ²⁰⁴	2012	205(8)	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{205,206}	2012	406(24)	1.3 - 2.62
<i>Mairhofer and Sadus</i> ²⁰⁷	2013	282(8)	1.36 - 3.05
<i>Thol et al.</i> ³⁷	2016	197(3)	0.7 - 9
<i>Deiters and Neumaier</i> ²⁰⁸	2016	255(2)	0.67 - 22.54
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(2)	1.01 - 30.0
<i>Ustinov</i> ²⁰⁹	2017	232(18)	0.76 - 1.14
<i>Schultz and Kofke</i> ²¹⁰	2018	404(93)	0.68 - 2272.73
<i>Stephan et al.</i> ¹¹	2019	655(8)	0.7 - 90
Internal energy u^{res}			
<i>Wood and Parker</i> ⁵	1957	13(9)	2.74
<i>McDonald and Singer</i> ¹⁸²	1967	27(19)	0.72 - 1.24
<i>McDonald and Singer</i> ⁹	1967	48(44)	1.45 - 3.53
<i>Verlet</i> ⁸	1967	39(11)	0.59 - 4.63
<i>Verlet and Levesque</i> ¹⁴⁷	1967	7(5)	1.05 - 2.74
<i>Wood</i> ¹⁸³	1968	41(15)	1.06 - 100

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Authors	Year	#	T
<i>Levesque and Verlet</i> ⁶¹	1969	25(10)	0.72 - 3.67
<i>McDonald and Singer</i> ¹⁸⁴	1969	28(8)	0.72 - 1.24
<i>Hansen</i> ¹⁸⁵	1970	9(5)	2.74 - 100
<i>McDonald and Woodcock</i> ¹⁸⁶	1970	6(2)	0.75 - 2.33
<i>Weeks et al.</i> ²¹¹	1971	5(2)	0.75 - 1.35
<i>McDonald and Singer</i> ⁶³	1972	56(19)	0.55 - 1.24
<i>Street et al.</i> ¹⁸⁸	1974	80(48)	0.75 - 3.05
<i>Adams</i> ¹⁸⁹	1975	12(11)	2 - 4
<i>Adams</i> ⁹⁷	1976	16(16)	1.0 - 1.2
<i>Torrie and Valleau</i> ²¹²	1977	7(6)	0.092 - 1.35
<i>Adams</i> ⁹⁹	1979	31(1)	1.15 - 1.35
<i>Nicolas et al.</i> ¹²	1979	108(24)	0.48 - 6.01
<i>Ree</i> ²⁸	1980	11(4)	0.81 - 2.7
<i>Yao et al.</i> ¹⁹¹	1982	12(7)	1.15 - 1.25
<i>Lucas</i> ¹⁹²	1986	10(4)	0.79 - 1.83
<i>Shaw</i> ¹⁹³	1988	265(68)	0.59 - 136.25
<i>Baranyai et al.</i> ¹⁹⁴	1989	18(0)	0.75 - 1.5
<i>Saager and Fischer</i> ¹⁹⁵	1990	38(0)	0.57 - 4
<i>Sowers and Sandler</i> ⁶⁷	1991	54(13)	1.35 - 6
<i>Lotfi et al.</i> ¹⁰⁴	1992	19(1)	0.7 - 1.3
<i>Giaquinta et al.</i> ¹⁹⁶	1992	12(0)	0.75 - 1.15
<i>Johnson et al.</i> ⁵⁶	1993	199(10)	0.7 - 6
<i>Kolafa et al.</i> ¹⁹⁷	1993	43(1)	0.72 - 4.85
<i>Miyano</i> ⁶⁹	1993	112(25)	0.45 - 100
<i>Kolafa and Nezbeda</i> ⁵⁷	1994	13(1)	0.81 - 10
<i>Lustig</i> ¹⁹⁸	1994	2(0)	1.18
<i>Mecke et al.</i> ⁷⁰	1996	12(0)	1.32 - 1.34
<i>Roccatano et al.</i> ¹⁹⁹	1998	10(6)	1.4 - 10.0
<i>Meier</i> ²⁰⁰	2002	351(7)	0.7 - 6
<i>Baidakov et al.</i> ²⁰²	2008	201(9)	0.35 - 2
<i>May and Mausbach</i> ²⁰⁴	2012	218(7)	0.68 - 6.17
<i>Yigzawe and Sadus</i> ^{205,206}	2012	346(96)	1.31 - 2.62
<i>Mairhofer and Sadus</i> ²⁰⁷	2013	282(0)	1.36 - 3.05
<i>Thol et al.</i> ³⁷	2016	197(3)	0.7 - 9
<i>Deiters and Neumaier</i> ²⁰⁸	2016	255(2)	0.67 - 22.54
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(11)	1.01 - 30.0
<i>Ustinov</i> ²⁰⁹	2017	232(105)	0.76 - 1.14
<i>Schultz and Kofke</i> ²¹⁰	2018	404(98)	0.68 - 2272.73
<i>Stephan et al.</i> ¹¹	2019	655(14)	0.7 - 90
Isochoric heat capacity c_v			
<i>Wood and Parker</i> ⁵	1957	11(6)	2.74
<i>McDonald and Singer</i> ¹⁸²	1967	26(16)	0.72 - 1.24
<i>McDonald and Singer</i> ⁹	1967	48(29)	1.45 - 3.53
<i>Adams</i> ¹⁸⁹	1975	12(5)	2 - 4
<i>Adams</i> ⁹⁹	1979	31(12)	1.15 - 1.35
<i>Saager et al.</i> ²¹³	1990	12(4)	1.1 - 1.35
Continued on next page			

Authors	Year	#	T
<i>Boda et al.</i> ²¹⁴	1996	9(0)	1.31 - 2
<i>Roccatano et al.</i> ¹⁹⁹	1998	10(2)	1.4 - 10.0
<i>Meier</i> ²⁰⁰	2002	327(12)	0.7 - 6
<i>Baidakov et al.</i> ²⁰²	2008	208(11)	0.35 - 2
<i>May and Mausbach</i> ²⁰⁴	2012	218(11)	0.68 - 6.17
<i>Yigzawe and Sadus</i> ^{205,206}	2012	406(32)	1.3 - 2.62
<i>Mairhofer and Sadus</i> ²⁰⁷	2013	282(3)	1.36 - 3.05
<i>Thol et al.</i> ³⁷	2016	197(5)	0.7 - 9
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(2)	1.01 - 30.0
<i>Stephan et al.</i> ¹¹	2019	515(4)	0.7 - 90
Isobaric heat capacity c_p			
<i>Boda et al.</i> ²¹⁴	1996	41(6)	0.65 - 1.9
<i>Lustig</i> ²⁰³	2011	6(0)	1.02 - 3.0
<i>May and Mausbach</i> ²⁰⁴	2012	202(4)	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{205,206}	2012	406(52)	1.3 - 2.62
<i>Mairhofer and Sadus</i> ²⁰⁷	2013	282(7)	1.36 - 3.05
<i>Thol et al.</i> ³⁷	2016	197(12)	0.7 - 9
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(2)	1.01 - 30.0
<i>Stephan et al.</i> ¹¹	2019	515(8)	0.7 - 90
Helmholtz energy $\tilde{a}^{\text{res}}$			
<i>Levesque and Verlet</i> ⁶¹	1969	8(4)	1.35
<i>Hansen and Verlet</i> ¹⁰	1969	25(13)	0.75 - 1.15
<i>Weeks et al.</i> ⁸⁸	1971	5(0)	0.75 - 1.35
<i>Weeks et al.</i> ²¹¹	1971	27(14)	0.75 - 1.35
<i>Torrie and Valleau</i> ²¹²	1977	16(6)	0.75 - 2.74
<i>Baranyai and Evans</i> ¹⁹⁴	1989	6(0)	1.15
<i>Cuadros et al.</i> ⁷³	1996	269(268)	0.7 - 2.6
<i>Hong and Jhon</i> ²¹⁵	1997	36(22)	0.59 - 2.89
<i>Hong and Jang</i> ²¹⁶	2003	22(11)	0.59 - 2.85
<i>Thol et al.</i> ³⁷	2016	197(10)	0.7 - 9
<i>Köster et al.</i> ²¹	2017	65(3)	1.3 - 30.0
<i>Stephan et al.</i> ¹¹	2019	655(18)	0.7 - 90
Chemical potential μ^{res}			
<i>Adams</i> ¹⁸⁹	1975	12(11)	2 - 4
<i>Adams</i> ⁹⁷	1976	16(7)	1 - 1.2
<i>Adams</i> ⁹⁹	1979	31(5)	1.15 - 1.35
<i>Yao et al.</i> ¹⁹¹	1982	12(0)	1.15 - 1.25
<i>Powles et al.</i> ⁹⁵	1982	37(35)	0.7 - 1.41
<i>Lotfi et al.</i> ¹⁰⁴	1992	19(1)	0.7 - 1.3
<i>Han</i> ²¹⁷	1992	3(1)	1.2
<i>Kolafa et al.</i> ¹⁹⁷	1993	7(1)	1.2 - 1.45
<i>Lustig</i> ¹⁹⁸	1994	2(2)	1.18
<i>Thol et al.</i> ³⁷	2016	197(7)	0.7 - 9

Continued on next page

Authors	Year	#	T
<i>Köster et al.</i> ²¹	2017	65(0)	1.3 - 30.0
<i>Ustinov</i> ²⁰⁹	2017	232(57)	0.76 - 1.14
<i>Stephan et al.</i> ¹¹	2019	656(20)	0.7 - 90
Thermal expansion coefficient α			
<i>McDonald and Singer</i> ¹⁸²	1967	20(9)	0.72 - 1.24
<i>Adams</i> ¹⁸⁹	1975	12(4)	2 - 4
<i>Yigzawe and Sadus</i> ^{205,206}	2012	406(48)	1.3 - 2.62
<i>Thol et al.</i> ³⁷	2016	197(9)	0.7 - 9
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(4)	1.01 - 30.0
<i>Stephan et al.</i> ¹¹	2019	515(11)	0.7 - 90
Isothermal compressibility β			
<i>McDonald and Singer</i> ¹⁸²	1967	22(14)	0.72 - 1.24
<i>Adams</i> ¹⁸⁹	1975	12(9)	2 - 4
<i>Adams</i> ⁹⁹	1979	31(21)	1.15 - 1.35
<i>Lotfi et al.</i> ¹⁰⁴	1992	19(3)	0.7 - 1.3
<i>Lustig</i> ¹⁹⁸	1994	2(0)	1.18
<i>Morsali et al.</i> ²⁰¹	2007	13(0)	3.76
<i>May and Mausbach</i> ²⁰⁴	2012	205(6)	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{205,206}	2012	406(43)	1.3 - 2.62
<i>Mairhofer and Sadus</i> ²⁰⁷	2013	282(6)	1.36 - 3.05
<i>Thol et al.</i> ³⁷	2016	197(7)	0.7 - 9
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(4)	1.01 - 30.0
<i>Stephan et al.</i> ¹¹	2019	515(6)	0.7 - 90
Thermal pressure coefficient γ			
<i>McDonald and Singer</i> ¹⁸²	1967	20(19)	0.72 - 1.24
<i>Adams</i> ¹⁸⁹	1975	12(10)	2 - 4
<i>Lustig</i> ¹⁹⁸	1994	2(0)	1.18
<i>Meier</i> ²⁰⁰	2002	326(14)	0.7 - 6
<i>Morsali et al.</i> ²⁰¹	2007	13(0)	3.76
<i>May and Mausbach</i> ²⁰⁴	2012	205(2)	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{205,206}	2012	406(20)	1.3 - 2.62
<i>Mairhofer and Sadus</i> ²⁰⁷	2013	282(9)	1.36 - 3.05
<i>Thol et al.</i> ³⁷	2016	197(8)	0.7 - 9
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(2)	1.01 - 30.0
<i>Stephan et al.</i> ¹¹	2019	515(5)	0.7 - 90
Speed of sound w			
<i>Meier</i> ²⁰⁰	2002	349(20)	0.7 - 6
<i>Lustig</i> ²⁰³	2011	8(0)	1.02 - 3.0
<i>Yigzawe and Sadus</i> ^{205,206}	2012	406(29)	1.3 - 2.62
<i>May and Mausbach</i> ²⁰⁴	2012	205(8)	0.69 - 6.17
<i>Mairhofer and Sadus</i> ²⁰⁷	2013	282(0)	1.36 - 3.05
<i>Continued on next page</i>			

Authors	Year	#	T
<i>Thol et al.</i> ³⁷	2016	197(6)	0.7 - 9
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(8)	1.01 - 30.0
<i>Stephan et al.</i> ¹¹	2019	515(8)	0.7 - 90
Joule-Thomson coefficient μ_{JT}			
<i>Lustig</i> ²⁰³	2011	8(0)	1.02 - 3.0
<i>May and Mausbach</i> ²⁰⁴	2012	205(5)	0.69 - 6.17
<i>Yigzawe and Sadus</i> ^{205,206}	2012	406(22)	1.3 - 2.62
<i>Mairhofer and Sadus</i> ²⁰⁷	2013	282(22)	1.36 - 3.05
<i>Thol et al.</i> ³⁷	2016	197(20)	0.7 - 9
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(2)	1.01 - 30.0
<i>Stephan et al.</i> ¹¹	2019	515(5)	0.7 - 90
Grüneisen parameter Γ			
<i>Emampour et al.</i> ²¹⁸	2011	26(18)	1.2 - 1.8
<i>Mausbach and May</i> ²¹⁹	2014	212(11)	0.69 - 6.17
<i>Thol et al.</i> ³⁷	2016	197(3)	0.7 - 9
<i>Mausbach et al.</i> ²²⁰	2016	110(9)	0.72 - 9
<i>Köster et al.</i> ²¹	2017	45(0)	1.01 - 30.0
<i>Köster et al.</i> ²¹	2017	65(4)	1.01 - 30.0
<i>Stephan et al.</i> ¹¹	2019	515(14)	0.7 - 90

APPENDIX B – PARAMETRIZATION OF NEW LJ EOS BASED ON THE PC-SAFT MONOMER MODEL

The LJ EOS developed in the present work is a re-parameterization of the PC-SAFT⁵⁸ monomer model, i.e. a spherical particle with soft repulsive and dispersive interactions. The universal constants of the PC-SAFT EOS⁵⁸ have been optimized several times in the literature^{38,78,166,170,171}. *Gross and Sadowski*¹⁷⁰, who developed the original version of the PC-SAFT EOS adjusted the universal constants to hard chain computer experiment data¹⁷⁰ and n-alkane VLE properties⁵⁸; *Liang and Kontogeorgis*^{166,171} fitted the parameters to VLE and speed of sound data of different real substances, and *Heier et al.*³⁸ fitted the parameters to VLE data of the Lennard-Jones truncated and shifted fluid. To include the PC-SAFT monomer model in the comprehensive comparison of the present work, its universal constants were re-parametrized such as to match computer experiment data of the Lennard-Jones fluid.

As most other theoretically-based LJ EOS, the PC-SAFT monomer model is based on perturbation theory^{86,89,172–174}. The PC-SAFT monomer model uses the perturbation theory

of *Barker and Henderson*^{86,87}, according to which the Helmholtz energy of the LJ fluid can be written as

$$\tilde{a} = \tilde{a}_{\text{id}} + \tilde{a}_{\text{res}} = \tilde{a}_{\text{id}} + \tilde{a}_{\text{ref}} + \tilde{a}_{\text{pert}} , \quad (20)$$

where $\tilde{a}_{\text{ref}}$ and $\tilde{a}_{\text{pert}}$ are the Helmholtz energy contribution of the reference system and the perturbation, respectively.

The Helmholtz energy of the hard sphere fluid of the PC-SAFT monomer is adopted from *Boublík*⁹¹ and *Mansoori et al.*⁹² as

$$\tilde{a}_{\text{ref}} = \tilde{a}_{\text{hs}} = \zeta_0^{-1} \left(\frac{3\zeta_1\zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1-\zeta_3) \right) , \quad (21)$$

where ζ_n is defined as

$$\zeta_n = \frac{\pi}{6} \rho d^n \quad \text{with } n = 0, 1, 2, 3 , \quad (22)$$

where $\zeta_3 = \eta$ is the packing fraction and ρ is the number density.

Following *Barker and Henderson*¹⁷⁵, the purely repulsively interacting reference fluid is that of a hard sphere, with an effective temperature-dependent hard sphere diameter d as

$$d(T) = \int_0^1 \left(1 - \exp \left(- \frac{u_{\text{LJ}}(r)}{T} \right) \right) dr . \quad (23)$$

This temperature-dependent diameter gives the repulsive hard sphere term its softness. The PC-SAFT monomer model simplifies Eq. (23) to an algebraic equation proposed by *Chen and Kreglewski*¹⁷⁶ to avoid the numerical integration to

$$d(T) = 1 - c_1 \cdot \exp \left(- \frac{c_2}{T} \right) . \quad (24)$$

The perturbation contribution $\tilde{a}_{\text{pert}}$ is modeled up to second order in the PC-SAFT monomer model, i.e.

$$\tilde{a}_{\text{pert}} = \frac{1}{T} \tilde{a}_1 + \frac{1}{T^2} \tilde{a}_2 . \quad (25)$$

As described in detail in Refs.^{87,175}, applying the *local compressibility-version* of *Barker and Henderson's* perturbation theory, the first and second order perturbation terms can be written as

$$\tilde{a}_1 = -2\pi\rho \int_1^\infty u_{\text{pert}}(r) g_0(r) r^2 dr , \quad \text{and} \quad (26)$$

$$\tilde{a}_2 = -\pi \rho \left(1 + \frac{8\eta - 2\eta^2}{(1 - \eta^4)} \right) \frac{\partial}{\partial \rho} \left[\rho \int_1^\infty u_{\text{pert}}(r)^2 g_0(r) r^2 dr \right]. \quad (27)$$

Following the ansatz of *Gross and Sadowski* made in their PC-SAFT equation of state^{58,170}, the integrals in Eq. (26) and (27) are simplified into a power series expansion in the packing fraction:

$$\int_1^\infty u_{\text{pert}}(r) g_0(r) r^2 dr = I_1 = \sum_{i=0}^N a_i \eta^i, \quad (28)$$

$$\frac{\partial}{\partial \rho} \left[\rho \int_1^\infty u_{\text{pert}}(r)^2 g_0(r) r^2 dr \right] = I_2 = \sum_{i=0}^N b_i \eta^i. \quad (29)$$

The parameters c_1 , c_2 , a_i , and b_i ($i = 1 \dots N$) are the state-independent universal constants of the PC-SAFT monomer model. We chose $N = 7$ for the present work. The 18 model parameters were adjusted in the present work to data of the LJ fluid. Only a subset of the computer experiment data compiled in Ref.¹¹ was used for that purpose. It comprises consistent and comprehensive data for the VLE and homogeneous fluid states^{11,37,164}.

The optimization was guided by the idea that a good representation of VLE properties should be accompanied by a good representation of bulk properties. Therefore, the data set used for the parametrization was a combination of the homogeneous state data and vapor-liquid equilibrium data. Not the full set of simulation data compiled in Ref.¹¹ that was used for testing the EOS as described in the main part of the paper was also used for the re-parameterization of the PC-SAFT monomer term. The large and consistent set of simulation data of *Thol et al.*³⁷ for homogeneous stable states was selected here, as it provides the residual Helmholtz energy $\tilde{a}^{\text{res}} = a^{\text{res}}/T$ and its derivatives with respect to the inverse temperature and the density for each state point. The vapor pressure and the saturated densities were taken from the correlations from Ref.¹¹ that describe the most precise computer experiment data within their combined scattering. Furthermore, data for the second and third virial coefficient in the range $T = 1.32 - 5$ with a discretization step of 0.005 were used for the parametrization.

The employed parametrization strategy uses elements from multi-criteria optimization to account for conflicts between the different objectives and is based on recent work of our group^{177–180}. It is described in detail in the Supplementary Material.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding of the present work by the ERC Advanced Grant ENRICO (grant agreement No. 694807) and by the Deutsche Forschungsgemeinschaft – DFG (grant IRTG 2057 – 252408385). The present research was conducted under the auspices of the Boltzmann-Zuse Society of Computational Molecular Engineering (BZS).

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