



Prediction of Thermodynamic Properties of Fluids at Extreme Conditions: Assessment of the Consistency of Molecular-Based Models

J. Staubach and S. Stephan^(✉)

Laboratory of Engineering Thermodynamics (LTD), RPTU Kaiserslautern, Kaiserslautern, Germany

{jens.staubach,simon.stephan}@rptu.de

Abstract. For machining processes, such as drilling, grinding, and cutting, fluids play a crucial role for lubrication and cooling. For adequately describing such processes, robust models for the thermophysical properties of the fluids are a prerequisite. In the contact zone, extreme conditions prevail, e.g. regarding temperature and pressure. As thermophysical property data at such conditions are presently often not available, predictive and physical models are required. Molecular-based equations of state (EOS) are attractive candidates as they provide a favorable trade-off between computational speed and predictive capabilities. Yet, without experimental data, it is not trivial to assess the physical reliability of a given EOS model. In this work, Brown's characteristic curves are used to assess molecular-based fluid models. Brown's characteristic curves provide general limits that are to be satisfied such that a given model is thermodynamically consistent. Moreover, a novel approach was developed, which uses pseudo-experimental data obtained from molecular simulations using high-accurate force fields. The method is generalized in a way that it can be applied to different force field types, e.g. model potentials and complex real substances. The method was validated based on the (scarcely) available data in the literature. Based on this pseudo-experimental data, different thermodynamic EOS models were assessed. Only the SAFT-VR Mie EOS is found to yield thermodynamically consistent results in all cases. Thereby, robust EOS models were identified that can be used for reliably modeling cutting fluids at extreme conditions, e.g. in machining processes.

1 Introduction

Cutting fluids experience extreme conditions in a contact zone of machining processes (cf. Fig. 1), i.e. large temperature and pressure as well as extreme gradients in these properties [8, 47, 49]. The pressure in a tribological contact zone can be up to several GPa and the temperature up to 1 000 K [6, 8]. For modeling such processes, reliable and robust models for describing the thermophysical properties of the fluids, e.g. the heat capacity, compressibility, and density at a given temperature and pressure are required. Yet, classical laboratory experiments for determining thermophysical properties at such conditions are practically not feasible. Also, empirical models fitted to the available data

© The Author(s) 2023

J. C. Aurich et al. (Eds.): IRTG 2023, *Proceedings of the 3rd Conference on Physical Modeling for Virtual Manufacturing Systems and Processes*, pp. 170–188, 2023.

https://doi.org/10.1007/978-3-031-35779-4_10

at moderate conditions often exhibit an unrealistic extrapolation behavior to extreme temperature and pressure. Hence, physical predictive and reliable models are required.

Models based on molecular thermodynamics can be favorably used for predicting thermophysical properties due to their physical kernel, i.e. mathematical structure. In particular, the strong physical background of these models often allows successful extrapolations to conditions that were not considered for the model development such as extreme pressure and temperature. Both molecular dynamics (MD) simulations and molecular-based equation of state (EOS) models are attractive candidates for such applications.

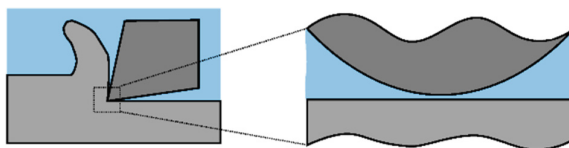


Fig. 1. Lubricated contact zone of a machining process between a workpiece (light gray) and a tool (dark gray). In the contact zone, extreme temperature and pressure prevail in the cutting fluid (blue).

The most popular modeling approach based on molecular thermodynamics is molecular simulation, i.e. molecular dynamics (MD) or Monte Carlo (MC) simulations based on classical molecular force fields. In molecular simulations, matter is modeled on the atomistic scale using a particle-based scheme. These particles interact with intermolecular potentials, i.e. the force fields. The accuracy of a molecular simulation primarily depends on the quality of the force field, which are available today for a large number of substances [46]. Molecular simulation has been extensively used for predicting thermophysical properties at extreme conditions, e.g. Refs. [32, 34, 35]. Due to the strong physical basis and reliability of the predictions, molecular simulations data is at times used as pseudo-experimental data where no ‘real’ experimental data is available [32, 34]. Yet, molecular simulations (MD or MC) are computationally expensive. For predicting thermophysical properties at a single state point, on the order of magnitude of 10^2 CPUh are required. An alternative modeling approach are molecular-based equation of state (EOS) models. They are algebraic models formulated in the Helmholtz energy as a function of the temperature and density, i.e. $a = a(T, \rho)$. Thereby, fluid properties at a given state point can be evaluated in milliseconds. Also, since the Helmholtz energy ansatz is a thermodynamic fundamental expression, all other thermodynamic properties can be derived from such a model – including phase equilibria, which are for example important for describing cavitation in a contact zone. Moreover, equation of state models can be favorably combined with further physical theories for modeling for example transport and interfacial properties, e.g. entropy scaling [20] and density gradient theory [40, 44]. In particular, molecular-based EOS models can be directly integrated for scale bridging in macroscopic models, e.g. in phase field or CFD simulations [15]. Molecular-based EOS come along with the drawback that approximations and assumptions are made

within the model formulation. Hence, compared to molecular simulation, molecular-based EOS have a less strong physical backbone. A good extrapolation behavior can therefore not be presumed *a priori*.

Different strategies have been proposed for the assessment of EOS models [1, 2, 17, 39, 48]. The thermodynamic consistency of a pure component model can for example be assessed using *ab initio* virial coefficients in the low-density limit and the Nezbeda compressibility or Clausius-Clapeyron test for the vapor-liquid equilibrium [30, 48]. An interesting strategy for testing the extrapolation behavior at extreme pressure and temperature liquid states is based on Brown's characteristic curves. Brown's characteristic curves define lines on the thermodynamic equilibrium surface and are named Zeno, Amagat, Boyle, and Charles curve. Each of the four characteristic curves has – for a given thermophysical property – the same behavior as the ideal gas [9]. These curves are located within a large pressure and temperature range. For a given molecular fluid, Brown's characteristic curves are known to exhibit certain thermodynamic features [9]. Therefore, Brown's characteristic curves have become an important tool for the assessment of the extrapolation behavior of new EOS [1, 39, 43]. Nevertheless, due to the extreme conditions, there is practically no experimental data available on the characteristic curves. Therefore, Brown's characteristic curves are usually only used for a qualitative assessment of the behavior of the model, i.e. evaluating the limits and the general shape. It should moreover be noted that providing thermodynamically consistent Brown's characteristic curves is a necessary, but not sufficient condition for a thermodynamic model being physically reasonable, which is also shown in an example in this work.

In this work, a novel approach was developed for testing the extrapolation behavior of EOS models based on Brown's characteristic curves using pseudo-experimental data obtained from molecular simulation. This approach conveniently combines the strong physical backbone and predictive capabilities of molecular force field models [32, 34, 35] with the computational advantages of molecular-based EOS. By using molecular simulation pseudo-experimental data, not only the thermodynamic consistency of the EOS model regarding Brown's characteristic curves can be assessed, but also the accuracy of the model can be simultaneously evaluated. The computational procedure for determining Brown's characteristic curves for a given force field model is adopted from [51]. The new approach for assessing EOS models with pseudo-experimental characteristic curve data was tested on both model fluids and real substances. This paper is outlined as follows: First, the methods used for determining the characteristic curves are described. Then, the results for the different substances are presented and discussed.

2 Methods

2.1 Brown's Characteristic Curves

The characteristic curves of a molecular fluid were postulated by E.H. Brown [9] as curves on the thermodynamic $p\nu T$ surface, along which the compressibility factor Z or its derivatives are identical to the values of an ideal gas. Brown's characteristic curves include state points at extreme conditions regarding temperature and pressure and can therefore be used as a tool for testing the extrapolation behavior of EOS. Moreover, on the

thermodynamically consistent surface, Brown deduced from physical arguments that the curves exhibit certain features and limits (details are given below) that can be favorably used for the assessment of models at extreme conditions. The four characteristic curves are:

- Zeno curve Z (also called ideal curve)
- Amagat curve A (also called Joule inversion curve)
- Boyle curve B
- Charles curve C (also called Joule-Thomson inversion curve)

Figure 2 shows a schematic representation of Brown's characteristic curves. The characteristic curves are shown in a double-logarithmic temperature-pressure (pT) diagram. Based on rational thermodynamic arguments, Brown derived several requirements for the characteristic curves to be thermodynamically consistent: Each characteristic curve exhibits a single pressure maximum. Furthermore, the Zeno curve crosses each of the other three curves in one point (cf. Fig. 2), whereas the Boyle, Charles, and Amagat curve do not intersect each other. Moreover, the Charles curve terminates on the vapor-liquid binodal and the Boyle curve terminates on the spinodal. The characteristic curves end at low pressure (corresponds to low densities) at specific temperatures, which are directly linked to the second virial coefficient B [43], which is often known with very high accuracy. In the virial expansion up to second order, the compressibility factor Z can be written as

$$Z = 1 + B\rho. \quad (1)$$

Hence, there is a direct link between the zero-pressure limit of the characteristic curves and the second virial coefficient [29, 43]. In the following, the definition and general features of the four characteristic curves are introduced. A comprehensive introduction to Brown's characteristic curves is given in Refs. [4, 5, 29, 43].

State points on the Zeno curve satisfy the relation

$$Z = \frac{vp}{RT} = 1, \quad (2)$$

where Z is the compressibility factor, v the molar volume, p the pressure, R the molar gas constant, and T the temperature. The definition can be rewritten in terms of the Helmholtz energy as

$$\rho \left(\frac{\partial \tilde{a}}{\partial \rho} \right)_T = 0, \quad (3)$$

where ρ is the molar density and $\tilde{a}$ is the molar Helmholtz energy defined as $\tilde{a} = \frac{A}{N_A k_B T}$ with the Boltzmann constant k_B and the Avogadro constant N_A .

The Zeno curve ends at the so-called Boyle temperature in the zero-pressure (and therefore zero-density) limit, cf. Fig. 2. At the Boyle temperature, the second virial coefficient is zero $B(T_{\text{Boyle}}) = 0$, which directly follows from comparing the definition of the Zeno curve Eq. (2) with the virial expansion Eq. (1). The Zeno curve intersects all other characteristic curves. The intersection of the Zeno and the Boyle curve is located in the zero-pressure limit at the Boyle temperature. The temperature of the

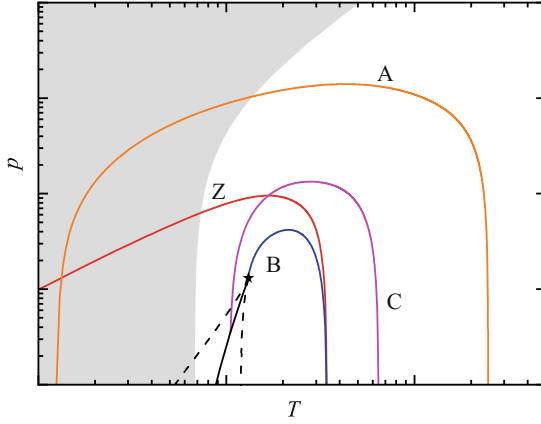


Fig. 2. Schematic representation of Brown's characteristic curves in the temperature-pressure (pT) projection. The Zeno curve Z (red), Amagat curve A (orange), Boyle curve B (blue), and Charles curve C (pink) are shown. The gray-shaded area indicates the solid phase region. The VLE, spinodals, and critical point of the fluid are indicated by the solid black line, the dashed black line, and the star, respectively.

intersection with the Charles curve is approximately the critical temperature of the fluid, cf. Fig. 2. The intersection of the Zeno curve with the Amagat curve is located at very low temperatures – for many substances in the solid phase region.

The Boyle curve is defined by the following relations:

$$\left(\frac{\partial Z}{\partial 1/\rho}\right)_T = 0, \quad \left(\frac{\partial Z}{\partial p}\right)_T = 0. \quad (4)$$

These definitions can be rewritten in terms of the Helmholtz energy as

$$\rho \left(\frac{\partial \tilde{a}}{\partial \rho}\right)_T + \rho^2 \left(\frac{\partial^2 \tilde{a}}{\partial \rho^2}\right)_T = 0. \quad (5)$$

The Boyle curve starts at the Boyle temperature in the zero-pressure limit, cf. Fig. 2. The Boyle curve has a bell shape and ends at the spinodal in the metastable region of the fluid, where the first and second density derivative of the Helmholtz energy are zero.

The Charles curve is defined by one of the following relations:

$$\left(\frac{\partial Z}{\partial 1/\rho}\right)_p = 0, \quad \text{or} \quad \left(\frac{\partial Z}{\partial T}\right)_p = 0, \quad \text{or} \quad \left(\frac{\partial H}{\partial p}\right)_T = 0, \quad (6)$$

where H is the enthalpy. These relations can be rewritten in terms of the Helmholtz energy as

$$\rho \left(\frac{\partial \tilde{a}}{\partial \rho}\right)_T + \rho^2 \left(\frac{\partial^2 \tilde{a}}{\partial \rho^2}\right)_T + \frac{\rho}{T} \frac{\partial \tilde{a}}{\partial \rho} \frac{\partial \tilde{a}}{\partial 1/T} = 0. \quad (7)$$

The Charles curve starts in the zero-pressure limit at high temperatures where the tangent to the second virial coefficient curve passes through the origin, i.e. the equation

$dB/dT = B/T$ holds. At low temperatures, the Charles curve ends at the vapor-pressure curve. The Charles curve has a bell shape and encloses the Boyle curve. The Charles curve is also known as the Joule-Thomson inversion curve, which is of fundamental importance for refrigeration technologies. There are several studies available in the literature investigating the Joule-Thomson inversion curve for refrigerants [10, 12, 13, 22, 52, 53].

The Amagat curve is defined by one of the following relations:

$$\left(\frac{\partial Z}{\partial T}\right)_\rho = 0, \quad \text{or} \quad \left(\frac{\partial U}{\partial 1/\rho}\right)_T = 0, \quad (8)$$

where U indicates the internal energy. These relations can be rewritten in terms of the Helmholtz energy as

$$\frac{\rho}{T} \frac{\partial \tilde{a}}{\partial \rho \partial 1/T} = 0. \quad (9)$$

The Amagat curve starts in the zero-pressure limit at high temperatures, where the second virial coefficient exhibits a maximum. At low temperatures, the Amagat curve ends at the vapor-pressure curve. The Amagat curve has a bell shape and encloses the Boyle curve and the Charles curve, cf. Fig. 2.

To be thermodynamically consistent, all four curves are required to exhibit a concave shape throughout in the double logarithmic pT projection. Moreover, for model fluids, the zero-pressure limit state point can be computed exactly using the virial route [51]. Hence, the zero-pressure limit is known exactly for model fluids.

2.2 Substances

In this work, both model fluids and real substances were studied to demonstrate and test the novel approach. As model fluids, the Lennard-Jones (LJ) fluid, the Lennard-Jones truncated and shifted (LJTS) fluid, and five Mie fluids were studied. For the studied model fluids, spherical molecules were considered that interact with the respective interaction potential. The model potentials used here can be employed for describing a large number of real substances, for example available in the MolMod force field database [46]. The underlying interaction potential are moreover important, as they are often used as building block in complex molecular force fields of real substances [28, 46]. Three real substances were studied in this work: toluene, ethanol, and dimethyl ether. The three substances strongly differ regarding the molecular structure and intermolecular interactions such that the novel approach is tested here for different situations.

The (full) Lennard-Jones potential u_{LJ} is defined as

$$u_{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \quad (10)$$

with the energy parameter ε , the size parameter σ , and the distance between two particles r . The LJ potential models repulsive interactions between particles at very small distances and attractive (dispersive) interactions at intermediate distances. The exponent

12 characterizes the repulsive interactions and the exponent 6 the attractive interactions between particles. The LJ potential is relatively simple, but a good approximation for intermolecular interactions. It has been extensively used since the early days of computer simulations and, accordingly, high quality benchmark data is available for the LJ fluid [48]. The Lennard-Jones truncated and shifted (LJTS) potential u_{LJTS} is computationally much cheaper, but simplifies the dispersive long-range interactions. The LJTS potential is defined as

$$u_{\text{LJTS}}(r) = \begin{cases} u_{\text{LJ}}(r) - u_{\text{LJ}}(r_c) & r \leq r_c \\ 0 & r > r_c, \end{cases} \quad (11)$$

with the cutoff radius $r_c = 2.5\sigma$. The Mie potential is a generalization of the LJ potential defined as

$$u_{\text{Mie}}(r) = C\varepsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_n} - \left(\frac{\sigma}{r} \right)^{\lambda_m} \right], \quad (12)$$

with

$$C = \frac{\lambda_n}{\lambda_n - \lambda_m} \left(\frac{\lambda_n}{\lambda_m} \right)^{\frac{\lambda_m}{\lambda_n - \lambda_m}}. \quad (13)$$

Hence, the Mie λ_n, λ_m potential has two additional parameters: the exponent for the repulsive interactions λ_n and the exponent for the attractive interactions λ_m . Often, $\lambda_m = 6$ is chosen, while λ_n is often used as an additional adjustable parameter. In this work, five Mie fluids were considered with $(\lambda_n, \lambda_m) = (8,6) (12,6) (20,6) (12,4) (12,8)$.

For the real substances, toluene, ethanol, and dimethyl ether were chosen as high-accurate force fields for these substances are available in the literature [18, 25, 38, 46]. The force fields for toluene, ethanol, and dimethyl ether are based on a united-atom approach and modeled as rigid bodies, where the hydrogen atoms are not explicitly modeled. The toluene force field [25] has seven Lennard-Jones interactions sites and six point quadrupoles modeling the π orbital. The ethanol force field [38] has three Lennard-Jones interactions sites and three point charges modelling the alcohol group and enabling h-bonding. The dimethyl ether force field [18] has three Lennard-Jones interactions sites and a single point dipole modeling the overall polarity of the molecule.

Also, equation of state models for these substances are available in the literature. All three substances are base components in the chemical industry. Moreover, the three substances have strongly different molecular architecture and interactions: ethanol strongly forms hydrogen bonds, toluene is an aromatic compound with strong quadrupolar interactions caused by π -orbitals, and dimethyl ether has strong dipolar interactions. Hence, the three substances challenge the predictive capabilities of the molecular-based EOS models regarding different aspects.

2.3 Molecular Simulation

In this work, reference data for the assessment of the EOS models was generated using molecular dynamics simulations. Hence, the MD data is considered as pseudo-experimental data for the characteristic curves. In particular, high accurate molecular force field models were used that are known to provide excellent agreement with experimental data [18, 25, 38].

For determining the characteristic curve state points from a given force field, a new simulation method was developed by our group [51]. For the development, a large number of sampling routes were compared. Based on this systematic approach, for each characteristic curve, the most favorable simulation route was determined [51]. The new method has several advantages, e.g. a rigorous method for determining the statistical uncertainties and evaluating the thermodynamic self-consistency of the results [51]. Nevertheless, it should be noted that also systematical uncertainties – as well-known from laboratory experiments – may affect the reproducibility of the simulation results [36, 42], e.g. the simulation engines and implemented algorithms may have some minor influence on the results.

Molecular dynamics simulations were performed with the molecular simulation tool *ms2* [21, 33] using at least $N = 2,000$ particles. For each characteristic curve, at least 14 state points were determined. For each characteristic curve state point, five state points in the vicinity of the initial guess characteristic curve were considered as a set. Each simulation of a simulation set was carried out at the same temperature. The simulations were carried out in the NVT ensemble for the Zeno, Boyle, and Charles curve. The NPT ensemble was used for the simulations of the Amagat curve. From the simulation results of a set, the characteristic curve state point was determined using the respective relations. In Table 1, the relations used for determining the characteristic curve state points are listed. For the zero-pressure limit, cluster integrals were evaluated for determining the characteristic curve state point via the virial route with high accuracy [51]. For the studied model fluids, these integrals can be evaluated exactly. For the real substance fluids, the integrals were evaluated using Monte Carlo simulations for sampling different orientations and distances between two molecules. For both, the model fluids and the real substances, the second virial coefficient was computed in a wide temperature range. From these results, the zero-pressure limit state points of the characteristic curves were obtained. Determining Brown's characteristic curves from molecular simulation for a given substance requires approximately 10^4 CPU hours. However, the force field type has a significant influence on that. Details on the molecular simulation methodology are given in Ref. [51].

Table 1. Conditions used for determining characteristic curve state points using MD simulations based on the method proposed in Ref. [51].

Zeno	Amagat	Boyle	Charles
$Z - 1 = 0$	$\left(\frac{\partial U}{\partial 1/\rho}\right)_T = 0$	$\left(\frac{\partial Z}{\partial 1/\rho}\right)_T = 0$	$\left(\frac{\partial H}{\partial p}\right)_T = 0$

2.4 Molecular-Based Equation of States

Molecular-based EOS have been primarily developed within the chemical engineering community for modelling in particular phase equilibria of mixtures [11, 14]. Yet, due to their physical general mathematical backbone, they can be favorably applied also in

other fields for modeling properties of fluids. The most popular molecular-based EOS is PC-SAFT [24]. Molecular-based EOS are formulated as

$$\tilde{a} = \tilde{a}_{\text{rep}} + \tilde{a}_{\text{att}} + \tilde{a}_{\text{chain}} + \tilde{a}_{\text{assoc}} + \tilde{a}_{\text{D}} + \tilde{a}_{\text{Q}}, \quad (14)$$

where $\tilde{a}$ indicates the configurational Helmholtz energy, $\tilde{a}_{\text{rep}}$ the contribution due to repulsive interactions between particles, $\tilde{a}_{\text{att}}$ the contribution due to dispersive attractive interactions, $\tilde{a}_{\text{chain}}$ the contribution due to the chain length of molecules, $\tilde{a}_{\text{assoc}}$ the contribution due to h-bonding interactions [19], $\tilde{a}_{\text{D}}$ the contribution due to dipole interactions [23], and $\tilde{a}_{\text{Q}}$ the contribution due to quadrupole interactions. Each contribution term has one or two substance-specific parameters that characterize features of the molecule or intermolecular interactions, e.g. the chain term $\tilde{a}_{\text{chain}}$ comprises chain length parameter m and the attractive contribution $\tilde{a}_{\text{att}}$ the dispersion energy ε . Details on the molecular parameters of this model class are given in the review of Economou [19]. Moreover, $\tilde{a}$ is a function of the temperature T and the density ρ (and for mixtures the composition vector $\underline{x}$), which also holds for the individual terms on the RHS of Eq. (14). According to Eq. (14), the Helmholtz energy contributions from the different molecular interactions and features are independent. This is an approximation made in the model, which may seem crude, but has proven reliable and flexible. Thermodynamic properties can be straightforwardly computed from Eq. (14) using well-known relations between the derivatives of the Helmholtz energy with respect to the density and inverse temperature, e.g. the pressure can be computed as $p = \rho TR(1 + \partial \tilde{a} / \partial \rho)$ and the heat capacity can be computed as $c_v = -(\partial^2 \tilde{a} / \partial (1/T)^2)$. Only derivatives of the Helmholtz energy with respect to the density and inverse temperature (and eventually composition) are required for the calculation of thermodynamic properties of interest from a given EOS. In this work, the characteristic curves were computed from different EOS models using the thermodynamic definitions given by Eqs. (3), (5), (7), and (9).

Two different molecular-based EOS frameworks were considered in this work: PC-SAFT [24] and SAFT-VR Mie [27]. The latter was directly used for describing the LJ and Mie model fluid as well as for the real substances toluene, ethanol, and dimethyl ether. For describing the LJ and LJTS model fluid within the PC-SAFT framework, the models from Refs. [26, 45] were used, which are re-parametrized PC-SAFT monomer models. For comparison, also empirical EOS models were used in some cases [37, 50, 54]. For the LJ fluid, the molecular-based EOS of Stephan et al. [45] and that of Lafitte et al. [27] were used. For the LJTS fluid, the molecular-based EOS of Heier et al. [26] and the empirical EOS of Thol et al. [50] were used. For the Mie fluid, the EOS of Lafitte et al. [27] was used. For modelling the three real substances, toluene, ethanol, and dimethyl ether, both the SAFT-VR Mie EOS and the PC-SAFT EOS were used. Moreover, for ethanol, the empirical EOS from Schroeder et al. [37] and, for dimethyl ether, the empirical EOS from Wu et al. [54] were used. The PC-SAFT and SAFT-VR Mie model parameters for all three real substances are summarized in Table 2. For dimethyl ether, a new SAFT-VR Mie model was parametrized within this work. The other model parameters were taken from the literature [3, 23, 24, 27].

Table 2. Model parameters used for the SAFT-VR Mie and PC-SAFT EOS. The model parameters were taken from Refs. [3, 23, 24, 27]. The model parameters for dimethyl ether for the SAFT-VR Mie EOS were obtained within this work. Columns indicate the dispersion energy ε , particle size parameter σ , attractive λ_n and repulsive λ_m exponent, chain length m , association volume κ , association energy ϵ , and dipole moment μ .

Substance	$\varepsilon/k_B/K$	$\sigma/\text{\AA}$	λ_n	λ_m	m	κ	$\epsilon/k_B/K$	μ/D
PC-SAFT								
Toluene	285.69	3.7169	-	-	2.8149	-	-	-
Ethanol	191.31	3.1477	-	-	2.4382	0.03481	2599.8	1.7
Dimethyl ether	210.29	3.2723	-	-	2.2634	-	-	1.3
SAFT-VR Mie								
Toluene	409.73	4.2770	16.334	6	1.9977	-	-	-
Ethanol	168.15	3.4914	7.6134	6	1.9600	0.34558	2833.7	-
Dimethyl ether	216.74	3.306	12	6	2.2340	-	-	-

3 Results

For the real substance fluids, classical SI units are used for presenting the results. For the model fluids, the Lennard-Jones units are used, i.e. using the potential well depth ε , the particle size parameter σ (cf. Eq. (10)), and the mass of the particle M as well as the Boltzmann constant k_B constitute the base unit system. Details on the LJ unit system are given in Ref. [48].

3.1 Lennard-Jones Fluids

Figures 3 and 4 show the results for the studied Lennard-Jones fluids: Fig. 3 for the (full) LJ fluid and Fig. 4 for the LJTS fluid. In both cases, results from different EOS and molecular simulation are shown. The latter is taken as reference.

For the LJ fluid (cf. Fig. 3), two molecular simulation data sets are compared. Overall, the data from Deiters and Neumaier [16] and the results using the new simulation method from our group [51] are in excellent agreement. In particular, both data sets are in excellent agreement with the zero-density limit data point obtained from the exact virial route. Moreover, the simulation results for all four characteristic curves exhibit a smooth trend. For the LJ fluid, two molecular-based EOS were used for predicting the characteristic curves. The EOS from Stephan et al. [45] (re-parametrized PC-SAFT monomer) yields a realistic Zeno, Boyle, and Charles curve. For the Amagat curve, however, the re-parametrized PC-SAFT monomer yields an erratic behavior, cf. Fig. 3. The EOS from Lafitte et al. [27], on the other hand, is in excellent agreement with the reference data. Moreover, this EOS yields physically realistic predictions for all four characteristic curves. Interestingly, the reference data and the EOS from Lafitte et al. agree very well even in the VLE metastable region.

For the LJTS fluid (cf. Fig. 4), only the data set determined by our group is available [51]. The simulation results show a very smooth trend and are also consistent with the

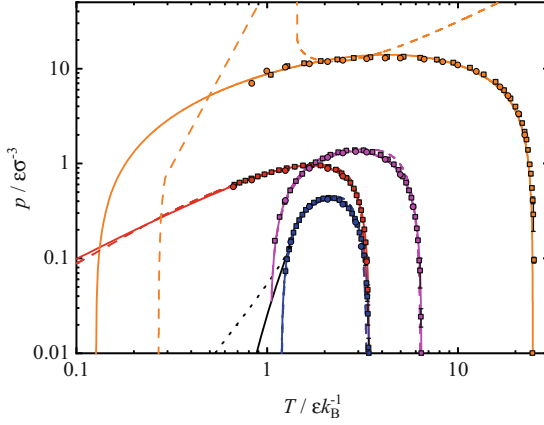


Fig. 3. Characteristic curves of the Lennard-Jones 12,6 fluid. Symbols indicate MD simulation results from Deiters and Neumaier (◐) [16] and from this work (◑). Lines correspond to predictions from the SAFT-VR Mie EOS (solid lines) and the EOS from Stephan et al. (dashed lines). Results for the Boyle curve (blue), Zeno curve (red), Charles curve (pink), and Amagat curve (orange). The vapor pressure curve (—) and the spinodal curves (---) as well as the critical point (★) are shown – computed from the EOS from Stephan et al.

exact zero-pressure limit results obtained from the virial route. Based on the molecular simulation reference data, two EOS models are assessed: the EOS of Thol et al. [50] and the EOS of Heier et al. [26]. The latter is also a re-parametrized PC-SAFT monomer, which is the reason that it yields a spurious Amagat curve. It was shown by Boshkhova and Deiters [7] that these defects are caused by a problematic formulation of the repulsive term of the underlying EOS framework. In the range of the Zeno, Boyle, and Charles curve, the EOS of Heier et al. [26] yields a realistic behavior. The EOS of Thol et al. [50] also exhibits an erroneous Amagat curve, but in the low-temperature regime. Brown showed that the Amagat curve is to intersect the Zeno curve in that regime, which is not the case for the EOS of Thol et al. Nevertheless, the EOS of Thol et al. is in reasonable agreement with the molecular simulation reference data in most cases.

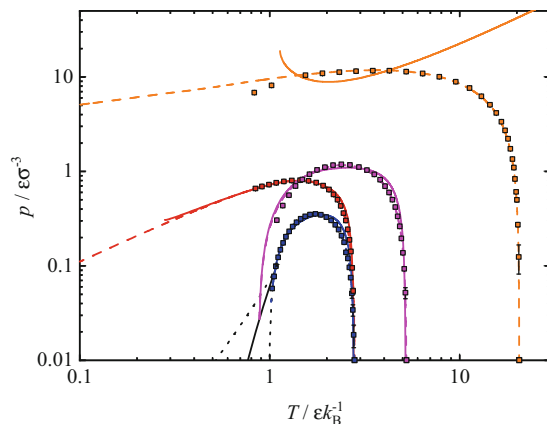


Fig. 4. Characteristic curves of the Lennard-Jones truncated and shifted (LJTS) fluid. Symbols $\square$ indicate MD simulation results [51]. Lines correspond to predictions from the LJTS EOS from Heier et al. (solid lines) and the EOS from Thol et al. (dashed lines). Results for the Boyle curve (blue), Zeno curve (red), Charles curve (pink), and Amagat curve (orange). The vapor pressure curve (—) and the spinodal curves (---) as well as the critical point (★) are shown.

3.2 Mie Fluids

Figure 5 and 6 show the results for the studied Mie fluids. Figure 5 shows the results for Mie fluids with different repulsive exponent λ_n ; Fig. 6 the results for Mie fluids with different attractive exponent λ_m .

While a large number of equations of state are available in the literature for the classical (full) LJ fluid, only some Mie EOS are presently available. Here, the Mie EOS from Lafitte et al. [27] was considered. Overall, the predictions from the Mie EOS are in excellent agreement with the molecular simulation reference data – for all studied λ_n , λ_m combinations. This is impressive considering the fact that only data for moderate conditions was used for the model development [27]. This highlights the advantage of the physically-based model to reliably extrapolate to extreme temperatures and pressures. Only, some small deviations to the reference data are observed for the Amagat curve, cf. Fig. 5 and 6.

Overall, the EOS of Lafitte et al. captures the effect of both the repulsive and the attractive exponent well and is in excellent agreement with the pseudo-experimental data – in a very wide temperature and pressure range. Hence, the EOS of Lafitte et al. is an excellent candidate for modeling real substance components and testing their extrapolation behavior.

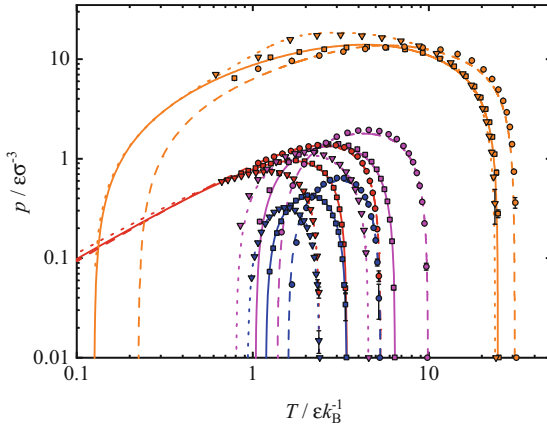


Fig. 5. Characteristic curves of the Mie $\lambda_{n,6}$ fluid. Symbols indicate MD simulation results [41]. Lines correspond to predictions from the SAFT-VR Mie EOS. Results for three $\lambda_{n,6}$ Mie fluids: 8,6 ($\circ$ and dashed lines), 12,6 ($\square$ and solid lines), and 20,6 (∇ and dotted lines). Results for the Boyle curve (blue), Zeno curve (red), Charles curve (pink), and Amagat curve (orange).

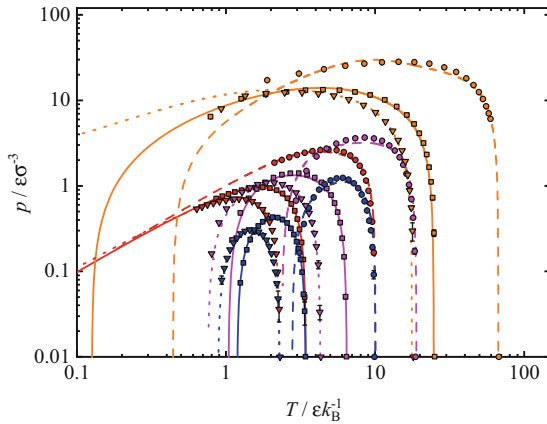


Fig. 6. Characteristic curves of the Mie $12,\lambda_m$ fluid. Symbols indicate MD simulation results [41]. Lines correspond to predictions from the SAFT-VR Mie EOS. Results for three $12,\lambda_m$ Mie fluids: 12,4 ($\circ$ and dashed lines), 12,6 ($\square$ and solid lines), and 12,8 (∇ and dotted lines). Results for the Boyle curve (blue), Zeno curve (red), Charles curve (pink), and Amagat curve (orange).

3.3 Toluene, Ethanol, and Dimethyl Ether

For the model fluids (cf. Sect. 3.2), the molecular-based EOS only used a repulsive and an attractive term for modeling the simple spherical particles. For the real substances discussed here, also the chain contribution and the association contribution were used. This significantly increases the complexity of the models.

Figure 7 shows the results for toluene. Again, molecular simulation data is taken as reference. These data are used for the assessment of the two EOS models: the PC-SAFT

EOS and the SAFT-VR Mie EOS. For the PC-SAFT EOS, a spurious Amagat curve is obtained. This is not surprising as this defect is inherited from the repulsive term (cf. Sect. 3.2). The SAFT-VR Mie EOS predictions, on the other hand, are physically reasonable and in good agreement with the pseudo-experimental data. Only, the temperature of the characteristic curves in the vicinity of the zero-pressure limit is overestimated by the SAFT-VR Mie EOS.

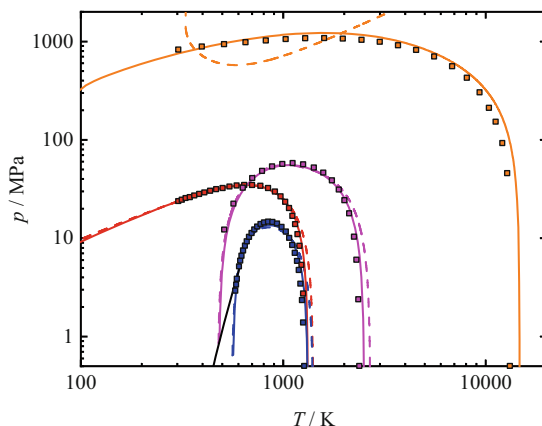


Fig. 7. Characteristic curves of toluene. Symbols ($\square$) indicate MD simulation results [51]. Lines are predictions from the SAFT-VR Mie EOS (solid lines) and the PC-SAFT EOS (dashed lines). Results for the Boyle curve (blue), Zeno curve (red), Charles curve (pink), and Amagat curve (orange). The vapor pressure curve (—) predicted from the SAFT-VR Mie EOS is shown.

For ethanol and dimethyl ether, only the Charles curve was studied, cf. Figures 8 and 9, respectively.

The molecular simulation reference data is compared with the predictions from three EOS. Both the PC-SAFT and SAFT-VR Mie EOS were used for both substances. Moreover, the empirical EOS from Schroeder et al. was used for modeling ethanol and the empirical EOS from Wu et al. was used for modeling dimethyl ether. Both empirical EOS yield an unphysical behavior, i.e. a convex shape at high pressure. The PC-SAFT EOS yields physically reasonable Charles curve for both components. For both the PC-SAFT and SAFT-VR Mie EOS, the results are qualitatively in accordance with Brown's postulates. For ethanol, the PC-SAFT results show best quantitative agreement with the pseudo-reference data. For dimethyl ether, the SAFT-VR Mie results show the best agreement with the reference data. This is probably due to the underlying substance model parameters, cf. Table 2.

4 Conclusions

In this work, the extrapolation behavior of physically-based thermodynamic models was studied. Therefore, a novel approach was developed that uses molecular dynamics simulations for generating pseudo-experimental data. Using that data as a reference, different

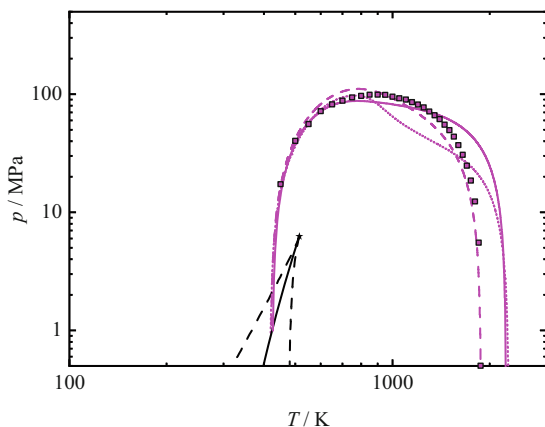


Fig. 8. Charles curve of ethanol. Symbols $\blacksquare$ indicate MD results [31]. Lines indicate predictions from different EOS: SAFT-VR Mie (solid line), PC-SAFT (dashed line), and the empirical multi-parameter EOS from Schroeder et al. [37] (dotted line). The vapor pressure curve (—) and the spinodal curves (---) as well as the critical point ($\star$) were computed from the EOS of Schroeder et al.

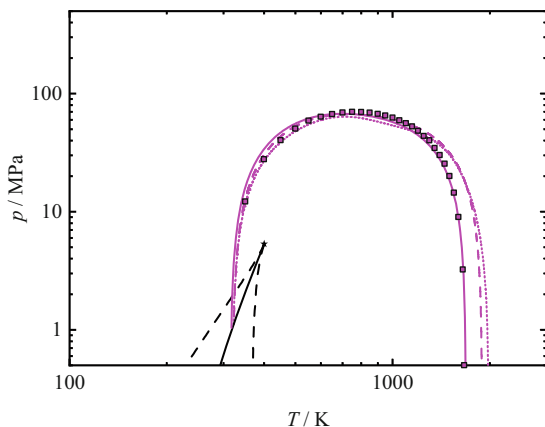


Fig. 9. Charles curve of dimethyl ether. Symbols $\blacksquare$ indicate MD results [31]. Lines indicate predictions from different EOS: SAFT-VR Mie (solid line), PC-SAFT (dashed line), and the empirical multi-parameter EOS from Wu et al. [54] (dotted line). The vapor pressure curve (—) and the spinodal curves (---) as well as the critical point ($\star$) were computed from the EOS of Wu et al.

molecular-based equation of state models were assessed regarding their applicability for modeling fluid properties at extreme temperature and pressure.

In a first step, a new simulation method was developed for determining Brown's characteristic curves from a given molecular force field model [51]. This method combines statistical mechanics for (exactly) computing the zero-pressure limit state point of

the characteristic curve via the virial route with classical MD simulations in the high-pressure regime. The method can be applied to both simple model fluids as well as complex real molecular substances. It has not yet been tested on electrolyte and polymer systems, which would be interesting for future work. Moreover, we have only addressed pure substances here. In technical applications, however, fluid mixtures are in practically all cases present. An extension of the computational approach to mixtures would therefore also be interesting for a future work.

The performance of two molecular-based EOS frameworks was compared, i.e. the PC-SAFT EOS and the SAFT-VR Mie EOS. The PC-SAFT model comprises more strongly simplifying approximations compared to the SAFT-VR Mie EOS. This is probably the reason that the SAFT-VR Mie EOS is found to extrapolate significantly better to extreme conditions regarding temperature and pressure. The PC-SAFT EOS, which is very frequently used in chemical engineering, on the other hand exhibits an artificial Amagat curve and should therefore not be applied at extreme temperatures and pressures. Hence, the SAFT-VR Mie EOS is found to be an excellent candidate for modeling fluid properties at extreme conditions, e.g. in tribological contact processes. Impressively, the SAFT-VR Mie EOS does not only satisfy the requirements of Brown's characteristic curves, the predictions of the EOS are in most cases in excellent agreement with the pseudo-experimental reference data. This is surprising considering the fact that the SAFT-VR Mie EOS was parametrized using data at moderate conditions alone. This supports the fact that models with a strong physical backbone can provide an excellent extrapolation behavior. In some cases, also empirical EOS were used for comparison and found to exhibit an unphysical behavior in some state region.

Based on the novel approach using MD pseudo-experimental reference data, for the first time, Brown's characteristic curves were used for a quantitative assessment of thermodynamic equation of state models. For future work, it would be interesting to study long chain alkane molecules, which are important substances used as lubricants. Moreover, it would be interesting to study the reproducibility of Brown's characteristic curves across different MD codes as well as the influence of the force field used for modeling a given substance.

Acknowledgement. The authors gratefully acknowledge access to the ELWE supercomputer at Regional University Computing Center Kaiserslautern (RHRK) under the grant TUKL-MTD.

References

1. Al-Saifi, N.M., Elliott, J.R.: Avoiding artifacts in noncubic equations of state. *Ind. Eng. Chem. Res.* **61**(42), 15661–15677 (2022)
2. Al-Saifi, N.M.: Simulation-based equations of state for the Lennard-Jones fluid: apparent success and hidden failure. *AIChE J.* **66**(7), e16244 (2020)
3. Al-Saifi, N.M., Hamad, E.Z., Englezos, P.: Prediction of vapor–liquid equilibrium in water–alcohol–hydrocarbon systems with the dipolar perturbed-chain SAFT equation of state. *Fluid Phase Equilib.* **271**, 82–93 (2008)
4. Apfelbaum, E.M., Vorob'ev, V.S., Martynov, G.A.: Virial expansion providing of the linearity for a unit compressibility factor. *J. Phys. Chem. A* **108**, 10381–10385 (2004)
5. Apfelbaum, E.M., Vorob'ev, V.S., Martynov, G.A.: Triangle of liquid-gas states. *J. Phys. Chem. B* **110**, 8474–8480 (2006)
6. Bair, S.: *High-Pressure Rheology for Quantitative Elastohydrodynamics*. Elsevier, Amsterdam (2007)
7. Boshkova, O.L., Deiters, U.K.: Soft repulsion and the behavior of equations of state at high pressures. *Int. J. Thermophys.* **31**(2), 227–252 (2010)
8. Brinksmeier, E., Meyer, D., Huesmann-Cordes, A.G., Herrmann, C.: Metalworking fluids – mechanisms and performance. *CIRP Ann. Manuf. Technol.* **64**, 605–628 (2015)
9. Brown, E.H.: On the thermodynamic properties of fluids. *Bulletin de l'Institut International du Froid Annexe* **1**, 169–178 (1960)
10. Chacin, A., Vazquez, J., Müller, E.: Molecular simulation of the Joule-Thomson inversion curve of carbon dioxide. *Fluid Phase Equilib.* **165**, 147–155 (1999)
11. Chapman, W.G., Gubbins, K.E., Jackson, G., Radosz, M.: New reference equation of state for associating liquids. *Ind. Eng. Chem. Res.* **29**, 1709 (1990)
12. Colina, C.M., Lisal, M., Siperstein, F.R., Gubbins, K.E.: Accurate CO₂ Joule-Thomson inversion curve by molecular simulations. *Fluid Phase Equilib.* **202**, 253–262 (2002)
13. Colina, C.M., Müller, E.A.: Molecular simulation of Joule-Thomson inversion curves. *Int. J. Thermophys.* **20**, 229–235 (1999)
14. Cotterman, R.L., Schwarz, B.J., Prausnitz, J.M.: Molecular thermodynamics for fluids at low and high densities. Part I: pure fluids containing small or large molecules. *AIChE J.* **32**(11), 1787–1798 (1986)
15. Diwald, F., et al.: Molecular dynamics and phase field simulations of droplets on surfaces with wettability gradient. *Comput. Methods Appl. Mech. Eng.* **361**, 112773 (2020)
16. Deiters, U.K., Neumaier, A.: Computer simulation of the characteristic curves of pure fluids. *J. Chem. Eng. Data* **61**(8), 2720–2728 (2016)
17. Deiters, U.K., De Reuck, K.M.: Guidelines for publication of equations of state I. Pure fluids. *Pure Appl. Chem.* **69**(6), 1237–1250 (1997)
18. Eckl, B., Vrabec, J., Hasse, H.: Set of molecular models based on quantum mechanical ab initio calculations and thermodynamic data. *J. Phys. Chem. B* **112**, 12710–12721 (2008)
19. Economou, I.: Statistical associating fluid theory: a successful model for the calculation of thermodynamic and phase equilibrium properties of complex fluid mixtures. *Ind. Eng. Chem. Res.* **41**, 953–962 (2002)
20. Fertig, D., Hasse, H., Stephan, S.: Transport properties of binary Lennard-Jones mixtures: Insights from entropy scaling and conformal solution theory. *J. Mol. Liq.* **367**, 120401 (2022)
21. Fingerhut, R., et al.: ms2: a molecular simulation tool for thermodynamic properties, release 4.0. *Comput. Phys. Commun.* **262**, 107860 (2021)
22. Figueroa-Gerstenmaier, S., Lisal, M., Nezbeda, I., Smith, W.R., Trejos, V.M.: Prediction of isoenthalps, Joule-Thomson coefficients and Joule-Thomson inversion curves of refrigerants by molecular simulation. *Fluid Phase Equilib.* **375**, 143–151 (2014)

23. Gross, J., Vrabec, J.: An equation-of-state contribution for polar components: dipolar molecules. *AIChE J.* **52**, 1194–1204 (2006)
24. Gross, J., Sadowski, G.: Perturbed-chain SAFT: an equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.* **40**, 1244–1260 (2001)
25. Guevara-Carrion, G., Janzen, T., Munoz-Munoz, Y.M., Vrabec, J.: Mutual diffusion of binary liquid mixtures containing methanol, ethanol, acetone, benzene, cyclohexane, toluene, and carbon tetrachloride. *J. Chem. Phys.* **144**, 124501 (2016)
26. Heier, M., Stephan, S., Liu, J., Chapman, W.G., Hasse, H., Langenbach, K.: Equation of state for the Lennard-Jones truncated and shifted fluid with a cut-off radius of 2.5 based on perturbation theory and its applications to interfacial thermodynamics. *Mol. Phys.* **116**(15), 2083–2094 (2018)
27. Lafitte, T., et al.: Accurate statistical associating fluid theory for chain molecules formed from Mie segments. *J. Chem. Phys.* **139**, 154504 (2013)
28. Mick, J.R., Barhaghi, M.S., Jackman, B., Rushaidat, K., Schwiebert, L., Potoff, J.: Optimized Mie potentials for phase equilibria: Application to noble gases and their mixtures with n-alkanes. *J. Chem. Phys.* **143**, 114504 (2015)
29. Neumaier, A., Deiters, U.K.: The characteristic curves of water. *Int. J. Thermophys.* **37**(9), 96 (2016)
30. Nezbeda, I.: Vapour–liquid equilibria from molecular simulations: some issues affecting reliability and reproducibility. *Mol. Phys.* **117**, 2814 (2019)
31. Rößler, J., Antolović, I., Stephan, S., Vrabec, J.: Assessment of thermodynamic models via Joule-Thomson inversion. *Fluid Phase Equilib.* **556**, 113401 (2022)
32. Rutkai, G., Thol, M., Lustig, R., Span, R., Vrabec, J.: Communication: Fundamental equation of state correlation with hybrid data sets. *J. Chem. Phys.* **139**, 041102 (2013)
33. Rutkai, G., et al.: ms2: a molecular simulation tool for thermodynamic properties, release 3.0. *Comput. Phys. Commun.* **221**, 343 (2017)
34. Saager, B., Fischer, J.: Predictive power of effective intermolecular pair potentials: MD simulation results for methane up to 1000 MPa. *Fluid Phase Equilib.* **57**(1), 35–46 (1990)
35. Schmitt, S., Fleckenstein, F., Hasse, H., Stephan, S.: Comparison of force fields for the prediction of thermophysical properties of long linear and branched alkanes. *J. Phys. Chem. B* (2023, in press)
36. Schappals, M., et al.: Round robin study: Molecular simulation of thermodynamic properties from models with internal degrees of freedom. *J. Chem. Theory Comput.* **13**, 4270 (2017)
37. Schroeder, J.A., Penoncello, S.G., Schroeder, J.S.: A fundamental equation of state for ethanol. *J. Phys. Chem. Ref. Data* **43**, 043102 (2014)
38. Schnabel, T., Vrabec, J., Hasse, H.: Henry’s law constants of methane, nitrogen, oxygen and carbon dioxide in ethanol from 273 to 498 K: prediction from molecular simulation. *Fluid Phase Equilib.* **233**, 134–143 (2005)
39. Span, R., Wagner, W.: On the extrapolation behavior of empirical equations of state. *Int. J. Thermophys.* **18**(6), 1415–1443 (1997)
40. Staubach, J., Stephan, S.: Interfacial properties of binary azeotropic mixtures of simple fluids: Molecular dynamics simulation and density gradient theory. *J. Chem. Phys.* **157**, 124702 (2022)
41. Stephan, S., Urschel, M.: Characteristic curves of the Mie fluid. *J. Mol. Liq.* **383**, 122088 (2023)
42. Stephan, S., Dyga, M., Alhafez, I.A., Lenard, J., Urbassek, H., Hasse, H.: Reproducibility of atomistic friction computer experiments: a molecular dynamics simulation study. *Mol. Simul.* **47**(18), 1509–1521 (2021)
43. Stephan, S., Deiters, U.: Characteristic curves of the Lennard-Jones fluid. *Int. J. Thermophys.* **41**, 147 (2020)

44. Stephan, S., Hasse, H.: Molecular interactions at vapor-liquid interfaces: Binary mixtures of simple fluids. *Phys. Rev. E* **101**, 012802 (2020)
45. Stephan, S., Staubach, J., Hasse, H.: Review and comparison of equations of state for the Lennard-Jones fluid. *Fluid Phase Equilib.* **523**, 112772 (2020)
46. Stephan, S., Horsch, M., Vrabec, J., Hasse, H.: MolMod - an open access database of force fields for molecular simulations of fluids. *Mol. Simul.* **45**, 806–814 (2019)
47. Stephan, S., Dyga, M., Urbassek, H., Hasse, H.: The influence of lubrication and the solid-fluid interaction on thermodynamic properties in a nanoscopic scratching process. *Langmuir* **35**, 16948 (2019)
48. Stephan, S., Thol, M., Vrabec, J., Hasse, H.: Thermophysical properties of the Lennard-Jones fluid: database and data assessment. *J. Chem. Inf. Model.* **59**, 4248–4265 (2019)
49. Stephan, S., Lautenschlaeger, M.P., Alhafez, I.A., Horsch, M.T., Urbassek, H.M., Hasse, H.: Molecular dynamics simulation study of mechanical effects of lubrication on a nanoscale contact process. *Tribol. Lett.* **66**(4), 1–13 (2018)
50. Thol, M., Rutkai, G., Span, R., Vrabec, J., Lustig, R.: Equation of State for the Lennard-Jones Truncated and Shifted Model Fluid. *Int. J. Thermophys.* **36**(1), 25–43 (2014)
51. Urschel, M., Stephan, S.: Determining Brown's characteristic curves using molecular simulation. *J. Chem. Theory Comput.* **19**, 1537–1552 (2023)
52. Vrabec, J., Kumar, A., Hasse, H.: Joule-Thomson inversion curves of mixtures by molecular simulation in comparison to advanced equations of state: Natural gas as an example. *Fluid Phase Equilib.* **258**, 34–40 (2007)
53. Vrabec, J., Kedia, G.K., Hasse, H.: Prediction of Joule-Thomson inversion curves for pure fluids and one mixture by molecular simulation. *Cryogenics* **45**, 253–258 (2005)
54. Wu, J., Zhou, Y., Lemmon, E.W.: An equation of state for the thermodynamic properties of dimethyl ether. *J. Phys. Chem. Reference Data* **40**, 023104 (2011)

Open Access This chapter is licensed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

