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Precise determination of LJ parameters and Eucken correction factors for a more accurate modeling of transport properties in gases

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Abstract

The kinetic gas theory, in particular the equations of Chapman and Enskog, proved to be good and widely applicable approximations for modeling transport properties like diffusion coefficients, viscosities and thermal conductivities. However, these equations rely on at least the Lennard-Jones parameters and for polar gases also the dipole moment. In the scientific literature, the Lennard-Jones parameters are fitted to only one experimentally determined transport coefficient. This approach leads to good agreement between the Chapman Enskog equations employing the so obtained parameters with the experimental data for this specific transport property. However, utilizing the same parameters for modeling different transport properties oftentimes leads to distinct deviations. In this work, it is shown that the subset of Lennard-Jones parameters with which the Chapman Enskog equations can predict the experimental results with deviations comparable to the experimental uncertainty are not identical for each transport property. Hence, fitting towards one property doesn't necessarily yield parameters that are suited to describe the other transport properties. In this publication, the Lennard-Jones parameters and a temperature dependent Eucken correction factor, leading to a significantly higher accuracy than the classical Eucken correction and also its modification by Hirschfelder, are therefore fitted towards all three transport properties simultaneously for seven exemplary gases. This approach leads to a significantly better agreement with experimental data for the three transport properties than the classical approach that relies on fitting to one single transport property and can be utilized to determine accurate sets of Lennard-Jones parameters and Eucken correction factors for any gas species. It provides a computationally inexpensive and practical method for the precise calculation of transport properties over a wide range of temperatures relevant for processes in the chemical industry.

Keywords Thermal conductivity · Diffusion coefficient · Viscosity · Kinetic gas theory · Lennard-Jones parameter · Eucken correction · Transport properties

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1 Introduction and theory

The accurate determination of diffusion coefficients, thermal conductivities and viscosities of gases has a decisive impact on the precision of computational models in chemical engineering. In recent years, the development of potential energy surfaces (PES) for interactions between two gas molecules using quantum mechanical ab initio calculations was employed extensively for calculating properties like the second virial coefficient, diffusion coefficients, thermal conductivities and viscosities of gases based on the kinetic theory for polyatomic gases [1, 2]. This approach is not only fully predictive but also showed good precision for a variety of gases [3, 4]. However, it is computationally very expensive and requires expert knowledge to be carried out. In the present work, a simple and computationally inexpensive approach is suggested that is based on the classical Chapman Enskog (CE)

theory and allows for the determination of binary diffusion coefficients, thermal conductivities and viscosities of gases with an accuracy comparable to the uncertainty of according experimental data. Furthermore, due to its simplicity, the here proposed approach can also be carried out by non-experts in the field for any desired gas species for which experimental data is available.

In chapter 1 of this work, the theoretical concepts of the CE theory with a focus on the calculation of the three transport coefficients are briefly delineated and the approach of fitting the Lennard-Jones parameters to experimental data of only one transport property is explained. Subsequently, chapter 2 focuses on the here proposed method of fitting towards all three transport mechanisms simultaneously, while in chapter 3 the results of this novel fitting procedure are presented and benchmarked versus the classical literature.

1.1 Kinetic gas theory

Chapman and Enskog have found an approximate solution of the Boltzmann equation which leads to the following mathematical expressions that are widely used for calculating thermal conductivities, viscosities and binary diffusion coefficients of gases in the scientific literature [5]. More information about their derivation can be found in Hirschfelder, Curtiss, and Bird and Chapman and Enskog [5, 6].

The binary diffusion coefficient [7]:

$$D_{12} = \frac{3}{16 \cdot \pi \cdot P} \cdot \left(\frac{2 \cdot \pi \cdot k_B^3 \cdot T^3}{\mu_{12}} \right)^{1/2} \cdot \frac{1}{\sigma^2 \cdot \Omega_{12}^{(1,1)*}} \quad (1)$$

The thermal conductivity of a pure gas [7, 8]:

$$\lambda = \frac{25}{32 \cdot \pi \cdot M} \cdot (\pi \cdot m \cdot k_B \cdot T)^{1/2} \cdot \frac{1}{\sigma^2 \cdot \Omega_{12}^{(2,2)*}} \quad (2)$$

The viscosity of a pure gas [7, 9]:

$$\eta = \frac{5 \cdot \sqrt{m \cdot \pi \cdot k_B \cdot T}}{16 \cdot \pi \cdot \sigma^2 \cdot \Omega_{12}^{(2,2)*}} \quad (3)$$

In these equations, M is the molar mass, m the mass of one molecule, μ the reduced mass of two gas molecules, k_b the Boltzmann constant, $\Omega_{12}^{(l,s)*}$ the reduced collision integral and σ, the collision diameter.

The collision integral of the order l, s can be described with the following eq. [5].

$$\Omega_{12}^{(l,s)} = \frac{1}{2\sqrt{\pi}} \int_0^\infty e^{\frac{-\mu \cdot v'^2}{2k_B \cdot T}} \cdot \left(\frac{-\mu \cdot v'^2}{2 \cdot k \cdot T} \right)^{s+1.5} \cdot Q^l_{(g)} \cdot dg \quad (4)$$

Hereby, v' is the relative velocity of two colliding molecules towards each other and $Q^l_{(g)}$ contains information about

the intermolecular potentials. More information on the collision integral can be found in the works of Chapman and Enskog and McGee [5, 7]. In the present work, the Lennard-Jones (LJ) potential was employed for non-polar gases and the Stockmayer potential for polar gases. In principal any other potential can be used as well, as long as it is spherically symmetric. These simple potentials were chosen to reduce the complexity of the approach and to make it easy to employ.

For the collision integral based on the LJ potential, numerous approximate solutions exist in the scientific literature. Kim and Monroe introduced the following equation, which is stated to be accurate to the seventh decimal place and is also used in the present work [9].

$$\Omega^{(l,s)*} = A^{(l,s)} + \sum_{k=1}^{6} \frac{B_k^{(l,s)}}{(T^*)^k} + C_k^{(l,s)} \cdot \ln(T^*)^k \quad (5)$$

In this equation, the asterisk denotes reduced quantities, which are obtained by dividing through the potential depth ε of the LJ potential. The parameters of Eq. (5) can be found in the work of Kim and Monroe [9].

For polar molecules, here described with the Stockmayer potential, the collision integral becomes more complicated [7, 10].

$$V_{(r,\Theta_1,\Theta_2,\phi)} = 4 \cdot \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} - \delta \left(\frac{\sigma}{r} \right)^{3} \right] \quad (6)$$

$$\delta = \frac{\mu^2}{4 \cdot \varepsilon \cdot \sigma^3} g_{(\Theta_1,\Theta_2,\phi)} \quad (7)$$

As can be extracted from Eqs. (6) and (7), the Stockmayer potential is a function of a third parameter δ in addition to the two LJ parameters, which depends on the dipole moment of the molecule μ and the angular dependent parameter $g_{(\Theta_1,\Theta_2,\phi)}$. More detailed information can be found from McGee [7] and Itean, Glueck, and Svehla [10]. For head to tail collisions in which the partially positive part of one molecule is colliding with the partially negatively charged part of the second molecule, $g_{(\Theta_1,\Theta_2,\phi)}$ assumes the value two. This is equivalent to a maximum value for δ, denoted as δ_{max}. Monchick and Mason [11] have tabulated approximate solutions for the collision integral as a function of the reduced temperature and δ_{max}, which are used in the present work. The dependence of the collision integral on δ_{max} and again the dependence of δ_{max} on the LJ parameters, makes the fitting process of the two LJ parameters towards experimentally measured transport properties more complicated. This is due to the fact that δ_{max}, is changing in every iteration step. Hence, a fit of the collision integral as a function of the reduced temperature and δ_{max} has to be constructed from the tabulated values and implemented into the fitting procedure for the LJ parameters. Many publications dealing with polar gases in the scientific literature either neglect the influence of the polarity for this reason and employ a potential for nonpolar gases, like the LJ potential

[12], or they fix δ_{max}, so that the collision integral is only a function of the reduced temperature and hence constant in each iteration of the fitting procedure for a given temperature [13]. In the latter case, one of the LJ parameters is then directly dependent on the other one, according to Eq. (7) and cannot be fitted in order to maintain physical coherence. Both approaches introduce errors into the fitting process that become more severe with an increasing polarity of the investigated gases. For highly polar molecules like hydrogen chloride, ammonia and water, the dependence of the collision integral on both, the reduced temperature and delta should therefore be taken into account, as done in the present work.

1.2 Mixing rules

While the viscosity and the thermal conductivity of pure gases can be directly calculated based on the LJ parameters and the collision integral, the binary diffusion coefficient involves parameters from two species i and j. Therefore, the following mixing rules are employed [6, 8]:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{8}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \cdot \varepsilon_j} \tag{9}$$

For the interaction of two polar gases, $\delta_{ij,\,max}$ can be calculated according to Eq. (10).

$$\delta_{ij,max} = \frac{\mu_i \mu_j}{2\varepsilon_{ij}\sigma_{ij}^3} = \frac{1}{2}\mu_{red,ij}^2 \tag{10}$$

In case of a mixture of a nonpolar with a polar gas, $\delta_{ij,\,max}$ is zero and the Stockmayer potential transitions into the LJ potential. To account for the polarity of one of the gas species, a correction factor ζ is introduced according to Hirschfeder et al. [6] from Fan [14]:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \cdot \zeta^{-\frac{1}{6}} \tag{11}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \cdot \varepsilon_j} \cdot \zeta^2 \tag{12}$$

$$\zeta = 1 + 0.25 \cdot \alpha_{red} \cdot \mu_{red}^2 \cdot \sqrt{\frac{\varepsilon_{polar}}{\varepsilon_{non-polar}}} \tag{13}$$

In Eq. (14), α_{red} is the reduced polarizability of the nonpolar species.

$$\alpha_{red} = \frac{\alpha}{\sigma_{non-polar}^3} \tag{14}$$

1.3 Eucken correction

The above introduced equations for the binary diffusion coefficient, the viscosity and the thermal conductivity based on the kinetic theory are only valid for monoatomic gases, since no internal degrees of freedom are taken into account. The effect of this approximation on the diffusion coefficients and viscosities of polyatomic gases can be neglected. Since in addition to the energy transport in the form of kinetic energy, also vibrational and rotational degrees of freedom can be excited in polyatomic gases, it is however necessary, to consider these internal degrees of freedom when describing the heat conductivity. The classical Eucken correction weights the translational degrees of freedom with the factor $f_{trans} = 2.5$, which follows directly from the relation between viscosity and thermal conductivity in the Chapman-Enskog theory [15]. The underlying assumption is that the transport of kinetic energy is unaffected by the internal degrees of freedom, meaning that an exchange of energy between the internal and translational energy only occurs rarely. This assumption has been supported by experimental investigations [16]. For reasons of simplicity, Eucken has weighted the internal degrees of freedom with a factor $f_{int} = 1$ [16, 17].

$$\lambda = \frac{\eta}{M}\left(f_{trans}C_{v,trans} + f_{int}C_{v,int}\right) \tag{15}$$

For a monoatomic gas this is equivalent to the expression that can be obtained by dividing Eqs. (2) and (3). Based on Eq. (15), the heat capacity of a polyatomic gas can then be calculated by multiplying the Chapman Enskog expression for monoatomic gases with the classical Eucken correction:

$$\lambda = \lambda_{monoatomic}\left(\frac{4}{15}\frac{C_v}{R} + \frac{3}{5}\right) \tag{16}$$

Hereby, C_v is the molar heat capacity of a gas at constant volume. However, according to Chapman and Enskog and Schäfer [5, 18], the transfer of internal energy is based on a diffusion mechanism [16]. Hence, $f_{int} = \frac{\rho D}{\eta}$ should be employed in the Eucken correction instead of $f_{int} = 1$ [16, 19]. In this case f_{int} assumes values of about 1.3 for most force laws and shows only a slight temperature dependence [15]. More specifically, Istomin, Kustova, and Mekhonoshina [20] have graphically depicted that f_{int} exhibits an almost linear temperature dependence at industrially relevant temperatures of up to 1500 K. More details can be found from Srivastava and Srivastava [16] and Hirschfelder [19]. Also, Srivastava and Srivastava [16] and Barua [17] have shown that the experimentally determined values for f_{int} are clearly dependent on the species and the temperature, contrary to the value following from Hirschfelder's approach [19]. Interestingly, the agreement of the experimental values with the classical Eucken correction is oftentimes better than with the approach from Hirschfelder [19]. Mason and Monchick [21] state that only at high temperatures the

theoretical value of 1.3 is approached and proposed a more complex approach in which both f_{int} and f_{trans} are variable. In the present work, a linear, species specific temperature dependence is assumed as supported by the dependence of f_{int} on the temperature in the data of from Istomin et al [20]. This simplified, semi-empirical approach is explained in more detail in section 3.

Besides the Eucken-like corrections for the thermal conductivity and the dipole moments, precise values of the Lennard-Jones parameters must be known in order for the CE theory to yield accurate values for the three transport coefficients.

1.4 Determination of Lennard-Jones parameters

In the scientific literature, the LJ parameters are fitted to experimentally determined values of only one property, preferably the viscosity due to the precise measurement methods available [8]. If no experimental data for the viscosity or thermal conductivity is available, physical properties like the second virial coefficient or boiling point temperatures can be used instead [8]. This approach is however problematic, since the CE equations for the respective transport properties utilizing the so obtained LJ parameters are then well able to describe the transport property they were fitted to but show clear deviations from experimental data when used to describe a different transport property. Mason and Monchick [22] for example calculated binary diffusion coefficients for a variety of gases with a given set of LJ parameters from literature. The binary diffusion coefficient for a water-oxygen mixture showed a mean relative deviation from experimental data of 9.5%, for water-methane mixtures it was even 15.5%. Hanley and Klein [23] determined LJ parameters for hydrogen from viscosity data and were able to reproduce the experimental data with a maximum deviation of less than 3% in a temperature range from 200 to 2000 K. However, when using the same LJ parameters to calculate the thermal conductivity, the maximum deviation ranged from +8% to −6%. In section 3, the calculated viscosity of nitrous oxide as well as its binary diffusion coefficient with nitrogen based on LJ parameters from Hirschfelder et al. [6] are compared to experimental data from Kestin and Wakeham [12], Johnston and McCloskey [24], and

Matsunaga, Hori, and Nagashima [25]. Also here, the same underlying problem can be observed. In many cases, as for example in the work of Hanley and Klein [23] it is argued that the uncertainty of the experimental data is too high in order to obtain precise parameters from a fit. This is true for some gases and transport properties. Also it has to be stated that for certain gases, the agreement between calculated and experimentally measured transport properties indeed lies within the experimental uncertainty when using LJ parameters from literature. Still there are numerous examples, like the ones mentioned above, where this is not the case, showing that there is room for an improved accuracy in determining the LJ parameters, which then leads to a better agreement between the CE theory and experimental measurements. Hence, the question arises where this disagreement is originating from.

As shown in section 3 and as can already be assumed from the Eqs. (1), (2), and (3), various combinations of LJ parameters lead to an agreement between experimental and calculated transport coefficients within the experimental uncertainty for each transport property. Hence, for all experimental uncertainties $\xi > 0$, a set $M \subseteq \mathbb{R}^2_{>0}$ can be defined as follows, taking the viscosity of a gas as an example:

$$M_\mu = \left\{ (\varepsilon, \sigma) \epsilon \mathbb{R}^2_{>0} : \left\| \frac{\eta_{CE}(\varepsilon, \sigma) - \eta_{experiment}}{\eta_{experiment}} \right\|_2 \leq \xi_\mu \right\} \quad (17)$$

Since the dependence of the different transport properties on the LJ parameters is not identical, the generated LJ parameters from fitting towards for example the viscosity, as done in the scientific literature, are not necessarily elements of the subsets $M_{D_{1,2}}$ and M_λ for the two remaining transport properties. The goal of this work is to investigate, whether physically meaningful parameters, which are able to fit all transport equations within the experimental uncertainty, can be obtained by simultaneously fitting towards all three transport properties. This will be the case, if there is an overlap between the above mentioned subsets of LJ parameters of the three different transport properties, here named M', which can be found through the fitting procedure proposed in this work.

$$M' = M_\mu \cap M_{D_{1,2}} \cap M_\lambda$$

$$= \left\{ (\varepsilon, \sigma) \epsilon \mathbb{R}^2_{>0} : \left\| \frac{\eta_{CE}(\varepsilon, \sigma) - \eta_{experiment}}{\eta_{experiment}} \right\|_2 \leq \xi_\mu, \frac{D_{1,2\ CE}(\varepsilon, \sigma) - D_{1,2\ experiment}}{D_{1,2\ experiment}} \Bigg\|_2 \leq \xi_{D_{1,2}}, \left\| \frac{\lambda_{CE}(\varepsilon, \sigma) - \lambda_{experiment}}{\lambda_{experiment}} \right\|_2 \leq \xi_\lambda \right\} \quad (18)$$

2 Methods

2.1 Parameters and optimization problem

For each gas, four parameters, the two LJ parameters as well as a and b for the weighting of the internal degrees of freedom in the Eucken correction, were fitted towards experimental data.

$$f_{int} = aT + b \qquad (19)$$

Hence,

$$\lambda = \frac{\eta}{M}\left(2.5 C_{v,trans} + (aT + b)C_{v,int}\right) \qquad (20)$$

The modified Eucken correction factor can then be formulated as follows:

$$\frac{\lambda}{\lambda_{monoatomic}} = \left(\frac{4}{15}\frac{C_v}{R}(aT + b) + \frac{\frac{5}{2}-(aT + b)}{\frac{5}{2}}\right) \qquad (21)$$

$$\min_{\varepsilon,\sigma,a,b}\left\{ f(\varepsilon,\sigma,a,b) = \frac{\eta_{CE}(\varepsilon,\sigma,T)-\eta_{experiment}(T)^2}{\eta_{experiment}(T)} + \frac{D_{1,2CE}(\varepsilon,\sigma,T)-D_{1,2experiment}(T)^2}{D_{1,2experiment}(T)} + \frac{\lambda_{CE}(\varepsilon,\sigma,a,b,T)-\lambda_{experiment}(T)^2}{\lambda_{experiment}(T)}\right\} \; s.t. \; \begin{array}{l} aT + b \geq 0 \\ a \geq 0 \end{array} \qquad (22)$$

The two constraints in Eq. (22) are based on the fact, that the internal degrees of freedom cannot be weighted negatively in the Eucken correction to ensure physical consistency. Furthermore, Istomin et al. [20] showed that f_{int} increases with temperature in the here investigated interval, which is the reason for enforcing a to be positive. In order to reduce the probability of finding local minima instead of a global minimum, the fitting process for each gas was carried out 200 times with different starting points. The obtained parameters indeed changed very slightly for the first few starting points. However, after already 20 different starting points the final result remained constant in all cases, indicating that using 200 starting points yields the global minimum. The collision integral for polar molecules in dependence of the reduced temperature and δ_{max} was fitted to the tabulated values in Table V from Monchick and Mason [11] by means of a linear spline-interpolation carried out in MATLAB.

2.2 Literature and fitting procedure

The accuracy of the fitting process strongly depends on the quality and availability of experimental data on transport coefficients. For this reason, the experimental data available in

Hereby, $\lambda_{monoatomic}$ is calculated according to the CE theory as described in Eq. (2). The same holds for the binary diffusion coefficients and viscosities which are calculated based on eq. 1 and 3 respectively. A major focus of this work is to simultaneously fit the diffusion coefficients, thermal conductivities and viscosities with an equal weight. Hence, if the amount of experimental data points differed for each transport property, the respective relative differences were weighted in a way that all three transport properties are considered equally in the fitting process. Using the least square method these relative deviations are then minimized in MATLAB.

the scientific literature was critically reviewed and the employed sources are given in Table 1 for each of the investigated gases, namely oxygen, nitrogen, chlorine, nitrous oxide, ammonia, hydrogen chloride and water vapor. This sample of gases intentionally contains polyatomic and non-polar as well as polar species to investigate whether the approach of this work is valid for a wide range of substances. For fitting the thermal conductivity, the polynomials from Yaws [26] based on experimental data were employed for all gases except for ammonia for which the experimentally based fit from Afshar, Murad, and Saxena [27] was used, since it employs experimental data in a wide temperature interval from 358 to 925 K. For some species additional experimental data is available in the scientific literature, e.g. for nitrogen from Le Neindre [36], for oxygen from Hirschfelder et al. [6], and for water from Brain [37], which all showed good agreement with the polynomials from Yaws [26]. Binary diffusion coefficients for the investigated gases in the scientific literature are mostly available in combination with nitrogen. For this reason, the fitting procedure was initiated with nitrogen and with the so generated LJ parameters and two parameters a and b from the modified Eucken correction, the equivalent parameters for the remaining gases were determined. The simplest monoatomic

Table 1 Values for the mean and maximum relative deviation between the calculated and experimentally determined transport properties for all seven investigated species and the literature sources used for the fitting procedure. The table additionally includes the temperature of the data point which showed the highest deviation between theoretical and experimental values

Species	Mean relative deviation, thermal conductivity / %	Maximum relative deviation, thermal conductivity / % and corresponding temperature / K
N_2	1.05 [26]	2.01 (950 K)
N_2O	3.47 [26]	6.27 (350 K)
O_2	0.71 [26]	2.31 (300 K)
Cl_2	1.24 [26]	2.47 (300 K)
H_2O	1.38 [26]	4.01 (400 K)
NH_3	0.1312 [27]	0.35 (400 K)
HCl	0.84 [26]	2.04 (300 K)

Species	Mean relative deviation, viscosity / %	Maximum relative deviation, viscosity / % at corresponding temperature / K
N_2	0.15 [28]	0.44 (500 K)
N_2O	1.22 [12]	3.16 (473.15 K)
O_2	1.21 [28]	1.83 (250 K)
Cl_2	1.15 [28, 29]	3.81 (600 K)
H_2O	3.14 [30]	5.35 (411.15 K)
NH_3	1.07 [28]	1.66 (300 K)
HCl	0.51 [13]	0.97 (523 K)

Species	Mean relative deviation, binary diffusion coefficient / %	Maximum relative deviation, binary diffusion coefficient / % at corresponding temperature / K
N_2	In He: 1.44 [31]	2.95 (415 K)
N_2O	In N_2: 5.46 [25]	6.56 (273.15 K)
O_2	In N_2O: 4.49 [25]	6.42 (273.15 K)
Cl_2	In Air: 2.02 [32]	2.02 (293 K)
H_2O	In N_2: 2.99 [33]	3.90 (312.94 K)
NH_3	In N_2: 2.35 [34]	5.64 (298 K)
HCl	In N_2: 1.50 [35]	2.26 (423.1 K)

gas, helium, was chosen as a partner species to fit the theoretical binary diffusion coefficient of an N_2-He mixture towards the experimental values from literature in order to obtain the LJ parameters and Eucken correction factor for nitrogen. The LJ parameters for Helium were taken from Hirschfelder et al. [6] and it was ascertained that these values from the literature fit experimental data for viscosity and thermal conductivity of Helium well. Since helium is a monoatomic gas, no Eucken correction is needed according to the CE theory. De Groot, Kestin, Sookiazian, and Wakeham [38] have experimentally investigated the thermal conductivity of noble gases and came to the conclusion that a minor Eucken correction of 1.5% would be needed even for these monatomic species. However, the experimental uncertainty for many gases, especially from the early literature, exceeds the extent of this correction markedly and hence it can be neglected. Helium is one of the few species for which LJ parameters from the scientific literature are well able to describe the transport properties within the experimental uncertainty. The advantage of this approach is therefore, that the utilization of a very well

investigated, simple gas like helium as a starting point for the fitting procedure leads to physically meaningful and not only mathematically optimal values for the parameters of nitrogen and from there on all other investigated gases.

3 Results and discussion

In the following, the necessity of fitting towards all three transport properties simultaneously is graphically demonstrated. Figure 1 shows the absolute values of the average relative deviation

$$\frac{\left|D_{NH_3-N_2,exp}-D_{NH_3-N_2,calc.}\right|}{D_{NH_3-N_2,exp}} \tag{23}$$

between the calculated binary diffusion coefficient of ammonia in nitrogen based on the CE theory and the experimentally determined values from Zhavrin et al. [34] for the three temperatures 400, 500 and 600 K in dependence of the two LJ
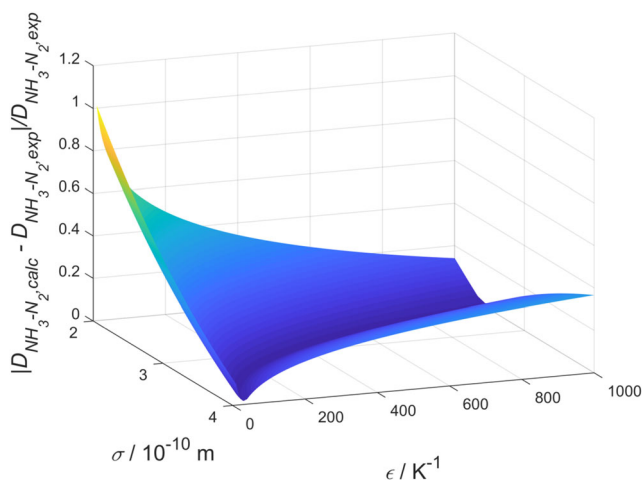
Fig. 1 Absolute values of the relative difference between experimental and calculated binary diffusion coefficients of NH_3 in N_2 in dependence of the two LJ parameters. Since the binary diffusion coefficient depends on the LJ parameters of both substances in the gas mixture, the parameters for nitrogen were fixed towards the values obtained from the fitting procedure of this work. This approach was chosen in order to be able to plot the according relative differences for all three transport properties in one single diagram in dependence of the LJ parameters of NH_3 as done in Fig. 6

parameters. The plotted deviation is an average over the three different temperatures.

Figure 2 depicts the same deviation for the subset of LJ parameters that are able to predict the binary diffusion coefficient with an accuracy of at least 3%, which is approximately the experimental uncertainty, showing that there is a wide interval of LJ parameters that lead to good agreement between CE theory and experiments. These subsets can be determined for each different transport property and since the diffusion coefficient is based on a collision integral with a different order than the thermal conductivity and the viscosity (please see Eqs. (1), (2), and (3)), these subsets can differ markedly.
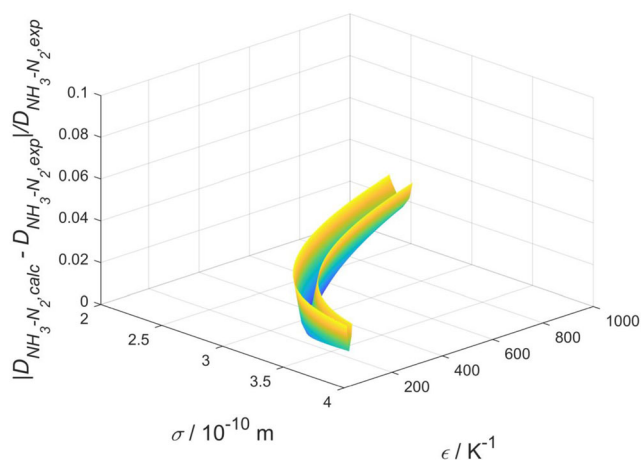
Fig. 2 Same deviation between experimental and calculated binary diffusion coefficients of NH_3 in N_2 as in Fig. 4, only showing the subset of LJ parameters that lead to the deviation being less or equal to the experimental uncertainty of 3%

To visualize this, the subsets that fulfill the precision criteria for each of the three transport properties are shown in Fig. 3 and Fig. 4 for two different accuracy criteria explained in the respective figure description.

It becomes clear that there is a significant overlap between the subsets (please see Figs. 3 and 4). However, if the LJ parameters were fitted to viscosity data alone, as it is often-times done in the literature, there is a chance that the obtained parameters are not suited for describing the thermal conduc-tivity or the binary diffusion coefficient. This is the case, if they are outside of the overlapping areas and hence only ele-ment of M_μ but not M' (please see Eqs. (17) and (18)). The chance of not obtaining suitable parameters for all transport properties increases, if the parameters were fitted to the exper-imental thermal conductivity data, as it is done when no accu-rate viscosity data is available for a gas species, due to the higher experimental uncertainty. Furthermore, Figs. 3 and 4 show that indeed there is a subset of parameters which predicts all three transport properties with an accuracy well within the experimental uncertainty. Therefore, fitting towards all three transport properties simultaneously, as done in the present work, will naturally yield parameters that are part of the subset M' introduced in Eq. (18) and therefore fulfill the criteria of being able to describe all three transport properties accurately.

The experimental uncertainty varies strongly in between liter-ature sources and also depends on the experimental method and the temperature. In earlier works the binary diffusion coefficients of gases were usually only accurate up to 5% for temperatures of
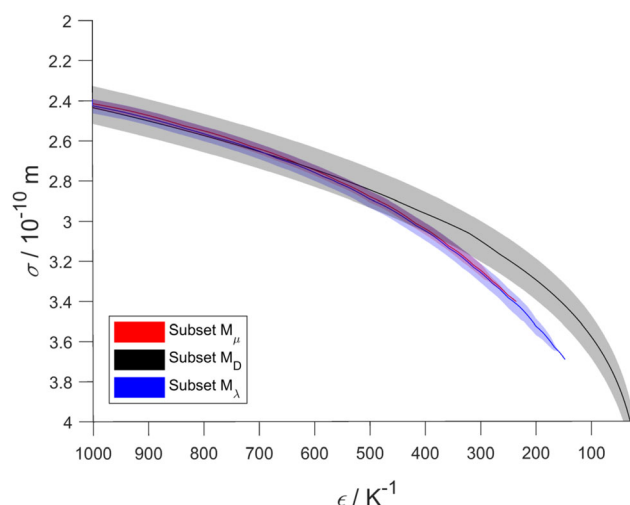

Fig. 3 Subsets that show an agreement between experimental and calculated transport properties within the experimental uncertainty for NH_3. Here, the experimental uncertainty was set to be 3% for the binary diffusion coefficient and the thermal conductivity and 2% for the viscosity. The subset for the diffusion coefficient is shown in grey, the one for the thermal conductivity in blue and the subset for the viscosity is displayed in red. The corresponding solid lines assign a value of σ to every value of ε for which the deviation between the experimental and the calculated transport property is lowest. Hence, the optimal parameter set for a certain transport property is found on the respective solid line
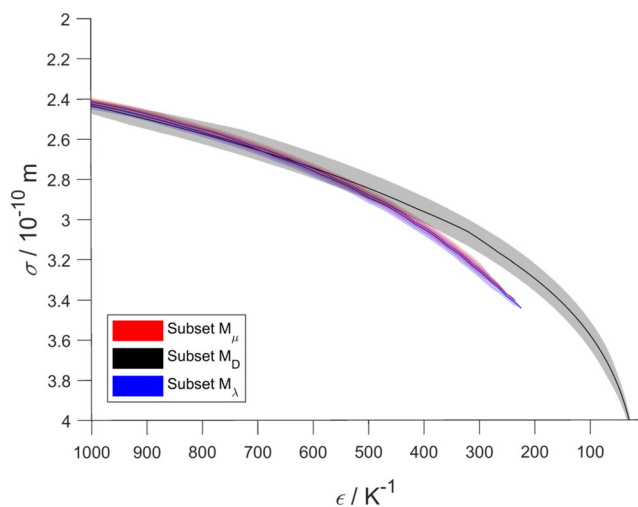
Fig. 4 Subsets that show an agreement between experimental and calculated transport properties within the experimental uncertainty for NH_3. Here, the experimental uncertainty was set to be 2% for all transport properties

Fig. 5 Comparison of the experimentally determined viscosity of nitrous oxide [12, 24] with the calculated values using the CE equations based on LJ parameters from Hirschfelder et al. [6] and the present work

up to 1000 K even in the measurements considered as most reliable as Marrero and Mason show in their comparison of different literature sources [39]. Also the thermal conductivity in some sources show experimental uncertainties of up to 4.5% depending on the temperature [27], while the viscosity measurements have always been the most precise of all the transport properties [8]. On the other hand, especially since the late twentieth century there are various scientific contributions that claim a significantly higher accuracy. Gotoh, Manner, Sørensen, and Stewart [40] for example state that their measurements of binary diffusion coefficients for various gas mixtures are accurate within 1%. Schley, Jaeschke, Küchenmeister, and Vogel [41] estimate the experimental uncertainty for their viscosity measurements of methane and natural gas to be between 0.3–0.5%. Lastly, De Groot, Kestin, and Sookiazian [42] believe that their measurements of thermal conductivities of gases have an accuracy of 0.2%. Besides these given examples there are many more with a comparably low experimental uncertainty. The consequence is that the subset of LJ parameters that leads to an agreement between experimental and calculated values within the experimental uncertainty for each transport properties is reduced with an increasing accuracy of the experimental measurements. This can be seen by comparing Figs. 3 and 4 where the shaded overlap is reduced with an increasing accuracy threshold of 2% in Fig. 4. Please note that some of the employed experimental data for this specific gas couple might not be accurate up to 2% over the whole temperature range, since not all of the employed literature sources state their accuracy. Therefore, Fig. 4 is more an example to visualize the decreasing overlap with changes in the experimental uncertainty than an absolutely accurate display of the subsets, which is only possible if the experimental uncertainty of the employed data is below 2% for all data points.
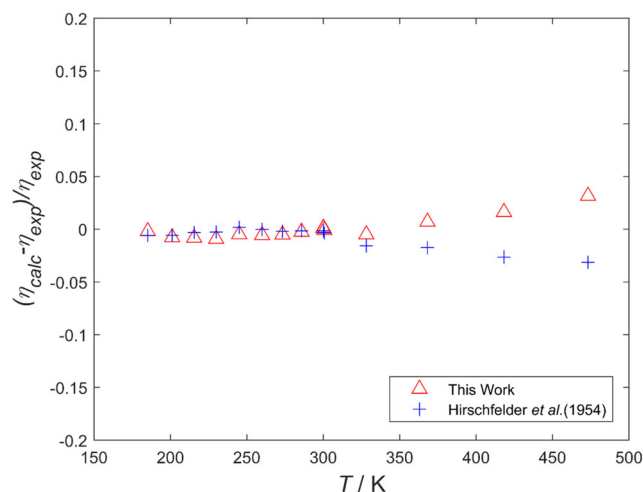
Therefore, with more and more accurate experimental data available in the scientific literature, the necessity of fitting towards all three transport properties seems to become more exigent in order to obtain LJ parameters that are an element of not only one of the subsets but all three of them and are therefore suited to describe all three transport properties accurately. It should be noted that the here presented fitting approach has intrinsic limits in its accuracy due to the approximations of the kinetic gas theory for monoatomic gases and the employed simple potential functions. However, as shown in the course of this section, an accuracy of 2–3% is achieved in most of the investigated examples with only a few exceptions where the experimental uncertainty was particularly high.

In order visualize the above discussed problems that arise when fitting towards only one transport properties in
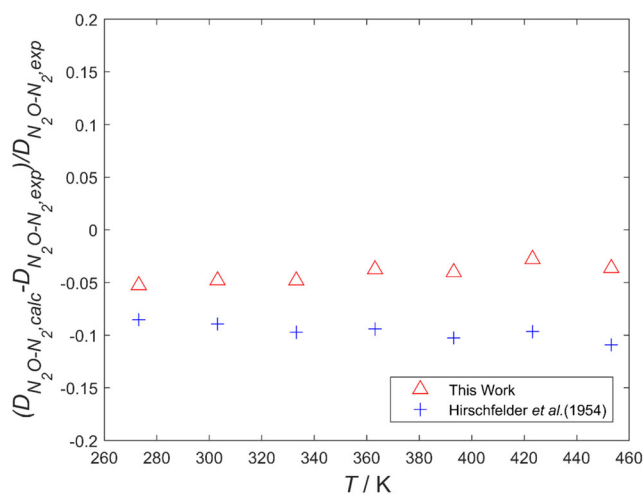

Fig. 6 Comparison of the experimentally determined binary diffusion coefficient of nitrous oxide in nitrogen [25] with the calculated values using the CE equations based on LJ parameters from Hirschfelder et al. [6] and the present work
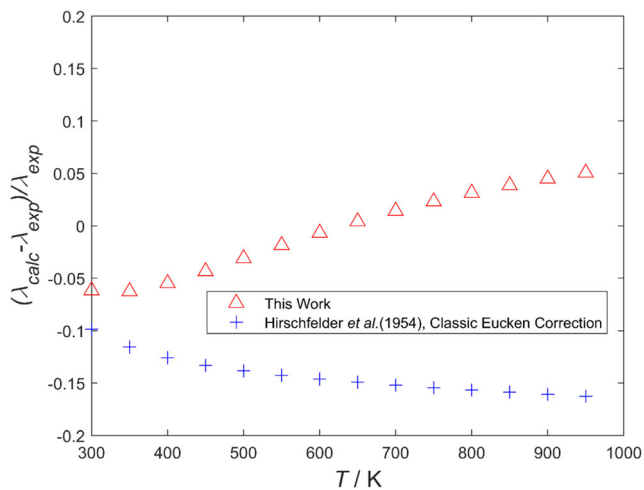
Fig. 7 Comparison of the experimentally determined thermal conductivity of nitrous oxide [26] with the calculated values using the CE equations based on LJ parameters from Hirschfelder et al. [6] using the classical Eucken correction and the present work, employing the modified Eucken correction presented in section 2

comparison to the approach proposed in the present work, nitrous oxide is investigated as an example species in the following: First, LJ parameters from Hirschfelder et al. [6] are used to calculate the three transport properties based on the CE theory. Good agreement between the calculated and experimental values was obtained only in the case of the viscosity, towards which the Lennard Jones parameters were originally fitted [6]. However, for the binary diffusion coefficient and the thermal conductivity, the deviation between calculated and experimental values is markedly greater than the experimental uncertainty. Figure 5-7 show the experimental values for the three transport properties as well as the values calculated with the CE equations using the LJ parameters from Hirschfelder and additionally the parameters determined in the present work. A more general discussion of the results for the fitting procedure for all 7 investigated species will follow later on in this section. Hirschfelder employed the classical Eucken correction for the calculation of the thermal conductivity (Fig. 7). Hence, the significant deviation between the

calculated data based on the parameters from Hirschfelder and the experimental data is to a certain extent also due to the insufficiency of the classical Eucken correction for predicting the thermal conductivity of polyatomic gases (this will be further elicited in section 3). In comparison, when using the temperature dependent modification proposed in this work, the thermal conductivity can be predicted more precisely (please see Fig. 7). In the case of the binary diffusion coefficient, the substantial mean deviation of 10% between CE theory based on the parameters from Hirschfelder and experiment can solely be deduced from the already discussed problematic approach of fitting the LJ parameters towards only one transport property. Contrary to the parameter set from Hirschfelder, the fitting procedure proposed in the present work yielded a good accuracy not only for the viscosity but also the binary diffusion coefficient and the thermal conductivity. The mean and maximum deviation of fitted and experimentally determined viscosities, thermal conductivities and binary diffusion coefficients are listed in Table 1 and the corresponding parameter set obtained from the fitting procedure based on eq. 22 is shown in Table 2.

As Table 1 shows, the mean deviation for all gases and all of the three transport properties is never greater than 5.5% and if N_2O is disregarded the mean deviation is even below 3.1% for all other gases. While the deviation in the diffusion coefficient of N_2O in N_2 is markedly higher than the deviations for the other gases, which are all between 0.6 and 3%, the mean deviation of 5.5% is still excellent in comparison to the results in the scientific literature. Using the Lennard Jones parameters from Hirschfelder et al. [6] for example, lead to a mean deviation of 10% as shown in Fig. 6. It seems that the reduced accuracy of the fit in the case of N_2O is most likely due to an increased uncertainty in the experimental work and not the fitting procedure itself. This is further underlined when specifically looking at the difference in the accuracy for the O_2-N_2 mixture (0.6% mean deviation) and the O_2-N_2O mixture. Kugler, Rausch, and Fröba [43] have published experimental data for the diffusion coefficients of the gas pair N_2O-N_2. However, their experimental uncertainty is very high, which

Table 2 Corresponding values for the LJ parameters σ and ε^*, as well as for a and b from the weighting factor f_{int} of the internal degrees of freedom in the Eucken correction obtained from the fitting procedure of the present work and the parameter δ for polar molecules

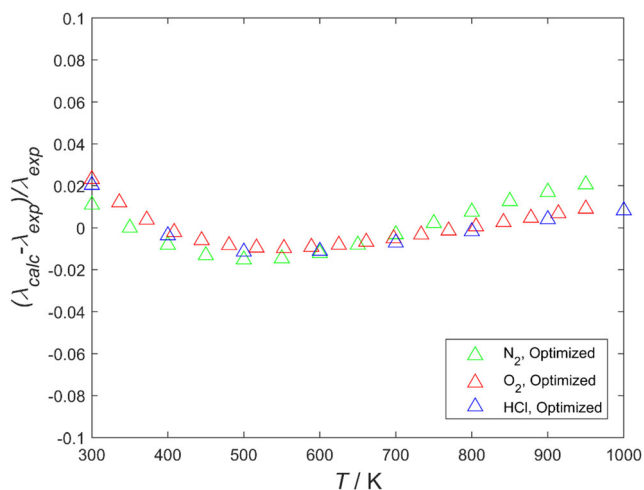| species	$\sigma/\mathring{A}$	$\varepsilon^*/\,K$	$a/1/K$	b	δ
N_2	3.5961	104.35	2.22E-14	1.1200	0
N_2O	3.2396	444.81	2.22E-14	1.1040	0
O_2	3.4770	96.92	0.000178	1.0473	0
Cl_2	3.2919	829.51	7.14E-08	1.3136	0
H_2O	3.2842	152.21	0.00103	8.12E-05	2.299
NH_3	2.9356	467.18	0.000969	0.3219	0.6622
HCl	3.0501	480.08	0.000102	0.7949	0.3101

Fig. 8 Comparison of experimental thermal conductivity and calculated thermal conductivity of HCl, N_2 and O_2 based on the obtained parameter set in Table 2

Fig. 10 Comparison of experimental viscosity and calculated viscosity of HCl, N_2 and O_2 based on the obtained parameter set in Table 2

is the reason why this data was not considered in the present work. Finally, the maximum deviations for all gases and all transport properties is always below 6.6%, the highest value again being the binary diffusion coefficient of N_2O in N_2. Since industrially relevant gases were purposefully chosen in the present work, a higher experimental uncertainty compared to simpler species, like the noble gases, must be accepted.

It can be concluded that the presented fitting procedure indeed leads to highly accurate LJ parameters and a significantly better agreement between the CE theory and experimental results compared to the fitting procedures of the previous scientific literature that relied on fitting to only one transport property. Furthermore, looking at the excellent agreement between experimental and calculated thermal conductivities, it seems that the modification of the Eucken correction proposed in this work is suitable for the wide range of investigated

temperatures and diverse gas species. This will be further underlined by looking at the graphically depicted temperature dependence of all three transport properties for three exemplary gases of this work in Fig. 8, 9, 10 amongst which is the highly polar substance HCl.

As already foreseeable from the data in Table 1, the theoretical and experimentally determined values show excellent agreement in the whole temperature range. This is also true for the thermal conductivity under consideration of the modified, temperature dependent Eucken correction. In comparison to the results from the present work, Fig. 11 shows the thermal conductivity of ammonia when the optimization is carried out with the classical Eucken correction and the modified version by Hirschfelder [19].

Figure 11 clearly shows that the classical Eucken correction and the modification from Hirschfelder, even though the

Fig. 9 Comparison of experimental binary diffusion coefficients and calculated binary diffusion coefficients based on the obtained parameter set in Table 2
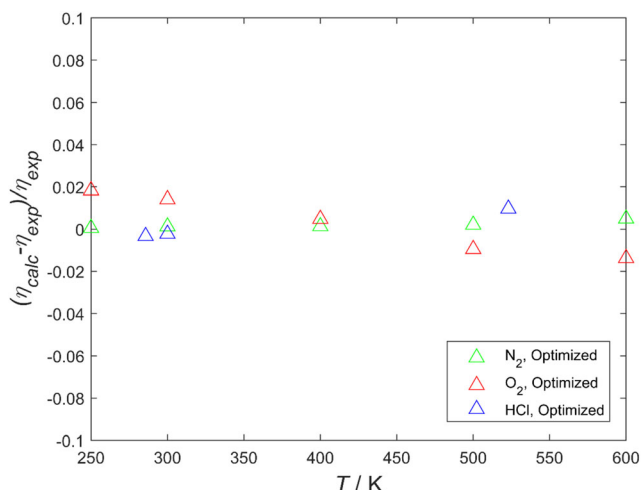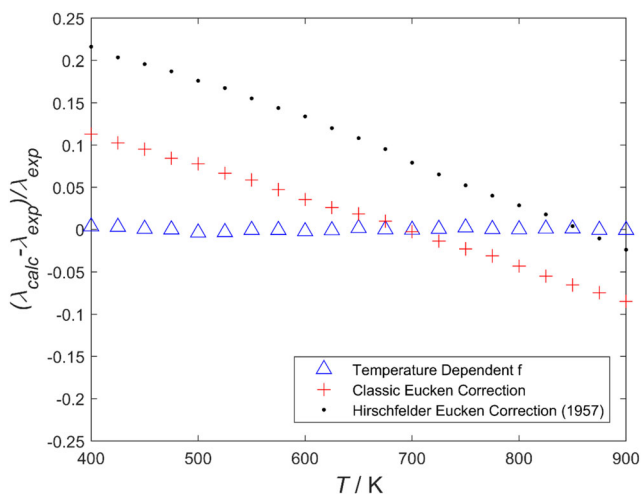

Fig. 11 Comparison of experimental thermal conductivity of Ammonia with the calculated ones based on a parameter fitting using the classical Eucken correction (cross), the modified version of Hirschfelder [16, 19] (dot) and the modified temperature dependent Eucken correction presented in this work (triangle)

LJ parameters were fitted towards experimental values for all three transport properties simultaneously, are not able to reproduce the experimentally determined thermal conductivity well. As explained in the introduction of this work, Hirschfelder [19] proposes a weighting of the internal degrees with the factor that assumes the value of 1.3 for most species and force laws. According to literature this factor shows only a negligible temperature dependence [20, 21]. Hence, it was assumed to be constant in the small temperature range considered here. It becomes clear that the temperature dependence of the experimentally determined data is not well described neither by the classical approach nor by Hirschfelder's variant, indicating that the temperature independent treatment of f_{int} is not justified. On the other hand, the temperature dependent treatment of the internal degrees of freedom while the translational degrees remain fixed in accordance with the Chapman Enskog theory, as presented in this work, leads to an excellent agreement between experimental and calculated results in the whole temperature range.

The method of developing a potential energy surface, as briefly explained in the introduction of this work, has been applied to some gas species and mixtures in the recent years. There are various examples where the agreement between experimentally determined and theoretically predicted transport properties is good [3, 4]. However, there are also various publications that show significant deviations. Hellman for example determined the thermal conductivity and viscosity of ethane [1]. When comparing the results based on his theoretical approach with experimental data of the thermal conductivity, deviations of up to 6% can be observed. In a similar article, Crusius et al. determined the transport properties for a CO_2-N_2 mixture and show maximum deviations of up to 8% from experimental data for the binary diffusion coefficient and also the thermal conductivity [2]. For nitrous oxide, they were able to predict the viscosity with in the experimental uncertainty, the second virial coefficient however, was predicted poorly [3]. It has to be mentioned that the experimental data scattered markedly, just as it is the case for some of the data of the gas species investigated in the present work. It can be concluded that the agreement between experimental data and both theoretical approaches, the here presented one and the method of developing a potential energy surface, is comparably good, except in a few cases where the experimental uncertainty is very high. As mentioned before, the approach presented in this work has a natural limit in its accuracy. However, as the low mean deviations listed in Table 1 show, the precision of this approach is not only significantly higher than the classical fitting approaches in the literature but is at the current state also mostly limited by the experimental uncertainty in measuring these transport properties. For most engineering applications, the presented approach therefore offers an accurate while still simple and computationally inexpensive way of calculating the transport properties over a wide range of temperatures.

3.1 Summary and outlook

The investigations of this chapter proved that the traditional approach of fitting LJ parameters towards only one transport property does not necessarily lead to a parameter set that is able to describe all three transport properties within the experimental uncertainty.

This is due to the fact that subset of LJ parameters with which the Chapman Enskog equations can predict transport coefficients with an accuracy that is within the experimental uncertainty, are not identical for each transport property. However it was demonstrated that there is an overlap between the subsets of all three transport properties which can be found by the fitting towards all three transport properties simultaneously, as proposed in the present work. The fitting procedure furthermore accounts for the dependence of the collision integral on the parameter δ_{max} in the case of polar species as well as a modified temperature dependent Eucken correction for determining thermal conductivities.

The so obtained Lennard Jones parameters and modified Eucken correction factors led to excellent agreement between calculated and experimental values for the three transport coefficients of the 7 exemplary gas species investigated in this chapter, clearly outperforming the classical fitting approach employed in the previous scientific literature. More specifically, the temperature dependent treatment of the Eucken correction shows significant advantages compared to the classical Eucken correction and the more sophisticated approach by Hirschfelder et al.

The presented approach can be extended to any gas for which experimental data are available. In future investigations the quality of these parameters could be even further refined by employing more precise experimental data and more sophisticated potential functions. Furthermore, it shows the advantage of being computationally very inexpensive and easily applicable in comparison to alternatives discussed in the foregoing sections. It is therefore not to be seen as a substitution of the more complex approach of developing a potential energy surface, but as a simple and yet still precise alternative that can be employed in various classical engineering applications.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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