

## **Correlation and Extrapolation of Dilute-Gas Properties of Simple Linear Molecules with the SSR-MPA Potential Model**

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A three-parameter angle-dependent pair potential referred to as the SSR-MPA is used to correlate and extrapolate the dilute-gas properties of the simple linear molecules nitrogen, oxygen, and ethane. The statistical mechanical equations are solved by direct numerical integrations. When the shape of the molecules and the anisotropic long-range forces are properly accounted for, all data are reproduced or predicted essentially within the experimental uncertainties.

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**KEY WORDS:** dilute-gas properties; mixtures; pair potentials; statistical mechanics.

### **1. INTRODUCTION**

Pair potentials in connection with statistical mechanics of dilute gases provide a useful tool for a consistent correlation and extrapolation of the thermophysical properties of gases. Much earlier work has been done in this area, although a consistent representation of the data of polyatomic gases has generally not been achieved. We believe that this rests on the choice of potential functions that has usually been made, e.g., either neglecting the anisotropy of molecular shape altogether or treating it by rather crude models. In this work, we demonstrate that a particular potential model, to which we refer as the SSR-MPA, is quite acceptable as a means for correlation and extrapolation of the dilute-gas properties of simple linear molecules.

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## 2. THE POTENTIAL MODEL

The SSR-MPA (site-site repulsion/multipole attraction) potential model, which we use in this work, uses the commonly known long-range contributions to the intermolecular forces, which are based on quantum mechanical perturbation theory and the multipole expansion. For linear molecules, all pair potential terms are documented in the literature; a comprehensive derivation is found in Ref. 1. Full account is taken of multipole induction and dispersion forces, the latter being restricted to the Lennard-Jones  $r^{-6}$  term plus anisotropic contributions. The short-range repulsive forces are modeled by a site-site interaction model, using the Lennard-Jones repulsive term, i.e.,

$$\phi^{\text{rep}}(r_{12}\omega_1\omega_2) = \sum_{a,b} 4\varepsilon_{ab} \left( \frac{\sigma_{ab}}{r_{ab}} \right)^{12} \quad (1)$$

where  $\varepsilon_{ab}$  and  $\sigma_{ab}$  are the potential parameters of the site-site interaction between site  $a$  and site  $b$ , and  $r_{ab}$  is the distance between two sites in different molecules. Using standard mathematical methods, the site-site repulsive model can be transformed into a model showing explicitly the excentricities  $r_a$ ,  $r_b$  of the molecule as well as its orientation angles [1]. The model contains three adjustable parameters. These are the center-to-center distance and energy parameters,  $\sigma$  and  $\varepsilon$ , respectively, and the elongation of the molecule, which is allowed to differ from the actual bond length. We denote with  $|r_a|$  and  $|r_b|$  the distances from the molecular center to the repulsive sites. As a relationship restricting the site-site parameters  $\varepsilon_{ab}\sigma_{ab}^{12}$ , we have the "boundary condition":

$$\sum_{a,b} \varepsilon_{ab}^* \sigma_{ab}^{*12} = 1 \quad (2)$$

with

$$\varepsilon_{ab}^* = \frac{\varepsilon_{ab}}{\varepsilon} \quad \text{and} \quad \sigma_{ab}^* = \frac{\sigma_{ab}}{\sigma}$$

Equation (2) ensures the proper limiting case of a pure Lennard-Jones repulsive potential for zero elongation of the molecule. For the simple linear molecules considered in this paper, this relation suffices to fix the site-site parameters universally to  $\varepsilon_{ab}^* \sigma_{ab}^{*12} = 0.25$ .

The three parameters of the model must be fitted to experimental data. In most earlier calculations this was done by using data of the second virial coefficient and of viscosity. While this is basically possible, a more sensible

route seems to be to use the second virial coefficient in combination with the Joule–Thomson coefficient [2], which is essentially the temperature derivative of the second virial coefficient. When consistent data sets of these two properties are used, the proper potential parameters are established [3] without being affected by possible inaccuracies of the statistical mechanical equation for the dilute-gas viscosity of polyatomic molecules.

### 3. NUMERICAL EVALUATION OF THE STATISTICAL MECHANICAL EQUATIONS

The second virial coefficient and the Joule–Thomson coefficient can be rigorously related to integrals over the pair potential. For rigid linear molecules, an integration over four variables is involved, and the problem of an effective numerical evaluation of the statistical mechanical equations presents itself. Most earlier work in this area has used a simplified procedure based on the Pople perturbation expansion [4]. In this approach, the second virial and the Joule–Thomson coefficients can be calculated analytically, once the angular integrations have been evaluated analytically in the spherical tensor formalism and the data of the universal

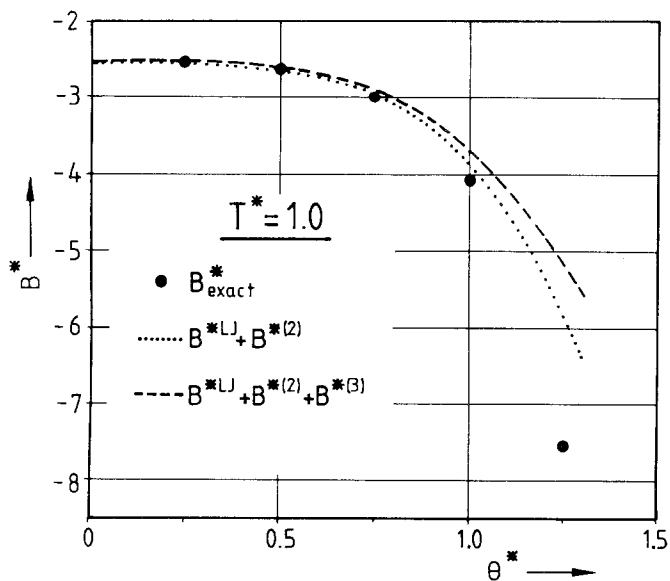


Fig. 1. Comparison of the Pople perturbation expansion with the exact calculated second virial coefficients for a Lennard–Jones plus quadrupole–quadrupole potential.

reference gas, e.g., Lennard–Jones, have been calculated. This perturbation expansion works quite well for the attractive part of the pair potential, but not so for the repulsive part. Figure 1 shows the convergence for a Lennard–Jones + quadrupole fluid for various reduced quadrupole strengths  $\theta^* \equiv (\theta/\sqrt{\epsilon\sigma^5})$  at  $T^* = 1.0$ . Convergence is satisfactory and, in fact, is better for the second-order expansion  $B^{*LJ} + B^{*(2)}$  than for the third-order expansion  $B^{*LJ} + B^{*(2)} + B^{*(3)}$ . Figure 2 shows a similar plot for a site–site repulsive + Lennard–Jones attractive potential for various reduced excentricities  $r_a^* = r_a/\sigma$ . It can be seen that the convergence is very poor. A Padé approximant [5]

$$B_{\text{Padé}}^* = B_{\text{LJ}}^* + B^{*(1)} + \frac{B^{*(2)}}{1 - B^{*(3)}/B^{*(2)}} \quad (3)$$

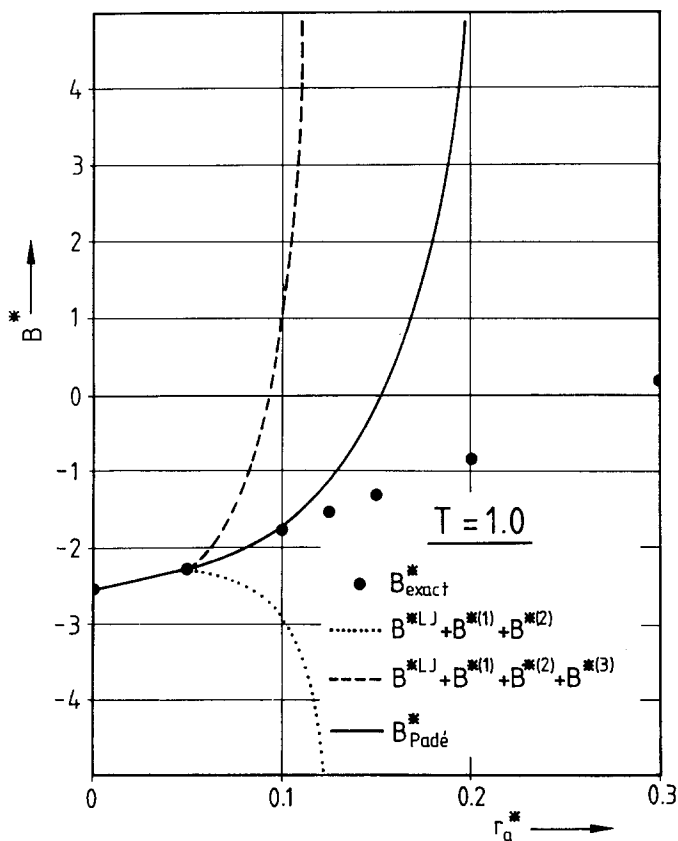


Fig. 2. Comparison of the Pople perturbation expansion with the exact calculated second virial coefficient for a site–site repulsive plus Lennard–Jones attractive potential.

where

$$B^* = B / (\frac{2}{3} \pi N_L \sigma^3)$$

helps but still does not carry further than  $r_a^* = 0.1$ . This is unacceptable, in view of a value of  $r_a^* \simeq 0.2$  for the molecules considered here. Thus, in this work, perturbation theory was rejected for the evaluation of the integrals. Instead, standard integration techniques were used [6], in spite of the considerable larger numerical effort. The dilute-gas viscosity can be calculated from a pair potential of polyatomic molecules by the Mason–Monchick approximation [7]. In this approximation, we calculate the collision integrals for particular orientations [8] and then perform an unweighted average over all of them. This procedure is not accurate but is probably the best practical method available today.

#### 4. RESULTS

In this work, we concentrate the detailed discussion on three characteristic gases of various molecular specifications, i.e., nitrogen, oxygen, and ethane.

Nitrogen is a small molecular which is often thought to be dominated by spherical interactions, although its elongation as well as its quadrupole contributes considerably to its thermophysical properties in the gases phase. Figures 3 and 4 show the simultaneous correlation of the second virial coefficient and the Joule–Thomson coefficient. The shaded area represents the estimated inaccuracy of the data, as given by Refs. 9–13. At temperatures below 150 K, we find the recommended data of [9] incon-

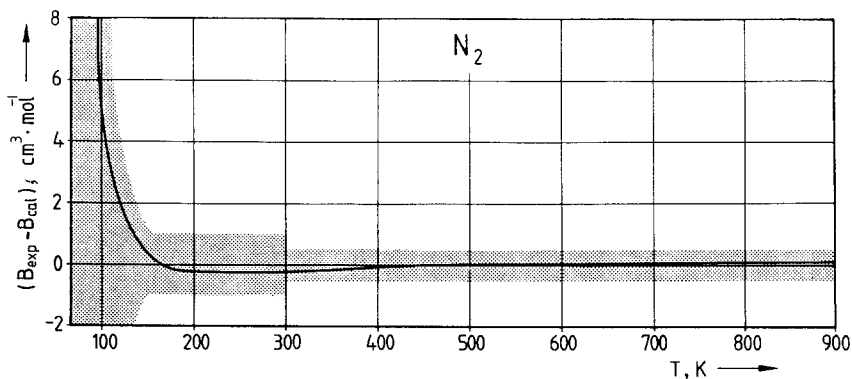


Fig. 3. Deviation plot of experimental second virial coefficients for nitrogen. Data: recommended values of Dymond and Smith [9] and Ref. 10.

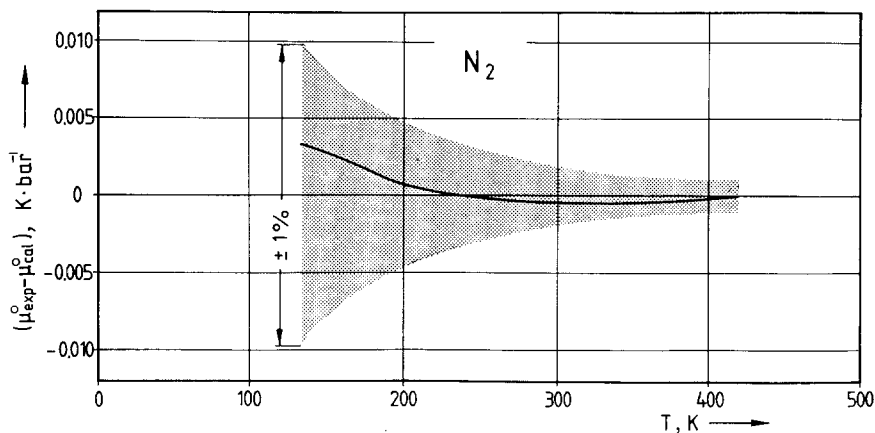


Fig. 4. Deviation plot of experimental Joule-Thomson coefficients for nitrogen. Data from Refs. 11–13.

sistent with others, in particular the Joule-Thomson coefficients. Since we depend on the combined errors of a second virial and Joule-Thomson coefficient, we increase the uncertainties cited in Ref. 9 accordingly and choose a 2.5% uncertainty in  $B$  below  $T/T_c = 0.8$ . The predicted viscosity is shown in Fig. 5 over a large range of temperatures. The accuracy of the prediction as compared to the data [14] is within the estimated accuracy of [14] and cannot nearly be achieved by any isotropic potential model.

Oxygen is a molecule rather similar to nitrogen, although its quadrupole effects are much smaller, i.e., by a factor of 3 in reduced units.

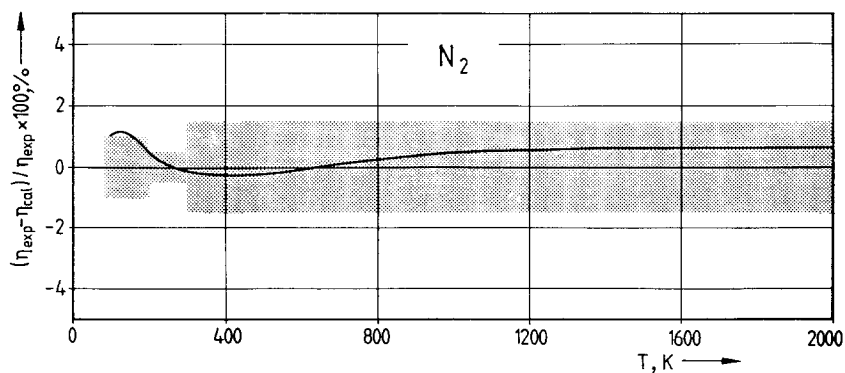


Fig. 5. Percentage deviation plot of experimental dilute gas viscosity coefficients for nitrogen. Data from Ref. 14.

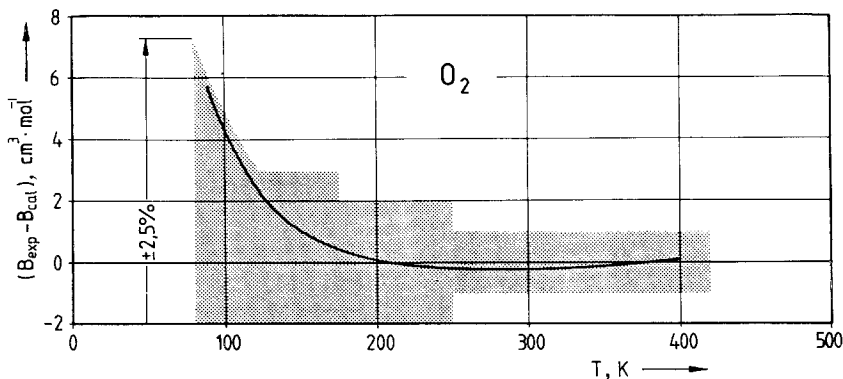


Fig. 6. Deviation plot of xperimental second virial coefficients for oxygen. Data from Ref. 10.

The angle dependence of the interaction energy will therefore be dominated by the repulsive forces. Figures 6 and 7 demonstrate that the second virial coefficient as well as the Joule–Thomson coefficient can be correlated within its experimental inaccuracy [9, 15]. The uncertainties of  $B$  are from Ref. 9, except for  $T/T_c < 0.8$ , where again 2.5% are assumed.

The Joule–Thomson coefficient of oxygen was calculated from an extended corresponding status correlation with an estimated inaccuracy of  $\pm 1\%$ . Figure 8 shows the predicted viscosity over a large temperature range. The predictions are again well within the error bounds of the data [14], which are stated to be  $\pm 1\%$  from 80 to 300 K and assumed to be  $\pm 2\%$  for higher temperatures.

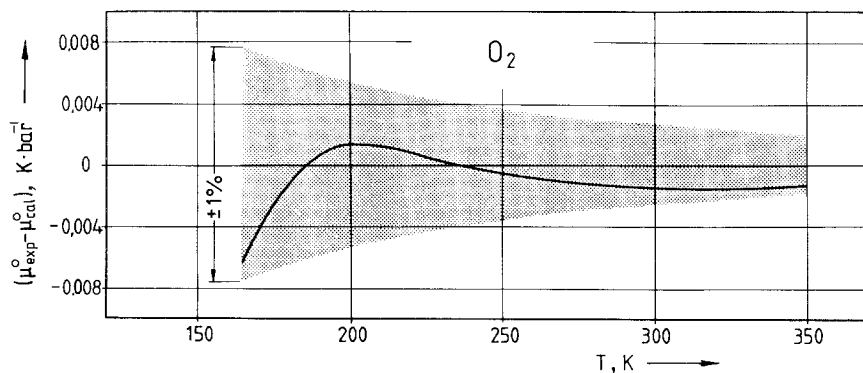


Fig. 7. Deviation plot of experimental Joule–Thomson coefficients for oxygen. Data from Ref. 15.

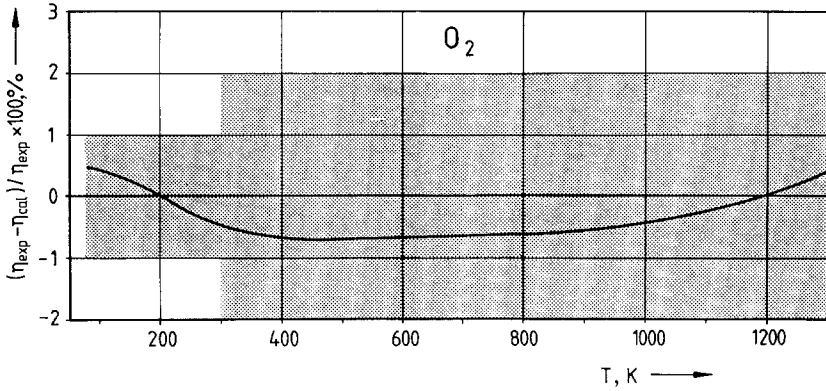


Fig. 8. Percentage deviation plot of experimental dilute-gas viscosity coefficients for oxygen. Data from Ref. 14.

Finally, ethane is a molecule with a rather complicated anisotropic shape, while the quadrupole and other long-range effects are almost negligible. We model the shape by considering ethane to be made up of two superatoms, the  $\text{CH}_3^-$  groups. Again, the simultaneous correlation of the second virial coefficient and the Joule-Thomson coefficient is essentially within the accuracy of the data [9, 16]; see Figs. 9 and 10. Higher deviations for the second virial coefficient at the lowest temperatures are

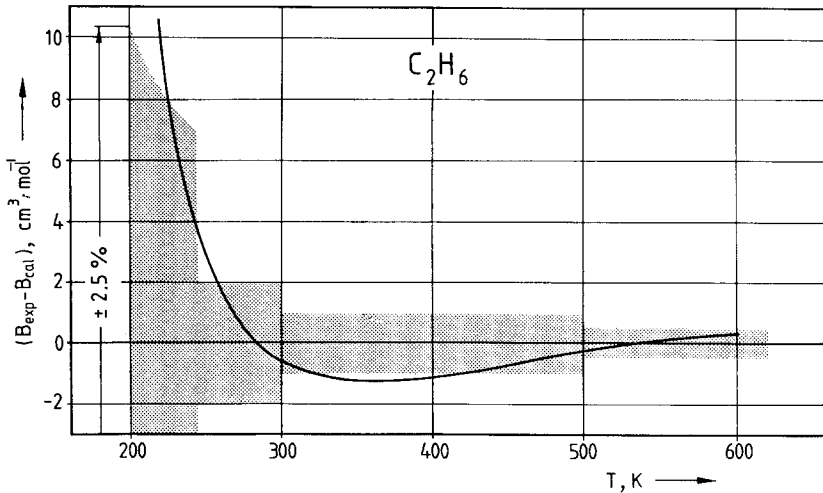


Fig. 9. Deviation plot of experimental second virial coefficients for ethane. Data from Ref. 9.



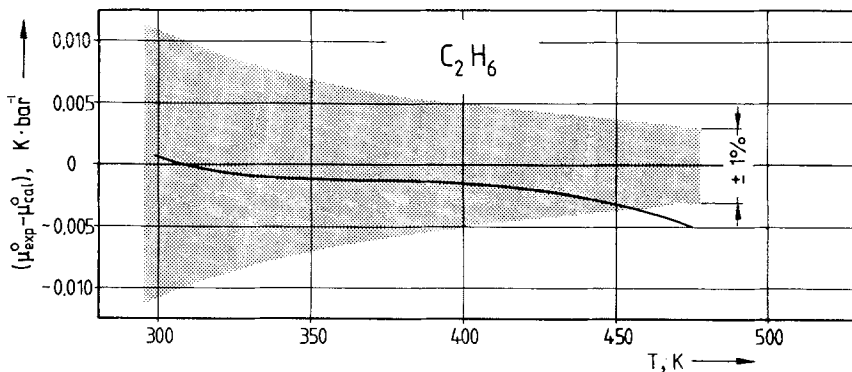


Fig. 10. Deviation plot of experimental Joule-Thomson coefficients for ethane. Data from Ref. 16.

found, but the given error bounds may be somewhat too optimistic and we again estimate the error below a reduced temperature of  $T/T_c = 0.8$  at least 2.5% from comparison with the data of other gases. The viscosity is predicted in perfect agreement with the available data [17, 18] and correlations [8], respectively. The uncertainty of the data has been stated [17] to be one of  $\pm 2\%$ , while we attributed an accuracy of  $\pm 1\%$  to the data of Ref. 18 in the limited temperature range shown.

### 5. CONCLUSIONS

We conclude that a simultaneous correlation of the second virial coefficient and the Joule-Thomson coefficient as well as a prediction of the

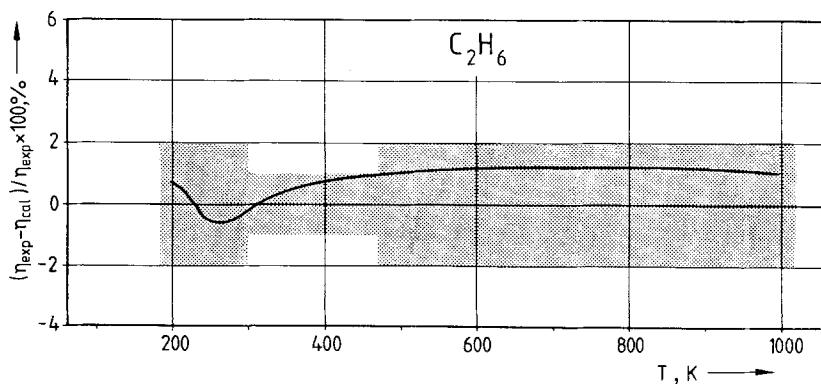


Fig. 11. Percentage deviation plot of experimental dilute gas viscosity coefficients for ethane. Data from Refs. 17-19.

**Table I.** Values of the Parameters of the SSR-MPA Potential Function for  $N_2$ ,  $O_2$ , and  $C_2H_6$  ( $\alpha$  = polarizability;  $\kappa = [(\alpha_{II} - \alpha_I)/3\alpha]$ )

Gas	$\epsilon/k$ (K)	$\sigma$ (Å)	$r_a/\sigma$	$\theta$ ( $10^{-26}$ esu · cm <sup>2</sup> )	$\alpha$ (Å <sup>3</sup> )	$\kappa$
$N_2$	257.89	2.9728	0.23455	-1.4	1.74	0.133
$O_2$	329.94	2.7678	0.22564	-0.4	1.58	0.232
$C_2H_6$	553.85	3.6438	0.22254	-1.2	4.44	0.0578

viscosity is possible within the claimed accuracy of the data for simple linear molecules with the SSR-MPA potential model. This is a nontrivial achievement for an anisotropic potential model with no more than three adjustable parameters. Uncertainties of the molecular constants, weakness of the Mason-Monchick approximation, slight inconsistencies of the data, etc., do not appear to have a noticeable effect on the gases investigated. It should be noted that neglecting anisotropic repulsive forces or even all angle-dependent contributions to the potential model results in errors in the viscosity predictions of up to 10%, while the simultaneous correlation of the second virial coefficient and the Joule-Thomson coefficient is still satisfactory. Table I summarizes the potential parameters and the molecular constants [19] that have been used in this work. A rather rigorous test of their physical significance will be the prediction of the third virial coefficients, which will be discussed in a separate paper.

We note that the accuracy obtained for the molecules treated in this paper relies on their simplicity. More complicated, even linear molecules require additional assumptions for relations between the various site-site parameters. Further, there is by no means conclusive evidence that the SSR-MPA model with the sites distributed qualitatively in accordance with the location of the atoms will be equally accurate for all rigid molecules, linear and nonlinear.

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