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Thermodynamic and Transport Properties of Gases from Sophisticated Potential Models[1]

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The statistical mechanical equations for the thermophysical properties of dilute gases are evaluated using sophisticated, but still practical potential models with no more than three adjustable parameters. Universal combination rules for these parameters are formulated. It is shown that some data of dilute gas thermophysical properties of monatomic and simple linear molecules yield potential parameters that can be used to predict all other thermophysical properties of the pure gases and their mixtures with excellent accuracy. For monatomic fluids, these potentials are shown to give excellent results of the thermodynamic functions also in the liquid and dense gaseous state.

KEY WORDS: gas properties; kinetic theory; pair potential; statistical mechanics.

1. INTRODUCTION

For simple molelcules, which can be considered to consist of rigid structures, statistical mechanics is developed to a high degree of sophistication. For a reasonable number of them, in particular, monatomic and linear molecules, we today find reliable values of the molecular constants in the literature. In the dilute gas region, we have accurate equations relating the thermodynamics to pair and triplet potentials [1]. Transport properties of polyatomic rigid molecules are not yet completely understood, but viscosity and diffusion coefficients can be calculated in the Mason–Monchick approximation with considerable accuracy [2]. In particular, the statistical

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mechanics of dilute gases provides us with accurate mixing rules for the thermophysical properties. It is, therefore, tempting to develop potential models along with universal combination rules for their parameters, in order to obtain a reliable scheme for the correlation and prediction of their thermophysical properties. In this paper, I review the results of this scheme.

2. MONATONIC GASES

For monatomic fluids, a large number of empirical pair potential functions have been suggested in the past. One that is particularly well suited for the purposes here is the one to which we refer as the MSK potential [3, 4]

$$\phi(r)=\frac{6}{n-6}\,\varepsilon\left[\left(\frac{r_m-d}{r-d}\right)^n-\frac{n}{n-6}\left(\frac{r_m-d}{r-d}\right)^6\right] \tag{1}$$

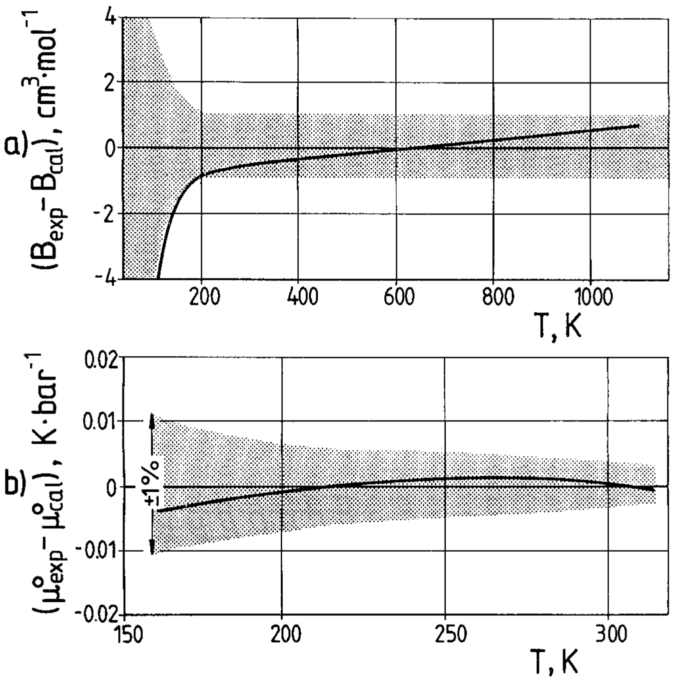

Fig. 1. Simultaneous correlation of dilute gas argon second virial coefficients (a) and Joule–Thomson coefficients with resulting MSK parameters (b) [4]. Shaded area represents experimental uncertainties. Parameters: $\varepsilon/k = 141.61$ K; $r_m = 3.746$ A; $d/r_m = 0.05864$.

with

$$n = 12 + 5\left(\frac{r}{r_m} - \frac{d}{r_m} - 1\right) \tag{2}$$

It contains three adjustable parameters, i.e., the depth of the potential ε, the associated distance between the atoms r_m at the potential minimum, and the hard spherical core diameter d.

As an example of what can be done with this potential, we consider the dilute gas properties of argon [3]. When we determine the three parameters of this potential from a consistent set of data of the second virial coefficient and the Joule–Thomson coefficient, we get a correlation essentially within experimental error as shown in Fig. 1. When we then

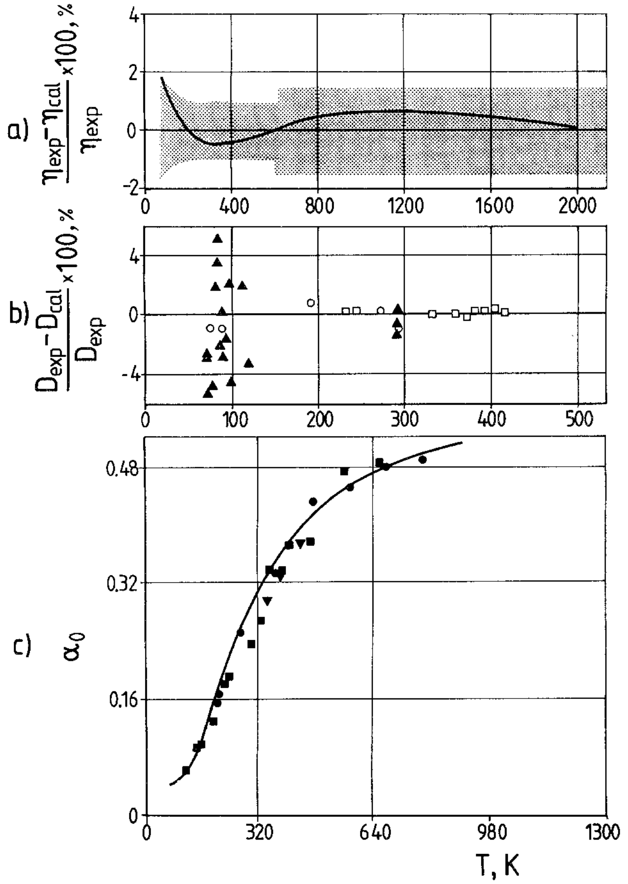

Fig. 2. Prediction of dilute gas argon viscosities (a), diffusion coefficients (b), and thermal diffusion factors (c) [4]. Shaded area represents experimental uncertainties; symbols represent data.

predict the dilute gas viscosity η, the diffusion coefficient D, and the thermal diffusion factor α_0 of argon, we obtain values which are in perfect agreement with the data, as shown in Fig. 2. At temperatures below 200 K there appears to be some uncertainty in the viscosity data and the shadow represents our estimate of probable error bounds. There is also substantial agreement for the predicted third virial coefficient, when we use the Axilrod–Teller term for the nonadditive three-body dispersion forces and eliminate its coefficient in favor of the pair potential parameters in the standard way [3]. This is shown in Fig. 3, where the considerable scatter of the experimental data is also evident. Similar results have been obtained for the other noble gases [4].

If we use the London dispersion formula adapted to a Lennard–Jones potential, we can derive the following combination rule for the potential parameters:

$$\varepsilon_{\alpha\beta}\sigma^6_{\alpha\beta} = \frac{2(\varepsilon_{\alpha\alpha}\sigma^6_{\alpha\alpha})(\varepsilon_{\beta\beta}\sigma^6_{\beta\beta})}{\varepsilon_{\alpha\alpha}\sigma^6_{\alpha\alpha}\alpha^2_\beta + \varepsilon_{\beta\beta}\sigma^6_{\beta\beta}\alpha^2_\alpha}\,\alpha_\alpha\alpha_\beta \qquad (3)$$

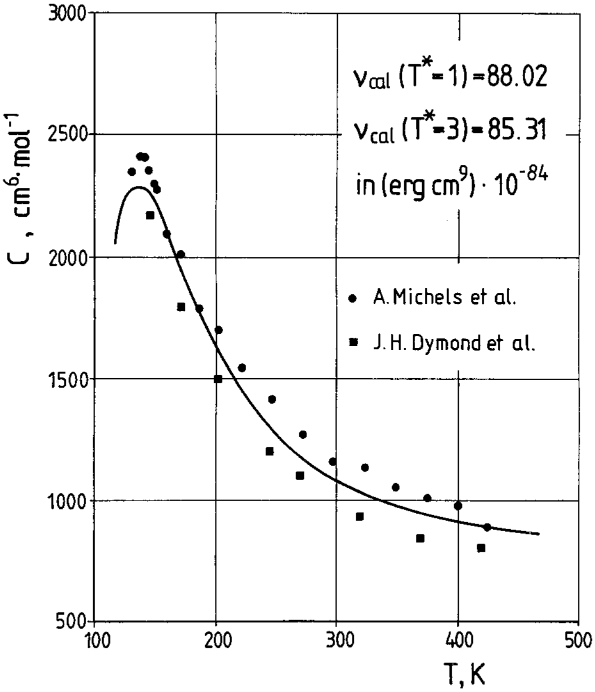

Fig. 3. Predicted argon third virial coefficient [4].

to which we refer as Kohler's rule [5]. Here the α's are the polarizabilities and the σ's are the distances at zero energy of the potential which are related to r_m. Further, representing the repulsive forces between two atoms by a spring model [6], a second combination rule for the Lennard–Jones parameters is easily derived:

$$\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^{12}=\left[\frac{(\varepsilon_{\alpha\alpha}\sigma_{\alpha\alpha}^{12})^{1/13}+(\varepsilon_{\beta\beta}\sigma_{\beta\beta}^{12})^{1/13}}{2}\right]^{13} \tag{4}$$

If we finally add the obvious combination rule for the hard spherical cores,

$$d_{\alpha\beta}=\frac{1}{2}(d_{\alpha\alpha}+d_{\beta\beta}) \tag{5}$$

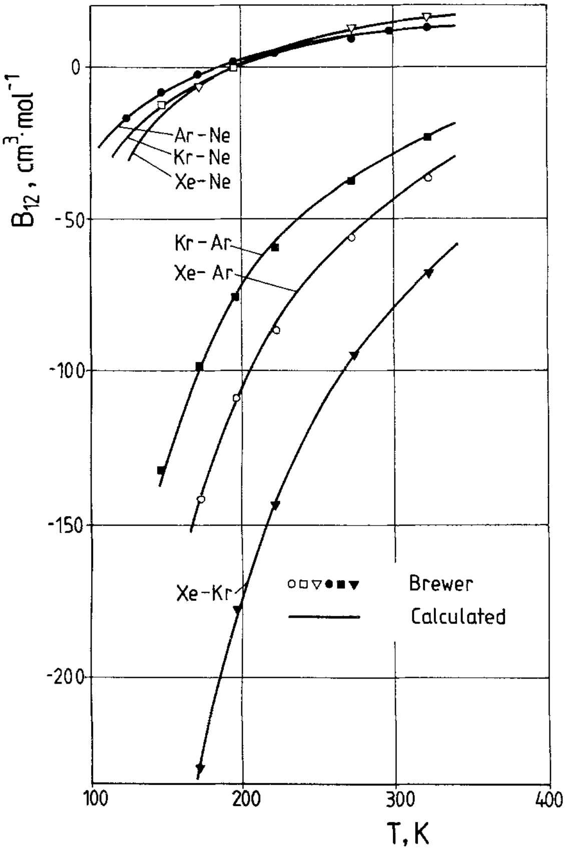

Fig. 4. Predicted second virial interaction coefficients for some noble gas mixtures [4].

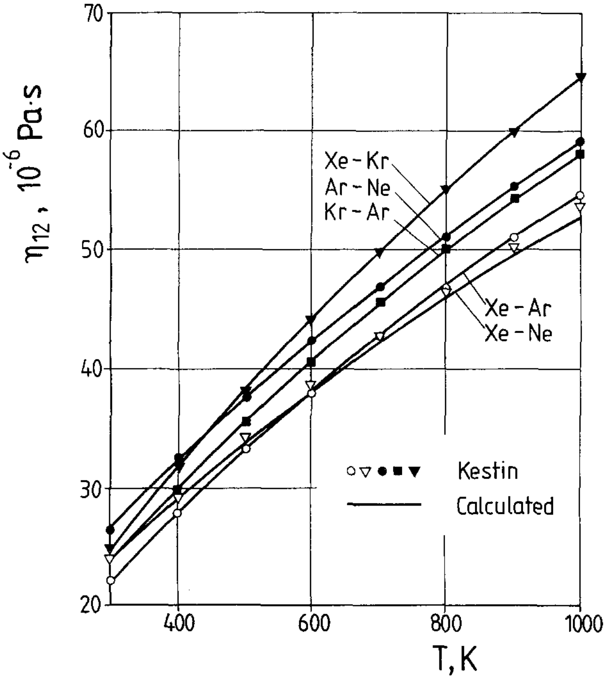

Fig. 5. Predicted viscosity interaction coefficients for some noble gas mixtures [4].

all binary unlike interactions are fully defined in terms of like interactions.

For the noble gases neon, argon, krypton, and xenon, the potential parameters have been obtained either from second virial coefficient plus Joule–Thomson coefficient data or from second virial coefficient plus viscosity data [4]. They are in reasonably good agreement with values established by much more sophisticated theoretical and experimental means. To demonstrate the usefulness of the approach, we show predicted interaction virial coefficients and interaction viscosity coefficients for some monatomic pair interactions in Figs. 4 and 5. There is excellent agreement with the data, and we conclude that the thermophysical properties of dilute gas mixtures can be predicted with considerable accuracy from the MSK potential along with the universal combination rules discussed [4].

3. SIMPLE LINEAR MOLECULES

Linear molecules have potential functions that deviate in several aspects from the simple spherically symmetric functions for the

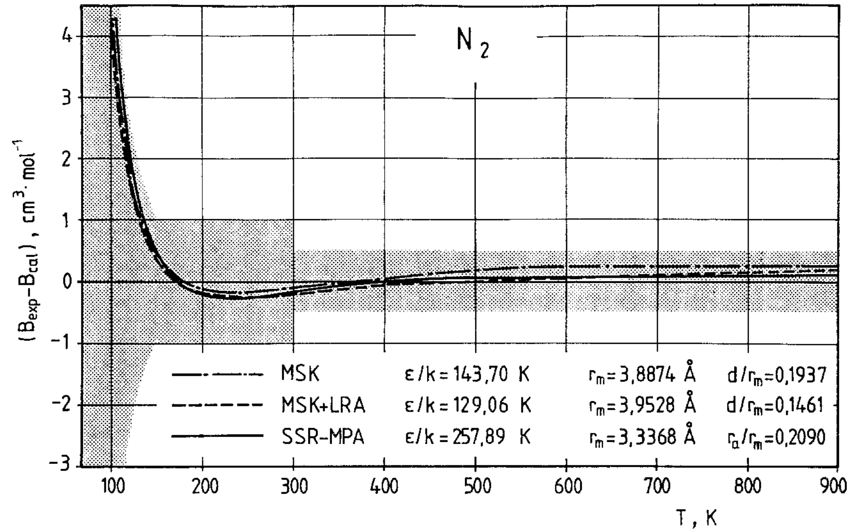

Fig. 6. Correlation of nitrogen second virial coefficient by various potential models [7]. Shaded area represents experimental uncertainty.

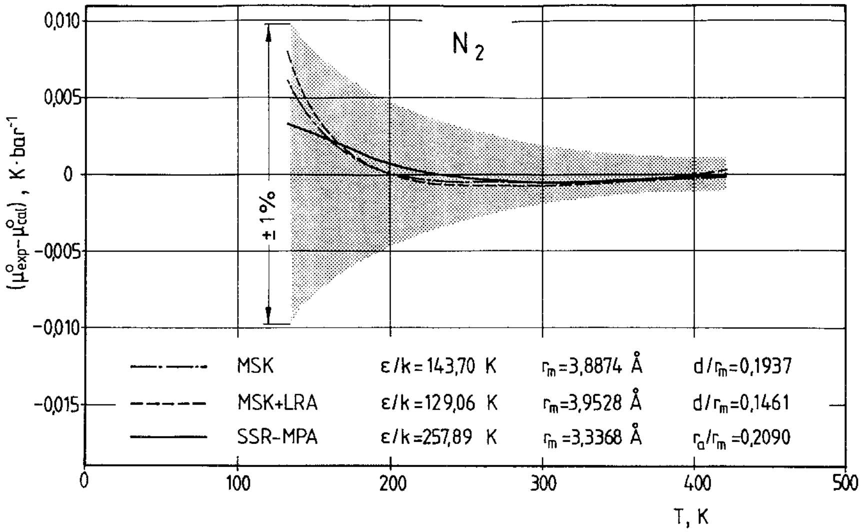

Fig. 7. Correlation of nitrogen Joule–Thomson coefficients by various potential models [7]. Shaded area represents experimental uncertainty.

monatomics. Basically they are angle dependent, due to an anisotropy of the long-range forces as well as of the short-range forces. A logical first step would be to assume that, due to rapid rotation of the molecules, an effective spherical force field will be sufficient to describe their thermophysical properties. However, this is not so, as can clearly be seen from Figs. 6–8, where a simultaneous correlation of the second virial coefficient and Joule–Thomson coefficient fails to predict accurately the dilute gas viscosity of a molecule as simple as nitrogen for the MSK potential.

Several authors have used a Stockmayer type of potential, by adding the long-range anisotropic forces dominated by the quadrupole term and using the Mason–Mochick approximation for the evaluation of the collision integrals. As can be seen from Fig. 8, this represents some improvement, although no further adjustable parameter is introduced. Still this Stockmayer model is not satisfactory, due to its total neglect of the anisotropy of molecular shape.

To include the effects of anisotropic repulsive forces for simple linear molecules, we propose an angle-dependent potential, to which we refer as the SSR-MPA (site–site repulsion/multipole attraction) [7]. This model uses the established long-range contributions to the intermolecular forces, as obtained from quantum mechanical perturbation theory and the multipole expansion. Full account is taken of multipole, induction, and disper-

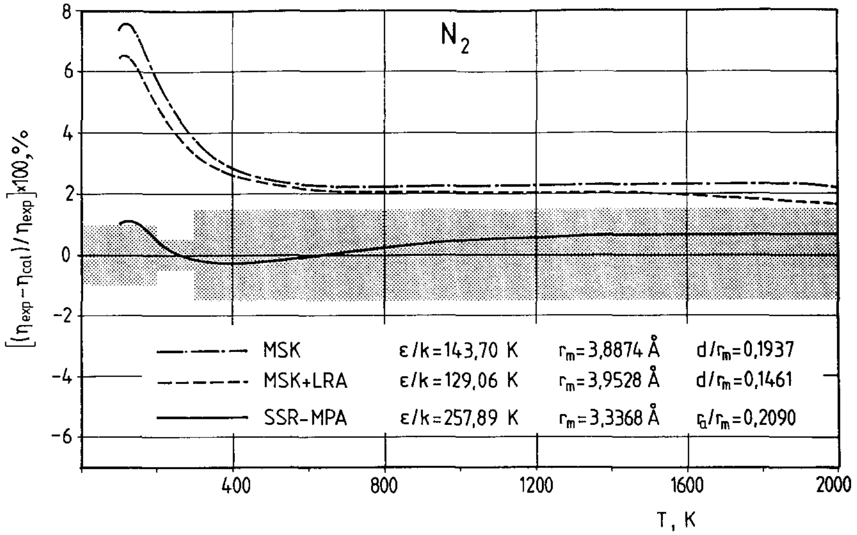

Fig. 8. Prediction of nitrogen viscosities by various potential models [7]. Shaded area represents experimental uncertainty.

sion forces, the latter being restricted to the Lennard–Jones r^{-6} term plus anisotropic contributions. The short-range repulsive forces, due to the anisotropy of molecular shape, are modeled by a site–site interaction model, using the Lennard–Jones repulsive term, i.e.,

$$\phi^{\mathrm{rep}}(r_{12}\omega_1\omega_2)=\sum_{\mathrm{a,b}}4\varepsilon_{\mathrm{ab}}\left(\frac{\sigma_{\mathrm{ab}}}{r_{\mathrm{ab}}}\right)^{12} \tag{6}$$

Here r_{12} is the center-to-center distance, and ω_1 and ω_2 are the orientational angles of the two molecules. Further, $\varepsilon_{\mathrm{ab}}$ and σ_{ab} are the potential parameters of the site–site interaction between site a of one molecule and site b of the other, and r_{ab} is the distance between these sites. The distance

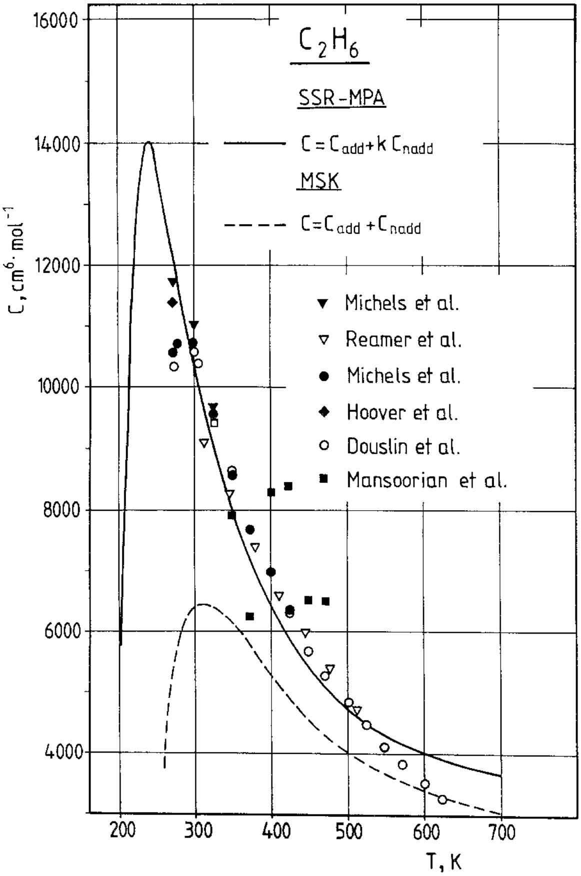

Fig. 9. Predicted third virial coefficient of ethane [8].

r_{ab} can be transformed into an equation containing the distance between the molecular centers and the orientational angles of the molecules by standard mathematics. The SSR-MPA model, like the MSK and the MSK + Stockmayer, then contains three adjustable parameters. These are the center-to-center distance and energy parameters, σ and ε, respectively, and the elongation of the molecule. The parameters for the site–site repulsion interactions are restricted by

$$\sum_{a,b} \varepsilon_{ab}\sigma_{ab}^{12} = \varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^{12} \tag{7}$$

which ensures the proper limiting case of a pure Lennard–Jones repulsive potential for zero elongation of the molecule. Clearly, for all homonuclear

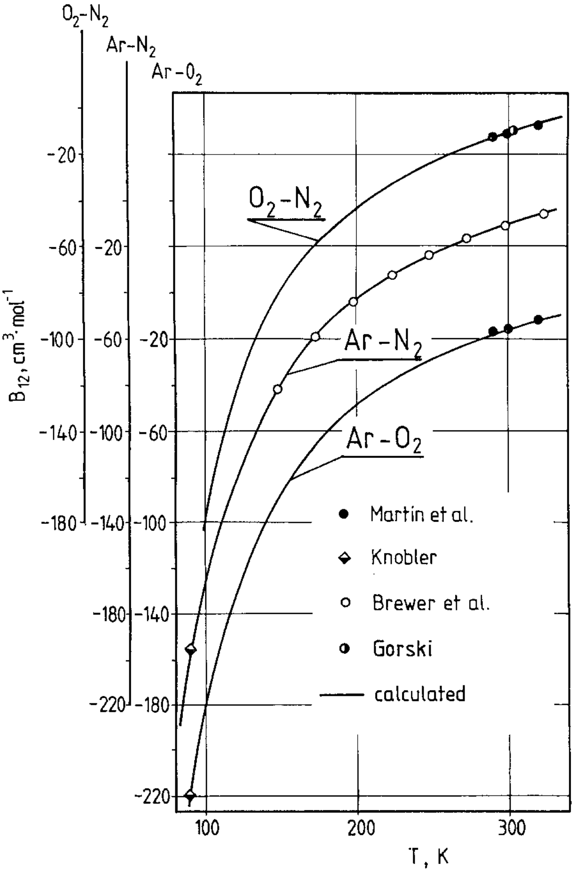

Fig. 10. Predicted second virial interaction coefficients in the air model mixture [9].

diatomic molecules $\varepsilon_{\mathrm{ab}}\sigma_{\mathrm{ab}}^{12}=0.25\,\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^{12}$ for any site–site term, and no additional assumptions have to be made.

Using the SSR-MPA model requires direct numerical integrations to be performed for the virial coefficients, since the usual Pople perturbation expansion does not converge well for site–site interactions [7]. It can be seen from Fig. 8 that an excellent prediction of the nitrogen viscosity is found and, so, its gas data are simultaneously described within their estimated experimental uncertainty. At temperatures below 130 K, the data of the second virial coefficient and the Joule–Thomson coefficient are inconsistent, resulting in unusually large error bounds for the second virial coefficient there. Quite analogous results are found for the two other simple linear molecules, oxygen and ethane, investigated [7]. Their second virial coefficients and Joule–Thomson coefficients can be correlated very well within the mutual error bounds, and the predicted viscosities are in perfect

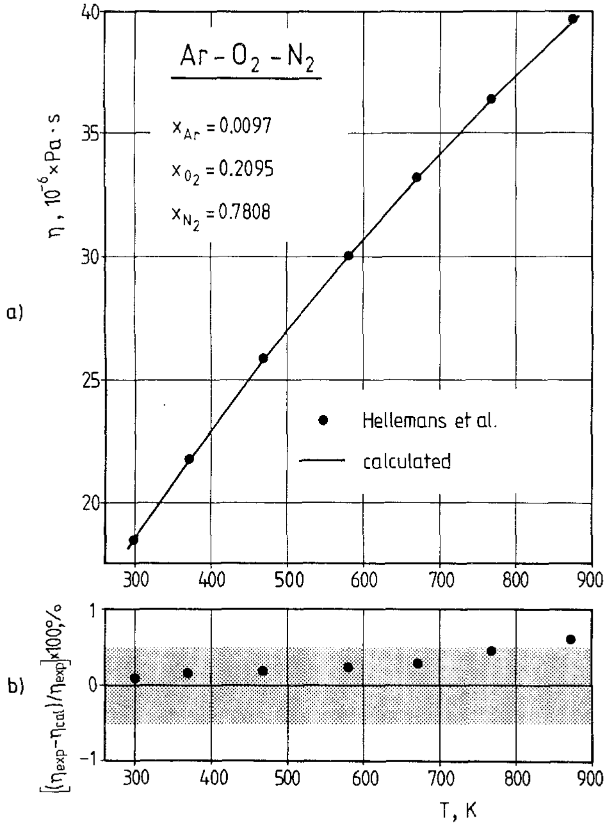

Fig. 11. Predicted viscosity of the air model mixture [9].

agreement with the data for the SSR-MPA model, but not so for the MSK or the Stockmayer model.

Again, a rather sensitive test of the SSR-MPA model is obtained from predicting the third virial coefficient. Figure 9 shows the excellent agreement of the predicted third virial coefficient of ethane with the data, contrary to the MSK prediction, which is considerably too low. In the calculations for the SSR-MPA model only a fraction of the nonadditivity contribution has been taken into account, in agreement with what is known for spherical Lennard–Jones interactions [8].

The extension to mixtures is straightforward. For the center-to-center parameters ε and σ, we use the combination rules Eqs. (3) and (4). The site–site interactions do not require any further combination rules, if Eq. (7) is used. We then get a value for $\varepsilon_{ab}\sigma_{ab}^{12}/\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^{12}$ of 0.25 for N–N, N–O, and O–O, while a value of 0.5 is obtained for Ar–O and Ar–N. As an example of a prediction of gas mixture properties, we look at the model mixture of air, consisting of 0.0097 mol% argon, 0.2095 mol% oxygen, and 0.7808 mol% nitrogen. The predicted interaction second virial coefficients of the binary interactions are compared with data in Fig. 10. They are essentially within experimental error. The same is true for the viscosity of the mixture, which is shown in Fig. 11. Similar results are obtained for other mixtures containing simple linear molecules [9].

4. CONCLUSIONS

With three potential parameters, fitted to data of the second virial coefficient plus the Joule–Thomson coefficient or, alternatively, to the second virial coefficient plus the viscosity, a representation of these data and a prediction of others are possible essentially within the stated uncertainties of the available data for monatomic and simple linear molecules. Extrapolations are possible from pure gases to gaseous mixtures and to higher and lower temperatures. While all these calculations are considerably more accurate than those on an empirical basis [10], this increase in accuracy is not dramatic in the gaseous state and they may seem to be of little consequence in practical work. Considerably stronger effects are found in liquids [11, 12]. Still, when setting up a sensible potential model, one may get more than just a reasonable interpolation and extrapolation scheme for the dilute gas thermophysical properties.

As an example for the independent use of such a potential model, we look at the MSK potential for argon and apply it to the prediction of its high-pressure gaseous thermodynamic properties, for which data are difficult to obtain. Table I shows the pressure calculated from the MSK potential, as determined from dilute gas data, at sufficiently high tem-

Table I. High-Temperature, High-Density Pressures of Argon According to Experiment and WCA Perturbation Theory [13]

T	v	p (bar)	
(K)	(cm$^3\cdot$mol^{-1})	Exp.	Cal.
160.47	28.82	1317	1271
	24.22	3846	3761
180.21	30.10	1282	1247
	23.71	4916	4820
201.29	31.59	1266	1212
	23.20	6203	6036
273	39.99	931	909
	34.99	1411	1397
323	62.22	502	493
	34.99	1825	1820
373	186.65	168	169
	34.99	2223	2226
423	559.97	63	63
	37.33	2177	2182

peratures to be able to use the WCA perturbation theory [13]. It can be clearly seen that with increasing temperature and decreasing volume, the predictions become almost perfect. In this region, the equation of state of a substance is represented primarily by its hard-sphere part. The hard-sphere diameter is determined from the WCA criterion in the standard way [13]. Quite analogous results are obtained for the other noble gases although the potential parameters must be slightly modified to model dilute gas and liquid region simultaneously. Clearly the potential fitted to dilute gas properties is useful in the high-temperature, high-density region as well.

Table II. Liquid Argon Thermodynamic Functions from Monte Carlo Simulations and Experiment [3]

	T	bar		kJ$\cdot$mol^{-1}	
(K)	(cm$^3\cdot$mol^{-1})	p_{MC}	p_{exp}	$u^{\mathrm{c}}_{\mathrm{MC}}$	$u^{\mathrm{c}}_{\mathrm{exp}}$
100	27.04	663	661	-5.84	-5.99
	27.86	427	432	-5.71	-5.84
140	30.65	583	591	-4.98	-5.08

The same is true in the normal liquid range, as shown in Table II [3]. Similar calculations have been performed for systems of polyatomic molecules by monte carlo simulations recently with encouraging results [14].

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