International Journal of Thermophysics, Vol. 12, No. 1, 1991

The Initial Density Dependence of Transport Properties: Noble Gases

E. Bich[1] **and E. Vogel**[1]

Received January 16, 1990

The usual procedure that the transport properties at atmospheric pressure are identified with values in the limit of zero density cannot be accepted for all reduced temperatures T^*. It is shown in the framework of the Rainwater–Friend theory for noble gases, as a good example, that for $T^* < 1$ the effect of the initial density dependence has different signs for viscosity and thermal conductivity and amounts to a few percent, when data at atmospheric pressure are compared with zero-density values. An improved representation of the monomer-dimer contribution to the second transport virial coefficients of the Rainwater–Friend theory is presented in the paper. This is based, among others, on the author's own experimental data of the initial density dependence of viscosity of polytomic gases.

KEY WORDS: noble gases; second transport virial coefficients; thermal conductivity; viscosity.

1. INTRODUCTION

Modern correlation and prediction schemes for transport properties are often based on the extended theorem of corresponding states, which is found to be valid for spherically symmetric pair potentials between structureless particles, where the potential has a universal reduced form

$$\frac{U(r/\sigma)}{\varepsilon} = U^*(r^*) \tag{1}$$

For monatomic gases a two-parameter law of corresponding states, characterized by energy and distance scaling parameters ε and σ, has been found

---

[1] Sektion Chemie der Universität Rostock, Buchbinderstr. 9, Rostock 1, DDR-2500, German Democratic Republic.

very useful for the zero-density properties [1, 2]. But it has been shown that for reduced temperatures $T^* < 1.2$ and $T^* > 10$, an extension is necessary even for noble gases, because their pair potentials are not exactly conformal [3, 4], and that in the case of polyatomic gases the inelasticity of intermolecular collisions has to be taken into account [2, 5]. Nevertheless, a two-parameter law of corresponding states is a reasonable and useful basis for the purpose of correlating and extending data beyond the temperature range of direct measurements. Since values at zero density are not accessible to direct measurements, values at relatively low densities are often identified with zero-density data in practice. Here it is assumed that the influence of the initial density dependence of transport properties is small and negligible in comparison with the uncertainties associated with the high-precision experimental methods under discussion. In principle, such a procedure cannot be accepted because the initial density dependence must surely affect the low-density values.

The transport properties of moderately dense gases may be represented at temperature T and density ρ by expressions of the form

$$\mu = \mu_0(T) + \mu_1(T)\rho + \cdots = \mu_0(T)[1 + B_\mu(T)\rho + \cdots] \tag{2}$$

where μ is either the viscosity η or the thermal conductivity λ, μ_0 represents the zero-density transport properties, and μ_1 the initial-density slope of the respective transport property. As a consequence of the collisional process between pairs of monomers, the density series of transport properties starts with its value in the zero-density limit, which is considered in the kinetic theory of dilute gases [2, 6]. But collisional processes between two monomers also contribute to the linear-in-density correction μ_1 through collisional transfer. Furthermore, collisions among three monomers and between a monomer and a dimer also contribute to this density correction.

Rainwater and Friend [7–9] have proposed a microscopically based theoretical model for the classical second transport virial coefficients B_μ and presented numerical results for the Lennard–Jones 12–6 potential. In this paper, we present an improved representation of the monomer–dimer contribution to B_μ and include our own experimental results for B_η of polyatomic molecules as well as new experimental values from the literature for B_λ of monatomic gases. Using this result, we also explore the influence of the initial density dependence on the low-density transport coefficients, espectially for noble gases at low redcuced temperatures and at atmospheric pressure.

2. THE MONOMER–DIMER CONTRIBUTION TO THE SECOND TRANSPORT VIRIAL COEFFICIENTS

The second transport virial coefficients are subdivided as follows:

$$B_\mu = B_\mu^{(2)} + B_\mu^{(3)} + B_\mu^{(\mathrm{M-D})} \tag{3}$$

The superscripts refer to the three already mentioned contributions to the initial density dependence of transport properties. Starting with the basic premise that moderately dense gases can be modeled as a mixture of monomers and dimers, Rainwater and Friend [7–9] have published an exact calculation of the collisional transfer contribution of two monomers $B_\mu^{(2)}$ by limiting the integration to the free portion of the relative phase space. According to an approximation proposed by Enskog [10] and applied by Hoffman and Curtiss [11], Rainwater and Friend [9, 12] have also computed the integrals of the three-monomer contribution $B_\mu^{(3)}$.

The treatment of the monomer–dimer contribution has been carried out according to the theory of Stogryn and Hirschfelder [13] via the first approximation for the transport properties of a dilute binary gas mixture [2, 6] consisting of monomers and dimers which are truly (b) and metastably (m) bound. It is assumed that the interaction potential between the monomer and the dimer is known and is of the same form as the monomer–monomer potential and characterized by the potential parameter ratios

$$\delta = \sigma_{\mathrm{M-D}}/\sigma_{\mathrm{M}} \tag{4}$$

$$\theta = \varepsilon_{\mathrm{M-D}}/\varepsilon_{\mathrm{M}} \tag{5}$$

The collision diameter σ and the well depth ε are used for reducing the temperature, the second pressure virial coefficients, and the second transport virial coefficients:

$$T^* = kT/\varepsilon \tag{6}$$

$$B^* = B/(\tfrac{2}{3}\pi\sigma^3) \tag{7}$$

$$B_\mu^* = B_\mu/\sigma^3 \tag{8}$$

On the condition that the proportion of dimers is small in comparison with that of the monomers in the mixture, the mole fraction of the dimers x_{D} is related to the equilibrium constant for the formation of dimers and their contribution to the second pressure virial coefficient as

$$x_{\mathrm{D}} \approx K\rho = -(B_{\mathrm{b}}^{\mathrm{Z}} + B_{\mathrm{m}}^{\mathrm{Z}})\rho \tag{9}$$

The superscript Z corresponds to the conventional subdivision of B due to Stogryn and Hirschfelder [14].

After expanding in powers of x_{D}, the viscosity of the mixture is given by

$$\eta = \eta_{\mathrm{M}} + \left[2 + \frac{3A^*_{\mathrm{M-D}}}{10 + 3A^*_{\mathrm{M-D}}}\left(\frac{9\eta_{\mathrm{M-D}}}{2\eta_{\mathrm{M}}} - \frac{20\eta_{\mathrm{M}}}{3A^*_{\mathrm{M-D}}\eta_{\mathrm{M-D}}} - 6\right)\right]\eta_{\mathrm{M}} x_{\mathrm{D}} + \cdots \tag{10}$$

η_{M} is the viscosity coefficient of the monomer and is equal to that in the zero-density limit η_0, whereas the interaction viscosity $\eta_{\mathrm{M-D}}$ and the collision integral ratios $A^*_{\mathrm{M-D}}$ and $B^*_{\mathrm{M-D}}$ (see below) can be expressed by means of δ and θ:

$$\xi = \frac{\eta_{\mathrm{M}}}{\eta_{\mathrm{M-D}}} = \frac{3^{1/2}\delta^2\Omega^{(2,2)*}(\theta^{-1}T^*)}{2\Omega^{(2,2)*}(T^*)} \tag{11}$$

$$A^*_{\mathrm{M-D}}(\theta^{-1}T^*) = \frac{\Omega^{(2,2)*}(\theta^{-1}T^*)}{\Omega^{(1,1)*}(\theta^{-1}T^*)} \tag{12}$$

$$B^*_{\mathrm{M-D}}(\theta^{-1}T^*) = \frac{5\Omega^{(1,2)*}(\theta^{-1}T^*) - 4\Omega^{(1,3)*}(\theta^{-1}T^*)}{\Omega^{(1,1)*}(\theta^{-1}T^*)} \tag{13}$$

Thus, the monomer–dimer contribution is represented for the viscosity as

$$\begin{aligned} B_\eta^{(\mathrm{M-D})*} &= -2/3\pi(B_{\mathrm{b}}^{\mathrm{Z}*} + B_{\mathrm{m}}^{\mathrm{Z}*})(1 + 0.3A^*_{\mathrm{M-D}})^{-1} \\ &\quad \times [2(1-\xi) + 0.3A^*_{\mathrm{M-D}}(4.5\xi^{-1} - 4)] \end{aligned} \tag{14}$$

In this paper we restrict our consideration of the thermal conductivity to monatomic gases. In the case of polyatomic gases, complications occur because of the sensitivity of this property to the anisotropy of the intermolecular potential and because of the existence of internal degrees of freedom and their interaction with the translational degrees of freedom (inelastic collisions). Suitable expressions have been developed for the thermal conductivity of dilute polyatomic gases by Mason, Monchick, and coworkers [15–17]. They include all of the information about the binary molecular interaction and account for internal contributions, internal energy relaxation, and spin polarization effects. Nevertheless, there are still problems in the accurate representation of the thermal conductivity of dilute gases, i.e., in the limit of zero density, which were discussed in terms of a theoretically based data assessment by Millat et al. [18]. Furthermore, up to now there exists no theory for the second virial coefficient B_λ for the thermal conductivity of polyatomic gases which suitably takes into consideration the effects mentioned above.

For a mixture of monomers and dimers the thermal conductivity can be given by a term according to the Chapman–Enskog theory for monatomic molecules together with another, which accounts for the effect that the molecular association is a chemical reaction, and, furthermore, with a Eucken-type correction term, which takes into consideration that the dimer is a quasi-polyatomic molecule. Two parts of the above terms cancel out, so that after expanding in powers of x_D the following equation is obtained:

$$\begin{aligned}\lambda = \lambda_M + 2\Bigg[& 1 - \frac{\lambda_M}{\lambda_{M-D}} + A^*_{M-D}\left(\frac{3\lambda_{M-D}}{10\lambda_M} - \frac{4}{15}\right) + \left(\frac{B^*_{M-D}}{5} + \frac{1}{12}\right) \\ & \times\left(\frac{\lambda_M}{\lambda_{M-D}} - 1\right) + \frac{3}{16A^*_{M-D}}\frac{\lambda_M}{\lambda_{M-D}}\left(B^*_{M-D} - \frac{25}{12}\right)\Bigg] \\ & \times\left[1 + \frac{4}{15}A^*_{M-D} - \frac{1}{2}\left(\frac{B^*_{M-D}}{5} + \frac{1}{12}\right) + \frac{1}{4}\right]^{-1}\lambda_M x_D \\ & + \rho R D_{M-D}\left[\frac{T^2}{B^Z_b + B^Z_m}\frac{d^2(B^Z_b + B^Z_m)}{dT^2} + \frac{5}{2}\right]x_D + \cdots \end{aligned} \tag{15}$$

Here, λ_M is the thermal conductivity of a monatomic monomer and, of course, equal to that in the zero-density limit λ_0. D_M is the self-diffusion coefficient. The interaction thermal conductivity λ_{M-D} and the binary diffusion coefficient D_{M-D} can again be formulated by means of δ and θ,

$$\xi = \frac{3}{4}\frac{\lambda_M}{\lambda_{M-D}} = \frac{3}{4}\frac{D_M}{D_{M-D}}\frac{A^*_{M-D}}{A^*_M} \tag{16}$$

With Eq. (15) and the following general relation of the Chapman–Enskog theory between thermal conducitivity and diffusion coefficient,

$$\rho R D = 8/25 A^* \lambda \tag{17}$$

the monomer–dimer contribution for the thermal conductivity is given by

$$\begin{aligned} B_\lambda^{(M-D)*} = -\frac{2}{3}\pi(B_b^{Z*} + B_m^{Z*})\Bigg\{2\Bigg[& 1 - \frac{4}{3}\xi + A^*_{M-D}\left(\frac{9}{40}\xi^{-1} - \frac{4}{15}\right) \\ & + \left(\frac{B^*_{M-D}}{5} + \frac{1}{12}\right)\left(\frac{4}{3}\xi - 1\right) + \frac{\xi}{4A^*_{M-D}}\left(B^*_{M-D} - \frac{25}{12}\right)\Bigg] \\ & \times\left[1 + \frac{4}{15}A^*_{M-D} - \frac{1}{2}\left(\frac{B^*_{M-D}}{5} + \frac{1}{12}\right) + \frac{1}{4}\right]^{-1} \\ & + \frac{6}{25}A^*_{M-D}\xi^{-1}\left[\frac{T^{*2}}{(B_b^{Z*} + B_m^{Z*})}\frac{d^2(B_b^{Z*} + B_m^{Z*})}{dT^2} + \frac{5}{2}\right]\Bigg\} \end{aligned} \tag{18}$$

Various methods have been used for estimating the parameters δ and θ. First, Stogryn and Hirschfelder [13] have calculated δ and θ by angular averaging for the Lennard–Jones 12–6 potential. Friend and Rainwater [8] have recommended as a better procedure to optimize δ and θ by fitting the theoretical expressions to experimental data for both second transport virial coefficients because of the uncertainty and complexity of the monomer–dimer collision process.

3. PROBLEMS AND RESULTS OF THE OPTIMIZATION OF δ AND θ

Making use of their theoretical results of $B_{\mu}^{(2)*}$ and $B_{\mu}^{(3)*}$ for the Lennard–Jones 12–6 potential as well as of the formulae of $B_{\mu}^{(\mathrm{M-D})*}$, Friend and Rainwater [8] have determined the parameter ratios for the Lennard–Jones 12–6 potential, of course, to be

$$\delta = 1.02 \qquad \text{and} \qquad \theta = 1.15$$

For this purpose they have used the experimental material summarized in 1969 by Hanley et al. [19] for the viscosity of the noble gases, nitrogen and hydrogen, and for the thermal conductivity of the noble gases. In addition, they have included some more recent data for the thermal conductivity of the noble gases. Their results for the whole reduced second transport virial coefficients B_{μ}^{*} are shown as curves in Figs. 1 and 2. We should like to point out that B_{μ}^{*} is most sensitive to temperature in the reduced temperature range $T^{*} < 2$ and, especially, for $T^{*} < 1$. In this range the largest differences between transport properties in the limit of zero density and data at atmospheric pressure are also to be expected. As the experimental material reviewed by Hanley et al. [19] is situated in the range $T^{*} > 1$, the behavior in the range $T^{*} < 1$ can be described by means of the monomer–dimer contribution of Rainwater and Friend only approximately.

Most problems connected with the optimization of δ and θ have already been discussed by Rainwater and Friend [9]. Nevertheless, we try to stress some special features from an experimentalist's point of view. The choice of common parameter ratios δ and θ by means of experimental data of different species implies that the procedure is based on the theorem of corresponding states. There is a further limitation in using the Lennard–Jones 12–6 potential. It is well-known that the Lennard–Jones 12–6 potential is unsuitable even for the noble gases and that potentials of the HFD type are able to represent simultaneously all macroscopic and microscopic properties of monatomic gases in an excellent manner [20–23].

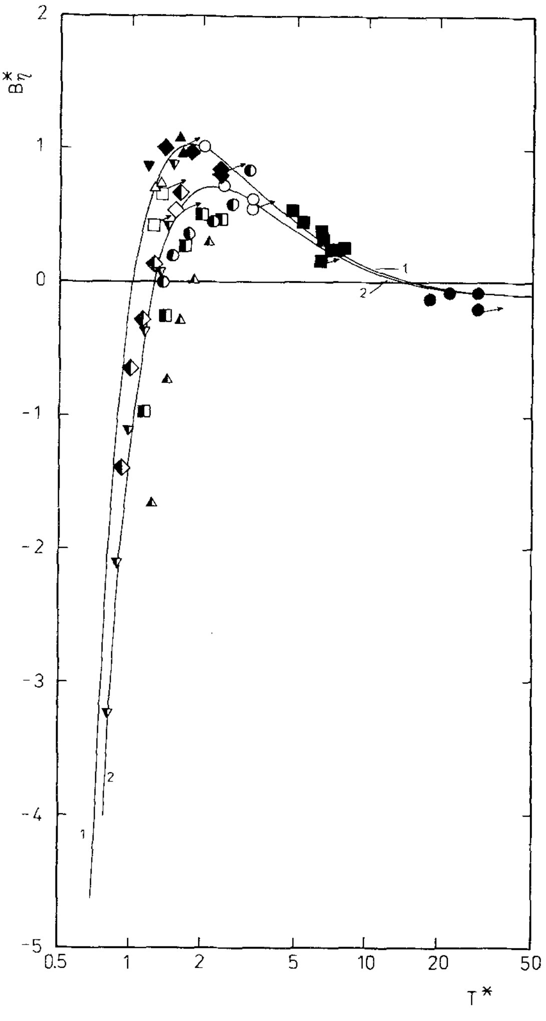

Fig. 1. Reduced second viscosity virial coefficient as a function of the reduced temperature for the Lennard–Jones 12–6 potential. Experimental data: ●, helium [30, 31]; ■, neon [32–34]; ◆, argon [30, 31]; ▲, krypton [35, 36]; ▼, xenon [36]; ○, nitrogen [30, 31]; □, carbon dioxide [37, 38]; ◇, ethane [38]; △, ethene [39]; ◐, sulfur hexafluoride [26]; ◧, neopentane [27]; ⬖, *n*-hexane [28]; ◭, cyclohexane [27]; ▽, benzene [29]. Curves according to the Rainwater–Friend theory: (1) $\delta = 1.02$, $\theta = 1.15$ [8]; (2) $\delta = 1.04$, $\theta = 1.25$ (this work).

The temperature range from which zero-density viscosity coefficients are chosen in order to determine σ and ε of the monomer for the Lennard–Jones 12–6 potential is of essential importance. To give an example we have determined σ and ε from values calculated according to the HFD potential and found for argon:

$$87.28 \leqslant T \leqslant 5000, \qquad \sigma = 0.3227\ \mathrm{nm}, \qquad \varepsilon/k = 176.3\ \mathrm{K}$$

$$87.28 \leqslant T \leqslant 1250, \qquad \sigma = 0.3312\ \mathrm{nm}, \qquad \varepsilon/k = 147.4\ \mathrm{K}$$

$$87.28 \leqslant T \leqslant 270, \qquad \sigma = 0.3418\ \mathrm{nm}, \qquad \varepsilon/k = 125.4\ \mathrm{K}$$

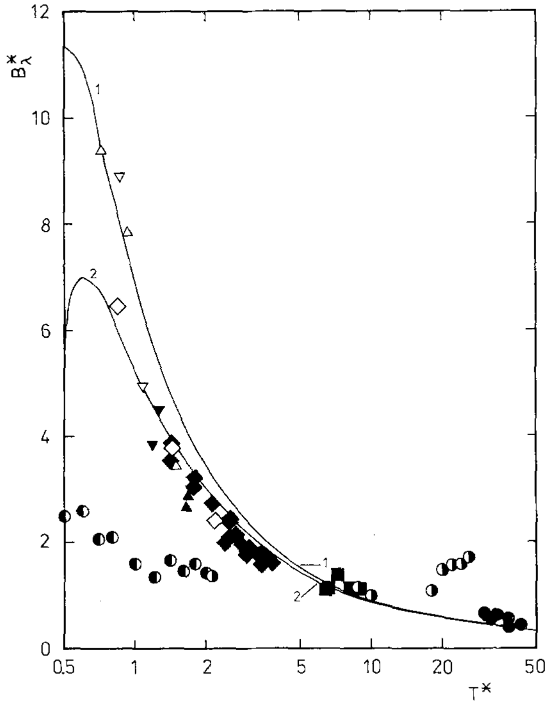

Fig. 2. Reduced second thermal conductivity virial coefficient as a function of the reduced temperature for the Lennard–Jones 12–6 potential. Experimental data: ●, helium [40–42]; ◑, helium [43]; ◐, helium [44]; ■, neon [40, 45]; ◆, argon [40, 46–49]; ◇, argon [50]; ▲, krypton [40, 51]; △, krypton [50]; ▼, xenon [40, 51]; ▽, xenon [50]. Curves according to the Rainwater–Friend theory: (1) $\delta = 1.02$, $\theta = 1.15$ [8]; (2) $\delta = 1.04$, $\theta = 1.25$ (this work).

where T is in K. The temperature range starts with the normal boiling point in each case because of the sensitivity for $T^* < 1$. The representation of the zero-density viscosity coefficients with the Lennard–Jones 12–6 potential is not sufficient, although it has been improved with decreasing temperature range. The largest deviation at 87.28 K has decreased from 8 to 2%. Furthermore, the values show the well-known fact that σ and ε cannot be determined independently and that the choice of the parameter set σ, ε is quite arbitrary. Therefore, we have decided to reduce the experimental second transport virial coefficients for the rare gases and nitrogen by means of the same parameters as Rainwater and Friend have done, i.e., the parameters of Hanley et al. [19], which are shown in Table I. The values of σ and ε for further substances discussed below are also listed in Table I with corresponding references.

In order to get reliable experimental second transport virial coefficients, one needs a sufficient number of low-density points along isotherms to resolve both slope μ_1 and zero-density limit μ_0. The single experimental points should have accuracies possibly better than 0.2% for viscosity and 0.5% for thermal conductivity. The range of reduced temperatures in which investigations can be done is of importance. Measurements are needed for the rare gases in temperature ranges in which the most reliable experimental techniques have not been applied up to now (He, $T < 11$ K; Ne, $T < 42$ K; Ar, $T < 143$ K; Kr, $T < 201$ K; Xe,

Table I. Lennard–Jones 12–6 Potential Parameters

Gas	Collision diameter σ (nm)	Well depth ε/k (K)	Ref. No.
Helium	0.263	10.0	19
Neon	0.272	47.0	19
Argon	0.341	125.0	19
Krypton	0.362	183.0	19
Xenon	0.396	250.0	19
Nitrogen	0.368	90.9	19
Carbon dioxide	0.3753	246.1	24
Ethane	0.4407	227.9	25
Ethene	0.4155	225.6	25
Sulfur hexafluoride	0.5205	215.0	26
Neopentane	0.6160	262.5	26
n-Hexane	0.6136	387.8	28
Cyclohexane	0.6267	289.4	This work
Benzene	0.5379	411.5	This work

$T < 282$ K). The reduced temperature range of $T^* < 1$ under discussion is simpler to attain for polyatomic species, for which, on the one hand, the Lennard–Jones 12–6 potential is even less suitable and, on the other hand, the thermal conductivity is complicated by the effects mentioned above. Our original contributions in this field consist in very accurate viscosity measurements on polyatomic gases and vapors in order to determine B_η for $0.8 < T^* < 3$. Results for the following substances are included in the present paper; sulfur hexafluoride [26], neopentane [27], *n*-hexane [28], cyclohexane [27], and benzene [29]. The Lennard–Jones 12–6 parameters of these substances determined by means of the zero-density viscosity data in Refs. 26–29 are given in Table I, too.

The experimental material used in this paper for the choice of optimized parameter ratios δ and θ has been selected with regard to the following considerations. In the insensitive temperature range the experimental data should have been obtained as results of measurements made with an apparatus of high precision. This means recent measurements with the transient hot-wire technique for thermal conductivity and with oscillating-disk or capillary viscometers for viscosity. In the case of thermal conductivity we have dealt only with monatomic gases. For viscosity, in addition to monatomic gases, results for polyatomic gases investigated in our laboratory as well as such from literature for simpler molecules, such as nitrogen, carbon dioxide, ethane, and ethene, have been included. If several series of measurements are available from one laboratory for approximately the same temperature range, we have chosen the more recent one. The references are reproduced in the legends to Figs. 1 and 2.

Figure 1 shows a comparison of experimental data with the reduced second viscosity virial coefficient B_η^* according to the results of Rainwater and Friend [9] (curve 1). Although this curve agrees quite well with data for the monatomic gases, there is a certain difference with the latest data for helium and argon [30], neon [34], and krypton [35], marked with an arrow. These data are lower than the results of Rainwater and Friend. Similar deviations are also found for recent data on the polyatomic gases nitrogen [30], carbon dioxide [37, 38], and ethane [38], marked with an arrow, too. Our data for the above-mentioned polyatomic gases also remarkably deviate from curve 1. Even if the Lennard–Jones 12–6 potential is inadequate for these polyatomic gases and the parameters σ and ε are arbitrarily determined, there seems to exist a tendency that a better representation of B_η^* or, more exactly, of $B_\eta^{(\mathrm{M-D})*}$ is necessary in order to describe the data for all monatomic and polyatomic gases. From Fig. 2 for the reduced second thermal conductivity virial coefficient B_λ^*, it becomes immediately obvious that all transient hot-wire data (filled symbols), apart from helium and neon, are lower than curve 1 due to Rainwater and

Friend. The results for both second transport virial coefficients show that the values of δ and θ have to be increased in order to improve the agreement. Thus, to arrive at a compromise we have chosen

$$\delta = 1.04 \qquad \text{and} \qquad \theta = 1.25$$

in the course of this work. The experimental B_λ^* data for the heavier noble gases are still lower than curve 2, whereas the B_η^* data for benzene and n-hexane are in close agreement with the corresponding curve 2 apart from some values at the highest temperature as a consequence of the increasing experimental uncertainty.

From Figs. 1 and 2, it emerges clearly that there is a need for experimental data in the range of $T^* < 1$ for all five noble gases. Therefore, we have looked for further data even if they are of a lower quality. For viscosity B_η^* data are missing for all five noble gases in this range. The B_λ^* values for the heavier noble gases by Keyes [50] seem to be in relatively close agreement with the results of Rainwater and Friend. But their uncertainty is very large so that they have failed to be accepted for the data collection of Hanley et al. [19]. In spite of the shortage of accurate data for both transport virial coefficients in the range $T^* < 1$, we are of the opinion that the Rainwater–Friend theory together with the new parameter ratios of δ and θ can be used for predictions of the classical behavior of the initial density dependence of transport properties, i.e., for the heavier noble gases.

In the case of helium and neon the situation is complicated because of quantum-mechanical effects, whose magnitude is very difficult to estimate. For neon it should be admissible to accept the classically calculated values because of the experimental uncertainty of B_μ^*. Some further remarks are necessary for helium. At low temperatures a quantum-mechanical monomer–dimer contribution $B_\mu^{(\mathrm{M-D})*}$ should be very small owing to the small percentage of dimers [20]. According to our knowledge corresponding calculations of $B_\mu^{(2)*}$ and $B_\mu^{(3)*}$ have not been carried out. Besides the three contributions of Eq. (3), there is a further density dependent term in quantum-mechanical calculations which results from the symmetrization of the wave function and the inclusion of higher terms in the quantum-mechanical Boltzmann intergrodifferential equation [52, 53]. For Bose–Einstein statistics this term is small and negative for both η and λ. As the sums of the classical values of $B_\lambda^{(2)*}$ and $B_\lambda^{(3)*}$ are also negative, whereas the experimental B_λ^* data of Acton and Kellner [44] between 5 and 20 K as well as B_λ^* of Roder [43] at 21 K are positive, it emerges clearly that $B_\mu^{(2)*}$ and $B_\mu^{(3)*}$ have to be calculated quantum-mechanically. In principle, all calculations of B_μ^* should be based on the individual HFD potential of helium including quantum effects. Because these calculations are not available, B_λ^* can be chosen in accordance with the data from Ref. 44, whereas B_η^* remains an open question.

4. THE INFLUENCE OF THE INITIAL DENSITY DEPENDENCE ON LOW-DENSITY TRANSPORT PROPERTIES

The zero-density transport coefficients belong to the basic information in order to generate the interatomic pair potential or the intermolecular potential energy surface because they depend on the interaction of only two monomers. The values in the limit of zero density can be determined via linear extrapolation of low-density data experimentally obtained. As measurements of transport coefficients at low or moderate gas densities have been carried out only during the last 10 years in such a way that values in the limit of zero density could be obtained at a high quality, earlier measurements at low densities have been accepted to give values in the limit of zero density. In most cases the influence of the initial density dependence has been comparable with the uncertainties of the experimental methods.

In order to demonstrate that the reduced second transport virial coefficients B_μ^* are of increasing importance for decreasing reduced temperature ($T^* < 2$), we have calculated the transport coefficients of neon, argon, krypton, and xenon at atmospheric pressure via Eqs. (2) and (3) with the classical B_μ^* for the Lennard–Jones 12–6 potential including the new parameter ratios δ and θ for $B_\mu^{(\mathrm{M-D})*}$. The relative departures from the zero-density transport coefficients of the corresponding HFD potentials are shown in Fig. 3. As the density at atmospheric pressure also increases with decreasing temperature, the differences amount to several percent and are much larger than the experimental uncertainties. In addition, in the case of thermal conductivity the differences for helium following from the experimental work of Acton and Kellner [44] are shown in Fig. 3.

Figure 3 makes it clear that, especially at low reduced temperatures, comparisons of experimental viscosity coefficients with thermal conductivity data or vice versa can be made only via the kinetic theory of dilute gases when accounting for the initial density dependence; otherwise large systematic differences are to be expected. The initial density dependence is also of importance if reference data are to be generated by means of correlation and prediction schemes based on the theorem of corresponding states. These schemes need data fitting the theoretical background. Therefore, low-density values, for which the influence of the initial density dependence is very large or negligible, cannot simultaneously be used as

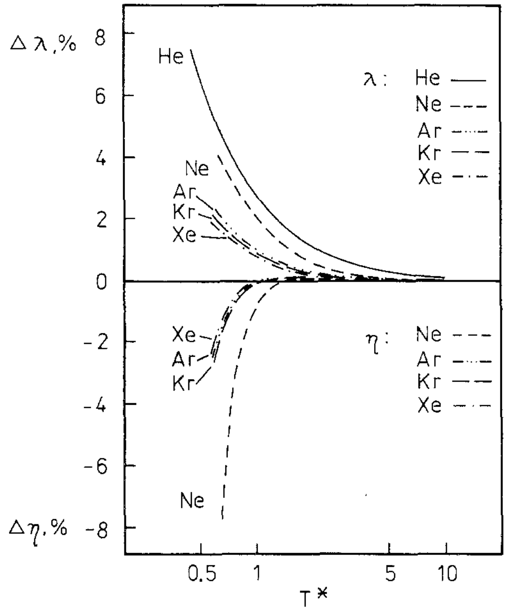

Fig. 3. Departures of the viscosity and thermal conductivity coefficients at atmospheric pressure from their values in the limit of zero density. $\Delta\eta = (\eta_{0.1\,\mathrm{MPa}} - \eta_0)/\eta_{0.1\,\mathrm{MPa}}$; $\Delta\lambda = (\lambda_{0.1\,\mathrm{MPa}} - \lambda_0)/\lambda_{0.1\,\mathrm{MPa}}$. Thermal conductivity for helium according to Ref. 44.

primary data in a scheme based on the kinetic theory of dilute gases. The contribution of the initial density dependence should be correlated separately by the use of the kinetic theory of moderately dense gases due to Rainwater and Friend. Thus, experimental data for transport properties should include the density or the pressure in addition to the temperature and transport coefficient itself.

5. CONCLUSIONS

In order to have reliable primary data for the prediction and correlation schemes for viscosity and thermal conductivity, it is necessary to make a very careful assessment of the experimental material. It is important to find out whether the effect of the initial density dependence of transport properties should be accounted for or not. The only practical method is to use the transport properties in the limit of zero density μ_0 in the framework of one correlation scheme together with the initial-density values μ_1 from another scheme.

In the case of gases for which deviations from the classical behavior occur due to quantum-mechanical effects, the situation is more complicated, because zero-density transport coefficients as well as initial-density transport coefficients are affected. Thus, Eq. (2) should be written as

$$\mu = \mu_{0,\mathrm{cl}}(T) + \Delta\mu_{0,\mathrm{QM}}(T) + \mu_{1,\mathrm{cl}}(T)\rho + \Delta\mu_{1,\mathrm{QM}}(T)\rho + \cdots \tag{19}$$

As a consequence we should like to stress that in prediction schemes on the basis of the theorem of corresponding states, not only $\mu_{0,\mathrm{cl}}$ and $\mu_{1,\mathrm{cl}}$, but also the quantum corrections $\Delta\mu_{0,\mathrm{QM}}$ and $\Delta\mu_{1,\mathrm{QM}}$ should be correlated separately.

Arising from this study, it can be seen that there is a need, especially at low reduced temperatures, to specify the densities for data in reference tables more exactly. Therefore, we intend to present tables for viscosity and thermal conductivity coefficients of the noble gases in the limit of zero density and at atmospheric pressure in the temperature range from the normal boiling point up to 5000 K [54].

In addition, this study shows clearly that very accurate measurements for viscosity and thermal conductivity are necessary over extended temperature ranges in order to fill the blank ranges in the experimental material. This should be supplemented by calculations which include the individual interatomic potentials, and in some cases an account for quantum-mechanical effects must be included.

ACKNOWLEDGMENTS

The authors are grateful for help from discussions with Dr. J. Millat at all stages of the work. The authors are indebted to Professor W. A. Wakeham for private communications of experimental data. The work was carried out under the auspices of the Subcommittee on Transport Properties of IUPAC Commission I.2.

REFERENCES

1. J. Kestin, S. T. Ro, and W. A. Wakeham, *Physica* **58**:165 (1972).
2. G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces: Their Origin and Determination* (Clarendon, Oxford, 1987).
3. B. Najafi, E. A. Mason, and J. Kestin, *Physica* **119A**:387 (1983).
4. E. Bich, J. Millat, and E. Vogel, *Wiss. Z. W.-Pieck-Univ. Rostock* **36**(N8):5 (1987).

5. A. Boushehri, J. Bzowski, J. Kestin, and E. A. Mason, *J. Phys. Chem. Ref. Data* **16**:445 (1987).
6. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).
7. J. C. Rainwater, *J. Chem. Phys.* **81**:495 (1984).
8. D. G. Friend and J. C. Rainwater, *Chem. Phys. Lett.* **107**:590 (1984).
9. J. C. Rainwater and D. G. Friend, *Phys. Rev.* **A36**:4062 (1987).
10. D. Enskog, *Kgl. Svenska Ventensk. Handl.* **63**:No. 4 (1922).
11. D. K. Hoffman and C. F. Curtiss, *Phys. Fluids* **8**:890 (1965).
12. D. G. Friend, *J. Chem. Phys.* **79**:4553 (1983).
13. D. E. Stogryn and J. O. Hirschfelder, *J. Chem. Phys.* **31**:1545 (1959).
14. D. E. Stogryn and J. O. Hirschfelder, *J. Chem. Phys.* **31**:1531 (1959).
15. E. A. Mason and L. Monchick, *J. Chem. Phys.* **36**:1622 (1962).
16. L. Monchick, A. N. G. Pereira, and E. A. Mason, *J. Chem. Phys.* **42**:3241 (1965).
17. L. A. Viehland, E. A. Mason, and S. I. Sandler, *J. Chem. Phys.* **68**:5277 (1978).
18. J. Millat, V. Vesovic, and W. A. Wakeham, *Int. J. Thermophys.* **10**:805 (1989).
19. H. J. M. Hanley, R. D. McCarty, and J. V. Sengers, *J. Chem. Phys.* **50**:857 (1969).
20. R. A. Aziz, F. R. W. McCourt, and C. C. K. Wong, *Mol. Phys.* **61**:1487 (1987).
21. R. A. Aziz and M. J. Slaman, *Chem. Phys.* **130**:187 (1989).
22. R. A. Aziz and M. J. Slaman, *Mol. Phys.* **58**:679 (1986).
23. R. A. Aziz and M. J. Slaman, *Mol. Phys.* **57**:825 (1986).
24. A. A. Clifford, P. Gray, and N. Platts, *J. Chem. Soc. Faraday Trans. I* **73**:381 (1977).
25. F. M. Mourits and F. H. A. Rummens, *Can. J. Chem.* **55**:3007 (1977).
26. T. Strehlow and E. Vogel, *Physica* **161A**:101 (1989).
27. E. Vogel, B. Holdt, and T. Strehlow, *Physica* **148A**:46 (1988).
28. E. Vogel and T. Strehlow, *Z. Phys. Chem. Leipzig* **269**:897 (1988).
29. E. Vogel, E. Bich, and R. Nimz, *Physica* **139A**:188 (1986).
30. J. Kestin, E. Paykoc, and J. V. Sengers, *Physica* **54**:1 (1971).
31. J. A. Gracki, G. P. Flynn, and J. Ross, *J. Chem. Phys.* **51**:3856 (1969).
32. G. P. Flynn, R. V. Hanks, N. A. Lemaire, and J. Ross, *J. Chem. Phys.* **38**:154 (1963).
33. N. J. Trappeniers, A. Botzen, H. R., van den Berg, and J. van Oosten, *Physica* **30**:985 (1964).
34. J. Kestin, Ö. Korfali, J. V. Sengers, and B. Kamgar-Parsi, *Physica* **106A**:415 (1981).
35. H. R. van den Berg and N. J. Trappeniers, *Chem. Phys. Lett.* **58**:12 (1978).
36. J. Kestin and W. Leidenfrost, *Physica* **25**:1033 (1959).
37. J. Kestin, Ö. Korfali, and J. V. Sengers, *Physica* **100A**:335 (1980).
38. H. Iwasaki and M. Takahashi, *J. Chem. Phys.* **74**:1930 (1981).
39. H. Iwasaki and M. Takahashi, *Proc. 4th Int. Conf. High Press.* (1974), p. 523.
40. J. Kestin, R. Paul, A. A. Clifford, and W. A. Wakeham, *Physica* **100A**:349 (1980).
41. M. Mustafa, M. Ross, R. D. Trengove, W. A. Wakeham, and M. Zalaf, *Physica* **141A**:233 (1987).
42. A. I. Johns, A. C. Scott, J. T. R. Watson, D. Ferguson, and A. A. Clifford, *Phil. Trans. Roy. Soc. Lond.* **325**:295 (1988).
43. H. M. Roder, NBS, private communication, cited in Ref. 21.
44. A. Acton and K. Kellner, *Physica* **90B**:192 (1977).
45. J. Millat, M. Ross, W. A. Wakeham, and M. Zalaf, *Physica* **148A**:124 (1988).
46. U. V. Mardolcar, C. A. Nieto de Castro, and W. A. Wakeham, *Int. J. Thermophys.* **7**:259 (1986).
47. A. I. Johns, S. Rashid, J. T. R. Watson, and A. A. Clifford, *J. Chem. Soc. Faraday Trans. I* **82**:2235 (1986).

48. J. Millat, M. Mustafa, M. Ross, W. A. Wakeham, and M. Zalaf, *Physica* **145A**:461 (1987).
49. J. Millat, M. J. Ross, and W. A. Wakeham, *Physica* **159A**:28 (1989).
50. F. G. Keyes, *Trans. Am. Soc. Mech. Eng.* **77**:1395 (1955).
51. M. J. Assael, M. Dix, A. Lucas, and W. A. Wakeham, *J. Chem. Soc. Faraday Trans. I* **77**:439 (1981).
52. J. de Boer, *Physica* **10**:348 (1943).
53. Ref. 6, p. 674.
54. E. Bich, J. Millat, and E. Vogel, (in press).