New Correlation Functions for Viscosity Calculation of Gases Over Wide Temperature and Pressure Ranges

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The viscosity of 14 supercritical gases over a wide temperature–pressure range is calculated with a new correlation scheme. Highly accurate realistic interatomic potentials of the noble gases are used in the Chapman–Enskog calculation of the zero-density viscosity and in the Rainwater–Friend theory to determine the initial density dependence of the viscosity. At densities beyond the range of the theory, a variant of the residual viscosity is developed. It is shown that the temperature dependence of the residual viscosity function increases with the number of atoms in the molecule. By including this temperature dependence, the accuracy of the predicted results improves significantly. The accuracy of this method is within the experimental uncertainties.

KEY WORDS: dense fluids; Rainwater–Friend theory; second viscosity virial coefficient; viscosity.

1. INTRODUCTION

Predictive methods for the transport coefficients provide correlations that can save untold hours of labor in the laboratory, in such a way that two hours in the library can save three months in the laboratory [1]. For a particular fluid, a reasonable means of satisfying the requirements of industry for values of the transport properties over a wide range of conditions is provided by accurate correlations, based on kinetic theory calculation of available experimental data. In the recent paper [2], the Rainwater–Friend theory and highly accurate realistic potentials were used to calculate the viscosity of some typical gases at moderate density (up to $2 \, mol \cdot dm^{-3}$). The

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range of validity was extended to very high densities (up to 40 mol·dm^{-3}) with the introduction of a corresponding states residual function.

This paper extends the accurate calculation of the viscosity of 14 gases from the zero-density limit up to a very high density range (up to 40 mol·dm^{-3} and 900 MPa) over a wide temperature range. Here, the viscosity, $\eta(T, \rho)$ is expressed as

$$\eta(T, \rho) = \eta_0(T)[1 + N_A \sigma^3 \rho B_\eta^*(T)] + D_\eta(T, \rho) \tag{1}$$

where η_0 is the viscosity in the zero density limit, B_η^* is the first order density correction, namely the reduced second virial viscosity coefficient, ρ is the molar density, N_A is Avogadro's constant, σ is the collision diameter, and D_η is the residual viscosity function which includes the higher density contributions. It is shown that by including a (weak) temperature dependence of D_η, the agreement of the predictions with experiment is improved significantly compared to the previous work [2].

1.1. Viscosity at Zero Density

In this work, the viscosity at zero density, η_0, is based only on the accurate interatomic potentials via the Chapman–Enskog theory. According to this theory, η_0 can be calculated from [3]

$$\eta_0 = \frac{5}{16} \left(\frac{mkT}{\pi} \right)^{1/2} \frac{f_\eta}{\sigma^2 \Omega^{(2,2)*}(T^*)} \tag{2}$$

Here m is the molecular mass, k the Boltzmann constant and T is the temperature. $\Omega^{(2,2)*}(T^*)$ is the reduced collision integral that acts as a first-moment approximation for the collision processes determining the viscosity, $T^* = kT/\varepsilon$, where ε is the depth of the potential well. The correction factor, f_η takes into account the higher-moment terms (Sonine polynomials) when solving the Boltzmann equation for the viscosity. Determination of η_0 via Eq. (2) is based on the calculations [4] of $\Omega^{(2,2)*}(T^*)$ which depend on the nature of the interaction potential and reduced temperature T^*. In this work, the most accurate potentials for helium (HFD-B3-FCI1) [5], (neon (HFD-B) [6], argon (HFD-D1) [7], argon (HFD-ID) [8], krypton (HFD-B2) [9] and xenon (HFD-B2) [10] are used for the calculation of the $\Omega^{(2,2)*}(T^*)$.

In Fig. 1 the calculated $\Omega^{(2,2)*}(T^*)$ for the noble gases using the above realistic potentials are plotted versus $\ln(T^*)$. As shown, to a fairly good approximation, all the curves coincide at $1 \leqslant T^* \leqslant 10$, which is consistent
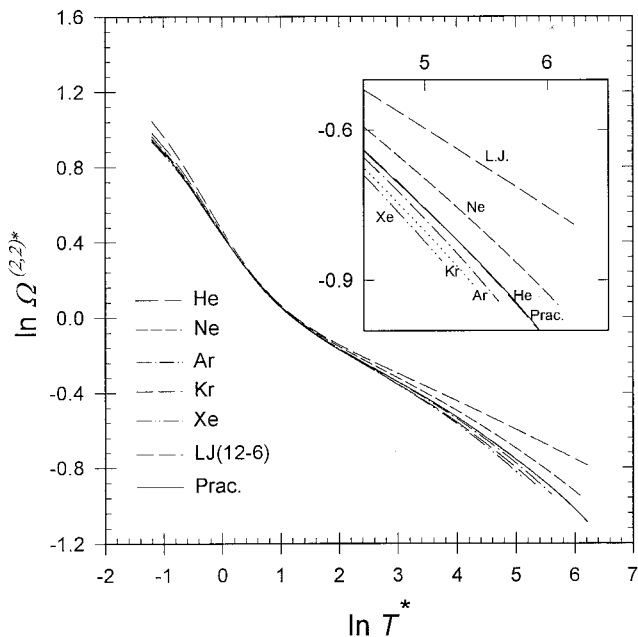
Fig. 1. The two-parameter correlation for $\ln \Omega^{(2, 2)*}(T^*)$ as a function of $\ln T^*$ for different interatomic potentials. The references for the potentials are given in the text.

with the fact that the reduced potentials coincide at intermediate interatomic distances; see Fig. 2.

There are two general procedures for the correlation of $\Omega^{(2, 2)*}(T^*)$ in the literature. One is based on scaling measured values of the viscosity using

$$\frac{\sigma^2 \Omega^{(2, 2)*}(T^*)}{f_\eta} = \left(\frac{mkT}{\pi}\right)^{1/2} \frac{5}{16\eta_0} \tag{3}$$

as a function of temperature for different gases onto a single curve with just two scale parameters ε/k and σ [11]. The most recent formulation of the two-parameter correlation [12] yields formulae for the range $1 \leqslant T^* \leqslant 25$.

The other procedure is based on the revised corresponding-states principle of Kestin et al. [11], which is a set of five parameters which characterize each pair-interaction, together with a fully consistent and asymptotically correct set of corresponding states collision integrals and functionals that appear in the rigorous kinetic theory. In order to take advantage of the correct asymptotic forms at low and high temperatures,
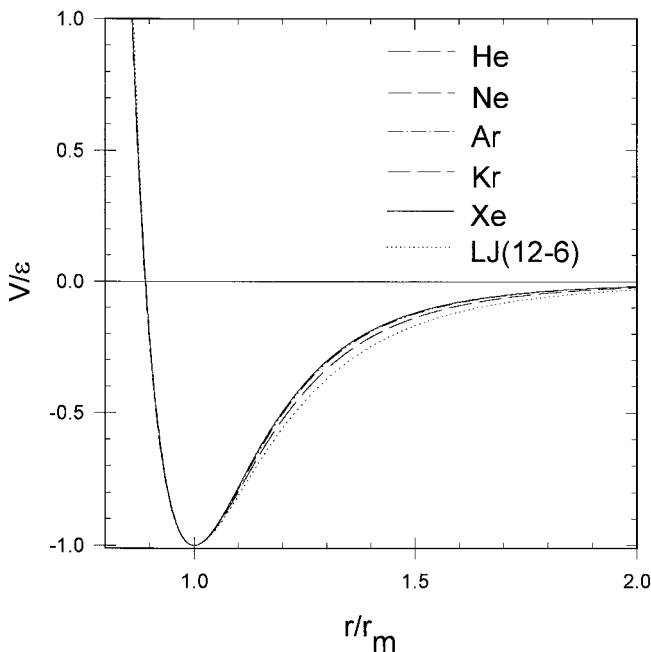
Fig. 2. Reduced plot of noble-gas potentials, showing deviations from congruence at large and small separations. r_m is the position of the potential minimum. The references for the potentials are given in the text.

different temperature regions are given for $\Omega^{(2,2)*}(T^*)$. The limitation is that the correlation is based on experimental data for helium at high T^* and also depends on the five parameters for each gas [13, 14].

At the suggestion of J. Kestin, Boushehri et al. carried out a direct inversion of the temperature dependence of the reduced viscosity to find the effective reduced intermolecular potential [15]. This inversion showed that the part of the interatomic potential that dominates the transport coefficient in the range $1 \leqslant T^* \leqslant 25$ is the relatively "featureless" repulsive wall, and that this rather featureless section of the potential could be fitted with only two parameters. Moreover, this result suggests that any attempt to extend the two-parameter correlation to lower temperature is likely to fail, since low-temperature transport properties are dominated by the attractive wells and tails of the potentials, and small deviations from perfect congruence are apparent at larger distances r/r_m, where r_m is the position of the potential minimum (Fig. 2). Since the correlation functions for the calculation of the viscosity depend on the potential parameters, ε and σ,

a "practical" two-parameter correlation function for the calculation of $\Omega^{(2,2)*}(T^*)$ for the temperature range $0.8 \leqslant T^* \leqslant 500$ is proposed.

1.2. Practical Correlation Function for $\Omega^{(2,2)*}(T^*)$

Due to the great advances in developing accurate realistic interatomic potentials for the noble gases, especially in the last decade, we derived a new correlation function for $\Omega^{(2,2)*}(T^*)$ with only two potential parameters, ε/k and σ, based on the calculation method of O'Hara and Smith [4]. $\Omega^{(2,2)*}(T^*)$ can be expressed for $0.8 \leqslant T^* \leqslant 500$ as

$$\Omega^{(2,2)}(T^*) = \exp \sum_{i=0}^{6} a_i (\ln T^*)^i \tag{4}$$

where

$$a_0 = 4.369 \times 10^{-1} \pm 7.8 \times 10^{-4}, \qquad a_1 = -4.505 \times 10^{-1} \pm 1.3 \times 10^{-3}$$

$$a_2 = 5.326 \times 10^{-2} \pm 8.1 \times 10^{-4}, \qquad a_3 = 3.519 \times 10^{-2} \pm 9.2 \times 10^{-4}$$

$$a_4 = -1.751 \times 10^{-2} \pm 4.0 \times 10^{-4}, \qquad a_5 = 2.773 \times 10^{-3} \pm 7.0 \times 10^{-5}$$

$$a_6 = -1.529 \times 10^{-4} \pm 4.3 \times 10^{-6}$$

The coefficients a_i have been obtained by a least-squares method. Since the available experimental viscosities of different noble gases are located at different reduced temperature ranges, the calculated values for $\Omega^{(2,2)*}(T^*)$ from light, intermediate (argon), and heavy noble gases are used mostly for the high, intermediate, and low temperature ranges, respectively in the least-square procedure. In Table I, the number of data points and the temperature range of each fluid which are used in deriving Eq. (4) and also the average and maximum differences between the calculated and correlated values are shown.

Table I. Temperature Range, Number of Data Points, and Deviations for the Practical Correlation Function, $\Omega^{(2,2)*}$, Eq. (4)

Gas	$T_{min}^* - T_{max}^*$	No. of points	Δ (%), avg. (max.)
He	20–500	250	0.30(1.0)
Ne	10–20	20	1.80(2.0)
Ar	1–10	30	0.45(0.84)
Kr	0.5–3	20	0.50(0.84)
Xe	0.5–3	10	0.32(0.90)

The values of the correction factor f_η have been determined by using the Aziz potentials [5, 7]. This correction does not depend on the used potential to a large extent, and f_η represents a contribution of no more than 1% in the zero-density values in most cases. f_η can be expressed for $0.8 \leqslant T^* \leqslant 500$ as

$$f_\eta(T^*) = \sum_{i=0}^{4} d_i(\ln T^*)^i \tag{5}$$

where the correlation coefficients are obtained via the least square method as

$$d_0 = 1.001 \pm 3.9 \times 10^{-4}, \qquad d_1 = 1.843 \times 10^{-3} \pm 3.6 \times 10^{-4}$$
$$d_2 = 1.793 \times 10^{-3} \pm 3.6 \times 10^{-4}, \qquad d_3 = -6.604 \times 10^{-4} \pm 1.2 \times 10^{-4}$$
$$d_4 = 5.818 \times 10^{-5} \pm 1.1 \times 10^{-5}$$

It must be noted that our correlation formula that covers the entire temperature range with a single formula is not in conflict with the previous correlation [13, 14] which gives different formulae for different temperature ranges. In fact, this correlation gives a more practical formula for the accurate calculation of η_0 of gases in those temperature ranges where most viscosity data are located. As we show later, this correlation function can be used to determine the potential parameters of gases.

1.3. Determination of Potential Parameters

It is well known that ε/k and σ cannot be determined independently and that there are different procedures for their determinations [3, 16]. In this work, when an accurate potential function for a gas is known, the ε/k and σ of that potential are used (for noble gases), otherwise they are regarded as adjustable parameters in order to give the best agreement between the calculated zero density viscosity from the Chapman–Enskog theory, Eqs. (2)–(5), and the accurate experimental zero-density viscosity values. These potential parameters are included in Table II for different gases. The calculated zero-density viscosity values using these potential parameters and our correlation function, via Eqs. (2), (4), and (5) are compared with the experimental data in Table II for the different gases.

2. VISCOSITY IN THE MODERATE DENSITY RANGE

The viscosity of gases at moderate densities (up to $2 \, \text{mol} \cdot \text{dm}^{-3}$) is calculated as

$$\eta(T, \rho) = \eta_0(T)[1 + N_A \sigma^3 \rho B_\eta^*(T)] \tag{6}$$

Table II. Average and Maximum Percent Error of the Zero-Density Viscosity Using Eq. (4)

Fluid	Ref.	σ (nm)	ε/k (K)	$T_{\min}$–$T_{\max}$ (K)	$100 \, |\eta^0_{\exp} - \eta^0_{\text{cal}}|/\eta^0_{\exp}$, avg. (max.)	No. of points
He	34	0.2641	10.956	100–5000	0.40(0.86)	30
Ne	34	0.2759	42.250	100–5000	2.9(5.30)	30
Ar	34	0.3350	143.23	100–5000	0.95(1.30)	30
Kr	34	0.3572	201.35	120–5000	0.35(0.75)	30
Xe	34	0.3890	282.80	165–5000	0.33(0.70)	30
O_2	39	0.3516	95.666	260–1400	0.17(0.73)	21
N_2	40	0.3728	85.229	180–1100	0.24(1.00)	18
F_2	41	0.3327	135.74	70–300	0.25(0.46)	18
CO	15	0.3678	93.480	273–3273	0.51(1.20)	21
NO	15	0.3507	118.75	273–3273	0.60(1.10)	21
NO_2	15	0.3703	266.80	333–3273	0.60(1.60)	18
CO_2	15, 47, 42	0.3800	233.03	313–3273	0.66(1.50)	59
CH_4	15, 47	0.3791	141.56	273–3273	0.50(0.92)	49
CF_4	15	0.4718	124.76	273–3273	0.81(1.60)	21
SF_6	15, 47	0.5340	184.93	220–3273	0.50(1.80)	48
CH_3OH	46	0.3410	668.19	363–593	0.85(1.70)	7
C_2H_4	15	0.4071	244.30	293–2273	0.53(1.20)	20
C_2H_6	15, 53	0.4371	241.90	273–2273	0.52(1.40)	20
C_3H_8	49	0.4721	353.35	230–600	0.44(0.86)	30
n-C_4H_{10}	48	0.4949	475.76	230–626	0.23(0.65)	27
C_6H_6	51	0.4898	651.02	333–623	0.22(0.54)	9
iso-C_4H_{10}	44, 48	0.5014	448.40	220–600	0.16(0.32)	17
c-C_6H_{12}	50	0.6056	353.20	353–623	0.30(0.94)	11
neo-C_5H_{12}	50	0.6071	288.71	298–633	0.30(0.94)	10
C_6H_5OH	52	0.5702	756.81	443–623	0.27(0.48)	10

In the Rainwater–Friend theory [2, 17, 18], which deals with realistic potentials, the reduced second viscosity virial coefficient, B_η^* is assumed to be the sum of three contributions

$$B_\eta^* = B_\eta^{(2M)*} + B_\eta^{(3M)*} + B_\eta^{(MD)*} \tag{7}$$

$B_\eta^{(2M)*}$ represents the contribution from the nonlocality of monomer–monomer collisions [19–22], $B_\eta^{(3M)*}$ accounts for the presence of a third particle during a monomer-monomer collision [23–25], and $B_\eta^{(MD)*}$ is the contribution from the monomer-dimer collisions [16, 26, 27]. In this work, the most accurate potentials for the noble gases [5–10] are used for the calculation of the $B_\eta^*(T^*)$. The reduced second viscosity virial coefficient $B_\eta^*(T^*)$ of a gas is a function of reduced potential and reduced temperature. As shown in Ref. 2, to a reasonable approximation, all of these curves coincide. The corresponding states behavior of $B_\eta^*(T^*)$ over the entire

range of T^* or the noble gases can be attributed to the superimposability of their reduced potentials. A good fit to the corresponding state function in powers of $(T^*)^{-1}$ or the range $0.8 \leqslant T^* \leqslant 500$ is the sixth-order polynomial

$$B_\eta^* = \sum_{i=0}^{6} b_i (T^*)^{-i} \tag{8}$$

where

$$b_0 = -0.2201 \pm 0.0057, \qquad b_1 = 2.075 \pm 0.20$$
$$b_2 = 5.512 \pm 1.2, \qquad b_3 = -13.91 \pm 2.6$$
$$b_4 = 10.82 \pm 2.2, \qquad b_5 = -4.263 \pm 1.2$$
$$b_6 = 0.5245 \pm 0.21$$

with the coefficients b_i again obtained via a least squares fit. It must be noted that due to the extended temperature range, these coefficients differ slightly from those of previous work [2]. In Fig. 3, B_η^* from Eq. (8) is
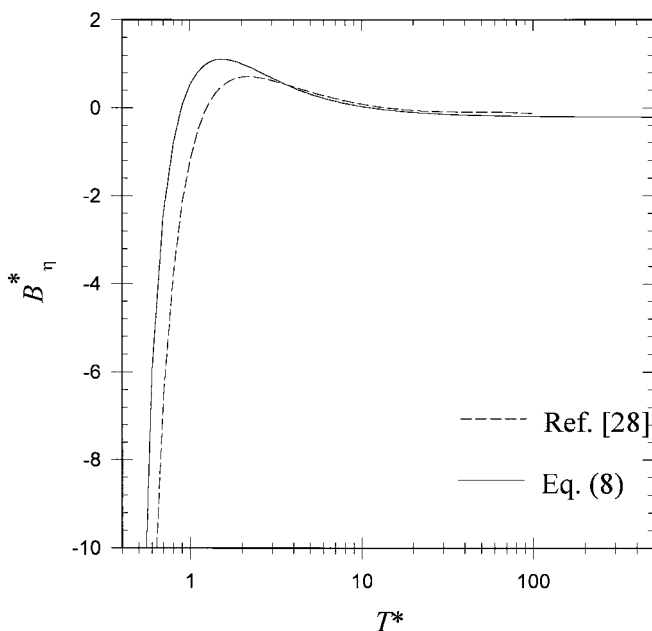

Fig. 3. Reduced second viscosity virial coefficient B_η^* versus reduced temperature using Eq. (8) and Vogel et al. correlation [28].

compared with a new empirical equation for B_η^*, which was presented by Vogel et al. [28].

In summary, according to this correlation, the viscosity of all gases at any specified temperature and density (pressure) can be easily calculated via the Eqs. (6) and (8). As shown before [2], the validity of Eq. (6), is up to $2 \, mol \cdot dm^{-3}$ and it is also applicable for calculation of the viscosity of gases other than the noble gases [2]. For consistency, the scaling parameters ε/k and σ used in Eq. (8) were chosen to coincide with those used for the zero-density viscosity representation. The potential parameters are given in Table II for gases.

3. VISCOSITY IN THE HIGH DENSITY RANGE

The viscosity behavior of supercritical gases at high pressures is unusual to some extent. At high densities, the viscosity-density isotherms of gases generally intersect at a common point, (with density of ρ_{com}) at which the viscosity of the gas is independent of temperature. As Figs. 4 and 5 show, this common point occurs at about $2.4\rho_{cri}$ for Ar and $2\rho_{cri}$ for
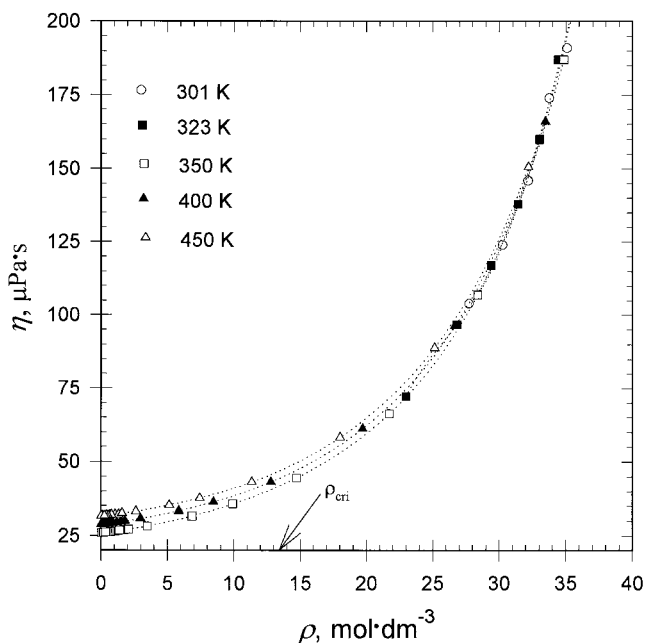
Fig. 4. Intersection of viscosity-density isotherms of argon at a common point. Note that the density of the common point is about $2.4\rho_{cri}$.

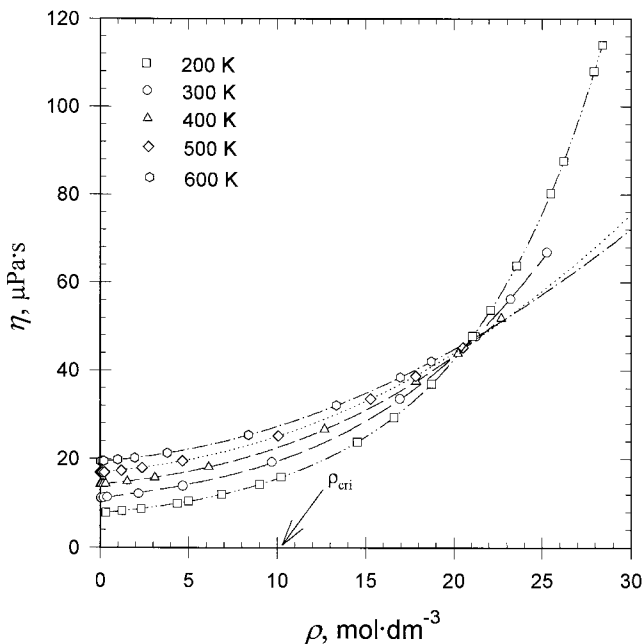**Fig. 5.**   Same as Fig. 4 for methane. Note that the density of the common point is about $2\rho_{cri}$.

CH_4, where ρ_{cri} is the critical density of the gas. It is also possible to show that ρ_{com} is about $2.4\rho_{cri}$ for Kr, $2.2\rho_{cri}$ for O_2, $2\rho_{cri}$ for Xe, CO_2, C_2H_6, and n-C_4H_{10}, and $1.8\rho_{cri}$ for C_3H_8. At densities greater than ρ_{com}, (which is between $1.8\rho_{cri}$ and $2.4\rho_{cri}$) the viscosity of gases decreases with increasing of temperature, similar to what happens in liquids. Of course a phase transition to liquids is impossible for supercritical gases.

In dilute gases, the most important mechanism for transport of momentum between layers of flowing fluid is the kinetic contribution. Molecules are transferred from one part of the fluid to another part and carry momentum along with themselves. As the temperature increases, the average momentum of the molecules increases and the mean free path of the molecules will increase, so the momentum transfer increases, and, as a result, the viscosity increases. As the density of the fluid increases, the mean free path is shorter and the molecules do not have much freedom of translational motion. In this case, the molecules are close together and the intermolecular potential between them becomes larger. To make the layers of fluid move over one another, a force has to be exerted to overcome the attractive forces between the layers. This is the origin of viscosity in liquids.

As the temperature increases at high density, the molecules have more kinetic energy and are able to overcome the "activation energy" of the forces between adjacent layers. Thus, at high density (higher than the common point density), "collisional transfer" rather than the kinetic transfer is the principal mechanism for viscosity, and the viscosity decreases with increasing temperature. At the common point, the increase of viscosity due to kinetic momentum transfer counterbalances the decrease of viscosity due to collisional transfer, and it is possible to consider the viscosity of the gas as being independent of temperature at this density.

At densities beyond the range of the Rainwater–Friend theory, use is made of the empirical observations that the transport properties show a regular dependence on density. The dependence of a transport property (here $\eta(T, \rho)$) can always be written [1] as the sum of three contributions

$$\eta(T, \rho) = \eta_0 + \Delta\eta(T, \rho) + \Delta\eta_c(T, \rho) \tag{9}$$

$\eta_0(T)$ is the zero-density limit of viscosity, $\Delta\eta(T, \rho)$ is the residual viscosity and $\Delta\eta_c(T, \rho)$ is the viscosity critical enhancement. Since in this work we
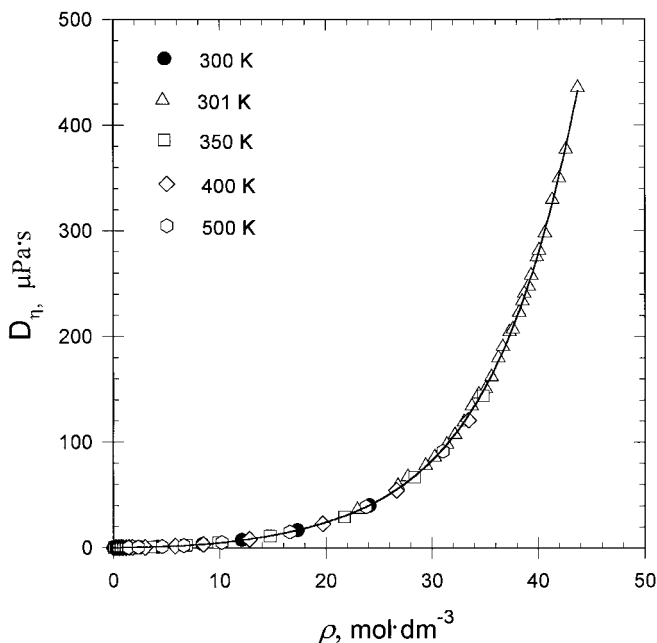

Fig. 6. The assumption of temperature independence of residual viscosity, Eq. (12), is valid for argon (a monatomic gas).

are dealing with gases outside their critical range, our discussion of the behavior of the gas can ignore $\Delta\eta_c(T, \rho)$, and residual viscosity is defined as

$$\Delta\eta(T, \rho) = \eta(T, \rho) - \eta_0(T) \tag{10}$$

The residual transport properties (here $\Delta\eta$) are often approximated as being only a function of density. This has been a useful basis for correlating data within stated density and temperature intervals [1, 2]. However, it should be noted that the residual properties are not rigorously independent of temperature, which can be observed when data are available over a wide range of temperatures at elevated pressures. Specifically, isotherms of the residual viscosity data do not lie on a single curve. In order to "weaken" this temperature dependence, we redefine the residual viscosity as

$$D_\eta(T, \rho) = \eta_{\exp} - \eta_0[1 + N_A \sigma^3 \rho B_\eta^*] \tag{11}$$

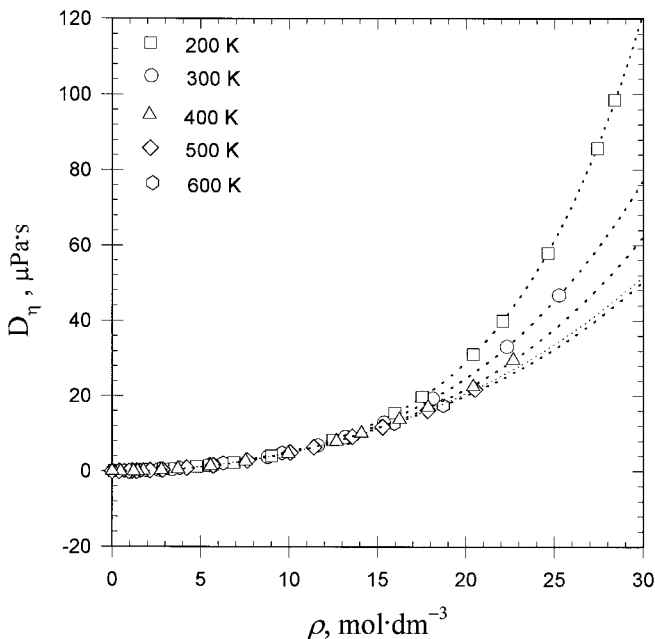Therefore, the viscosity of a gas (outside the critical region) can be written as Eq. (1).

Fig. 7.   The residual viscosity, Eq. (12), is temperature independent for densities up to about 15 mol·dm^{-3} for CH_4.

In previous work [2], the residual viscosity was taken as temperature independent. Now we show that this assumption is nearly valid for monatomic gases, such as argon (see Fig. 6), and the temperature dependence of the residual viscosity is significant for polyatomic gases. (See Figs. 7 and 8). In this work, we show that by including this (weak) temperature dependence of the residual viscosity, it is possible to improve significantly the results.

Once the residual viscosity data have been generated via Eq. (11), $D_\eta(T, \rho)$ can be fitted by a suitable polynomial. There is no theoretical guidance to the functional form of $D_\eta(T, \rho)$, Eq. (11), but we found that it can be fitted with the following polynomial which consists of a temperature contribution plus a density contribution (a Padé approximation),

$$D_\eta(T, \rho) = (1 + aT)^2 \frac{b_1\rho + b_2\rho^2}{1 + c_1\rho + c_2\rho^2} \tag{12}$$

All of the five polynomial coefficients for each gas are adjusted by fitting accurate viscosity data over a wide temperature-pressure range via Eq. (1). These coefficients, which are obtained via a least-square method, are given in Table III for different gases.
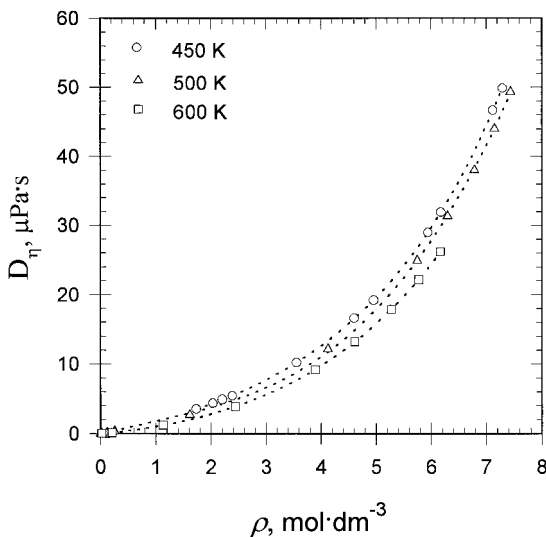

Fig. 8. The residual viscosity, Eq. (12), of iso-C_4H_{10} (a heavy polyatomic gas) is not temperature-independent over the entire density range.

Table III. Coefficients of the Residual Function, Eq. (12)

| Fluid	a (K^{-1})	b_1 $(\mu Pa \cdot s \cdot dm^3 \cdot mol^{-1})$	b_2 $(\mu Pa \cdot s \cdot dm^6 \cdot mol^{-2})$	c_1 $(dm^3 \cdot mol^{-1})$	c_2 $(dm^6 \cdot mol^{-2})$
He	-3.392×10^{-4}	0.2000	2.027×10^{-4}	1.226	-7.690×10^{-2}
Ne	1.170×10^{-2}	-0.0410	7.452×10^{-3}	1.000	-4.10×10^{-2}
Ar	-1.291×10^{-4}	0.2231	0.0181	-0.03442	3.0867×10^{-4}
Kr	-3.521×10^{-4}	0.1827	0.1171	-0.0116	-3.895×10^{-4}
Xe	-6.627×10^{-4}	0.9398	0.2237	-0.0420	4.278×10^{-4}
O_2	4.138×10^{-4}	0.1043	0.0207	-0.0177	-6.799×10^{-5}
N_2	4.817×10^{-4}	0.1349	0.0161	-0.0233	-2.518×10^{-4}
F_2	5.982×10^{-6}	0.0451	0.0993	-0.0159	2.092×10^{-3}
CO_2	-1.751×10^{-5}	-0.7070	0.1908	0.0635	-2.874×10^{-3}
CH_4	-3.034×10^{-4}	-0.1042	0.1201	0.0898	-3.033×10^{-3}
C_2H_6	1.712×10^{-4}	0.6993	0.0675	0.0152	-3.206×10^{-3}
C_3H_8	-4.485×10^{-4}	0.3317	0.3775	-0.0452	-4.802×10^{-4}
$n\text{-}C_4H_{10}$	-3.797×10^{-4}	1.072	0.1977	-0.1524	6.887×10^{-3}
$iso\text{-}C_4H_{10}$	-4.856×10^{-4}	1.863	0.2157	-0.1314	5.033×10^{-3}

Although there are some temperature dependent correlations for residual transport properties in the literature, our 5-coefficient correlation formula, Eq. (12), yields better results than other correlations with many coefficients. (For example, there are in the literature correlation functions for the residual viscosity with 30 coefficients for ethane [29], with 30 coefficients for nitrogen [30] and 32 coefficients for methane [31]).

In summary, according to this correlation, the viscosity of each gas at any specified temperature and density (pressure) can be easily calculated via the equation

$$D_\eta(T, \rho) = \eta_0[1 + N_A \sigma^3 \rho B_\eta^*] + (1 + aT)^2 \frac{b_1\rho + b_2\rho^2}{1 + c_1\rho + c_2\rho^2} \quad (13)$$

As we showed, η_0, B_η^*, and D_η can be obtained from Eqs. (2), (8), and (12) respectively without using any additional measured data. All the necessary parameters are given in Tables II and III for different gases.

In Fig. 9, calculated viscosity-density isotherms of CH_4 via Eq. (13) intersect at a common point. The density of this point is very close to the value obtained from the experimental data (see Fig. 5).
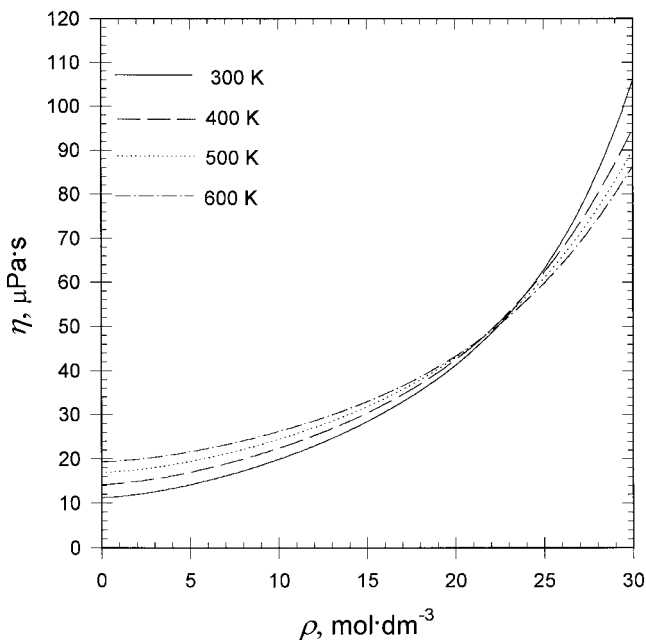
Fig. 9. Intersection of the calculated viscosity-density isotherms of CH_4, via Eq. (13). The parameters of the equation are from Tables II and III.

4. COMPARISON WITH EXPERIMENTAL DATA

The experimental and calculated values of η_0 based on the Chapmann–Enskog theory, Eqs. (2), (4), and (5) are compared in Table II for 25 gases over the temperature range up to temperatures as high as 5000 K. The average absolute percent deviation of the calculated values of η_0 (except for Ne, for which is about 3) is 0.4.
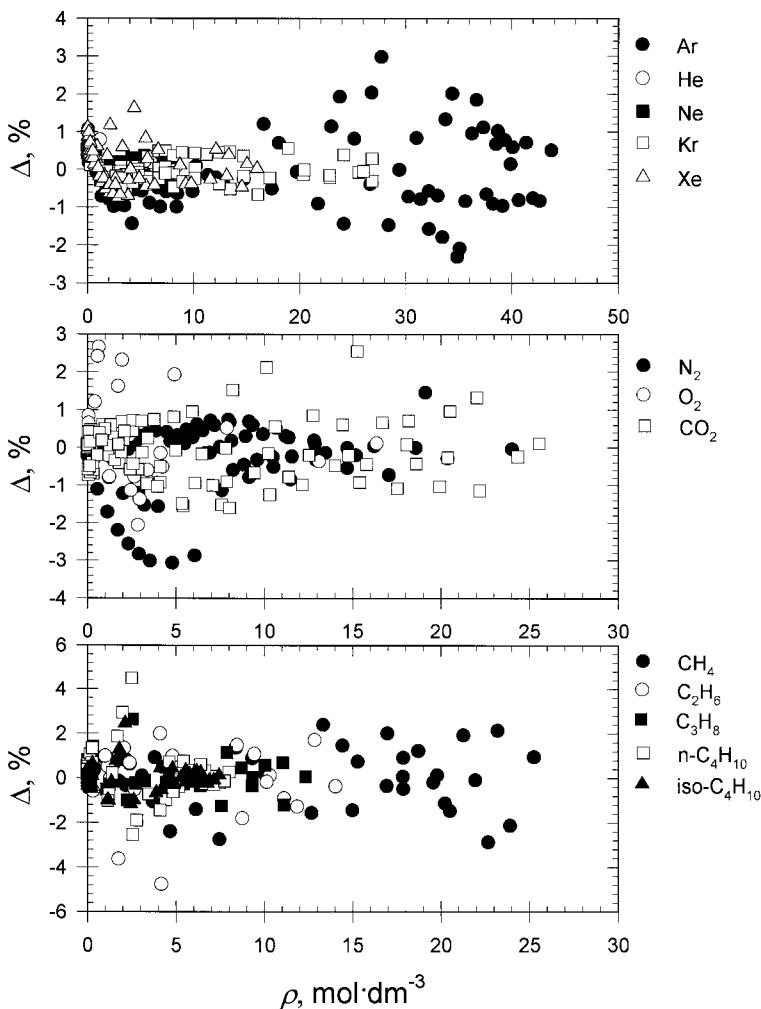
Fig. 10. The percent deviation between the experimental data and calculated values, Δ, % via Eq. (13) for different gases over a wide density range. The references for the experimental data are given in Table IV.

Table IV. Average and Maximum Percent Error of the Viscosity Using Eq. (13)

Fluid	Ref.	$\rho_{\text{Max.}}$ $(\text{mol} \cdot \text{dm}^{-3})$	$T_{\min}-T_{\max}$ (K)	$100\,|\eta_{\exp}^0 - \eta_{\text{cal}}^0|/\eta_{\exp}^0$, avg. (max.)	No. of points
He	35	8.3	223–337	0.15(0.80)	23
Ne	35	8.3	223–337	0.18(0.40)	11
Ar	36	44.0	300–500	0.65(3.00)	111
Kr	37	27.0	298–348	0.25(0.65)	70
Xe	38	16.0	300–500	0.50(1.60)	60
O_2	39	16.5	500–1300	0.18(0.80)	72
N_2	40	24.0	220–1100	0.52(3.00)	120
F_2	41	16.3	200–300	0.90(2.70)	27
CO_2	43, 44	25.5	380–1100	0.60(2.50)	91
CH_4	45	25.3	300–600	0.92(3.70)	66
C_2H_6	45	14.0	400–600	0.85(4.70)	71
C_3H_8	45	12.3	400–600	0.60(2.70)	71
$n\text{-}C_4H_{10}$	45	8.0	450–600	0.60(4.50)	60
Iso-C_4H_{10}	45	7.4	400–600	0.36(2.50)	71

The percent average deviation between the most accurate viscosity data of the monatomic, diatomic and polyatomic gases and calculated values via Eq. (13) is plotted in Fig. 10 over a wide density range. The results are also summarized in Table IV for different supercritical gases, including the maximum density $\rho_{\max}$, the temperature range, average absolute percent deviation of the calculated viscosity based on Eq. (13), along with the number of data points. The potential parameters are also given.

5. DISCUSSION

In this work, a correlation function for the calculation of the viscosity of supercritical gases is obtained which is valid over a wide temperature range and pressures up to 900 MPa (density up to 43 mol · dm^{-3}), with an accuracy that is within experimental uncertainty. Highly accurate realistic potentials are used for the calculation of the zero-density viscosity, η_0, and initial density dependence of the viscosity, ρB_η^*, using the Chapman–Enskog and the Rainwater–Friend theory, respectively. Since the realistic potentials used were generated on a sound theoretical basis and have been optimized using a large number of microscopic properties, including data for the viscosity and thermal conductivity, such a multiproperty fit ensures that the proposed potentials are useful throughout the entire temperature range, and therefore the correlation function, Eq. (4), for $\Omega^{(2,2)^*}(T^*)$ based

on these potentials can be taken as the most precise two-parameter correlation function that works over a very wide temperature range ($0.8 \leqslant T^* \leqslant 500$). This correlation function was used to adjust two potential parameters, ε/k and σ, for the polyatomic gases. Using this new correlation function, the zero-density viscosity, η_0, of different gases can be calculated over a wide temperature range, $80 \leqslant T \leqslant 5000$ K with a mean error estimate of 1 % (for neon 2 %).

The realistic potentials were also used for the calculation of the second virial viscosity coefficient over the wide temperature range, $0.8 \leqslant T^* \leqslant 500$ for the noble gases. Due to the similarity of the reduced potentials of the noble gases, B_η^* follows a corresponding states function over the whole range of reduced temperatures. It was demonstrated that this corresponding states function, B_η^*, which is based on the noble gas potentials, works very well for other gases [2]. This can be attributed to the dominant behavior of the "featureless" repulsive wall of the potentials on the thermophysical properties of dense fluids.

At high densities, beyond the range of the Rainwater–Friend theory, a residual viscosity function has been presented. Although it is usual to take this function to be temperature independent [32], it was shown that this can not be a suitable approximation and that the residual viscosity function is indeed temperature dependent, especially for polyatomic gases.

In the previous work [2], a corresponding states scheme based on a residual viscosity function, D_η, was developed for the prediction of the viscosity of different gases. As shown in Table IV of Ref. 2, the success of the corresponding states deteriorates with increasing number of atoms in the molecule and consequently with increasing number of internal degrees of freedom. Although, the thermal conductivity is affected significantly by the presence of the internal degrees of freedom, viscosity and diffusion are not appreciably affected. Thus the theory for monatomic gases may be applied to polyatomic molecules with considerable success, provided that the molecules are not too non-spherical [33].

This is in agreement with our observations that the assumption of a temperature-independent residual viscosity is valid for monatomic gases such as Ar over the entire density range (see Fig. 6). This assumption is also valid over a limited density range for a polyatomic gas such as CH_4 (see Fig. 7). This assumption is not valid for a heavy polyatomic gas such as iso-C_4H_{10} (see Fig. 8). Therefore, the extent of the success of the corresponding states for the calculation of the viscosity of polyatomic gases depends on the extent of the validity of the assumption of a temperature-independent residual viscosity function, D_η. In this work, it is shown by including a "weak" temperature dependence in this function, D_η, the accuracy of the results improved significantly. A correlation function for
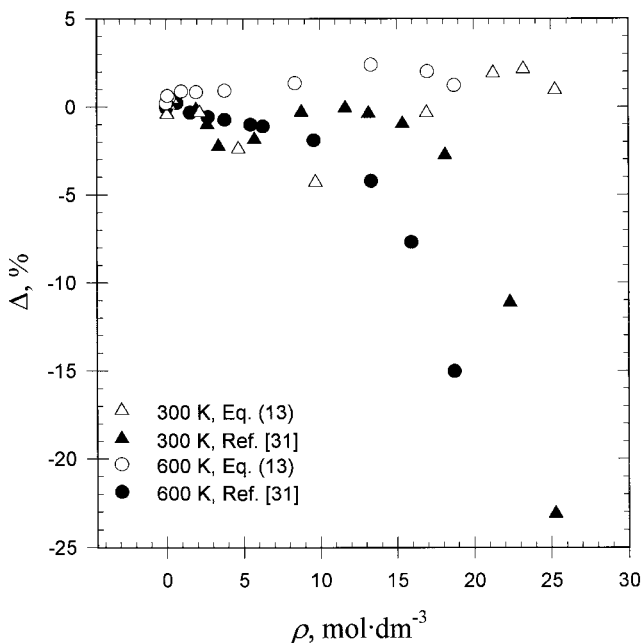
Fig. 11. Comparison of the percent deviation between the experimental data and calculated values, Δ, % of CH_4: (a) this work, via Eq. (13) and (b) via the residual function of Ref. 31.

the calculation of the residual viscosity function is presented for 14 supercritical gases, over a wide temperature range and pressures up to 900 MPa, with mean error estimate 0.5% and maximum error less than 5%. The accuracy of the predicted viscosity values using this residual viscosity function is higher than the predicted values with other residual viscosity functions with many parameters. In Fig. 11, the accuracy of the predicted viscosity values of CH_4 via Eq. (13) is compared with the values obtained with the 32-parameter residual function of Millat [31]. As shown, the accuracy of our residual function is higher especially at high densities.

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