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Reference Viscosity of Argon at Low Density in the Temperature Range from 290 K to 680 K

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Abstract An all-quartz oscillating-disk viscometer of very high precision was used to measure the temperature dependence of the viscosity of argon in the limit of zero density. The measurements were based on a single calibration value at 298.15 K, which was calculated theoretically using an accurate *ab initio* pair potential for argon and the kinetic theory of dilute gases. The uncertainty of the experimental data is conservatively estimated to be 0.15 % at room temperature increasing to 0.2 % at the highest temperature of 680 K. The new data, as well as viscosities determined in 2007 at the National Institute of Standards and Technology in the range from 200 K to 400 K, agree excellently within ±0.1 % with the theoretically calculated viscosity of argon at zero density. On the contrary, the widely accepted viscosity data recommended by Kestin et al. (J Chem Phys 56:4119, 1972) deviate by as much as 0.9 %.

Keywords Argon · Measurement · Oscillating-disk viscometer · Viscosity

1 Introduction and Motivation

It is extensively accepted that the transport properties of argon are well established. In 2004, Lemmon and Jacobsen [1] reported formulations for the viscosity and thermal conductivity of argon with uncertainties of 2 % over its liquid and vapor states, except in the critical region. Most of the experimental dilute-gas viscosity data of 47 considered papers, generally taken to be at a pressure of about one atmosphere, could be described within ±1 % at temperatures up to 1000 K, although Lemmon and Jacobsen concluded from Fig. 2 of their paper a representation within ±0.5 %. Thus,

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the question arises why the dilute-gas viscosity of argon should be measured once again.

One reason for examining the transport properties of dilute argon was discussed at the National Institute of Standards and Technology (NIST) by May et al. [2,3]. They stated that argon-based primary acoustic thermometry and acoustic redeterminations of the universal gas constant require very accurate dilute-gas thermal conductivity values. Since the thermal conductivity can only be measured with greater uncertainty than the viscosity, May et al. preferred to measure the viscosity and to use these data to calculate thermal conductivity values by means of the kinetic theory of dilute gases. But in order to decrease the uncertainty of their viscosity measurements, they based the evaluation of their data in the fully measured temperature range from 200 K to 400 K on viscosity values for helium, derived theoretically by Hurly et al. [4,5] using an *ab initio* helium–helium interatomic potential and the kinetic theory of dilute gases. May et al. estimated the uncertainty of their argon data to be 0.084 % so that reference zero-density viscosities became available in the temperature range 200 K to 400 K, but not in a larger one.

A second reason is to improve the knowledge about the argon–argon interatomic potential which was developed empirically by Aziz [6] and by Boyes [7] using an analytical potential function in a fit to different experimental data. But *ab initio* calculations of the pair potential energy curves for the monatomics are developing rapidly. Thus in our group, highly accurate pair potentials were calculated purely from theory for helium [8] and neon [9], and very recently for argon [10,11]. Subsequently, we calculated the thermophysical properties of helium [12] and neon [13] and found the theoretical values to be more accurate than all available experimental data and suitable to be used for the calibration of high-precision measuring instruments. The extension of this research to a number of thermophysical properties of argon is currently being performed [14]. The comparison with the best experimental data enables a stringent test of the pair potential of argon.

A third reason for the investigation is associated with differences between viscosity data obtained by means of an all-quartz oscillating-disk viscometer in our group at the University of Rostock in 1984 [15] and data measured with another all-quartz oscillating-disk viscometer [16] by the group of Kestin at Brown University, Providence, RI, USA, in the 1970s. Kestin et al. [17] recommended best estimated values for the temperature range 25 °C to 700 °C together with an estimation of the over-all uncertainty, given to be 0.1 % for 25 °C and 100 °C and 0.15 % for 200 °C, 300 °C, and 400 °C. Whereas the uncertainty of the Rostock group data was estimated to be (0.2 to 0.3) % at 600 K, the differences to the Brown University data exceeded the mutual uncertainties. The viscosity data determined at Brown University for all monatomic gases were higher than the Rostock data, with the highest deviations between 400 K and 500 K and increasing with the decrease in their thermal conductivities up to nearly 1 % (see figures and references in Ref. [15]).

In further papers of our group, Bich et al. [18,19] developed an improved version of the extended theorem of corresponding states for the rare gases, which was originally proposed by Kestin, Ro, and Wakeham (KRW theorem) [20–22], and showed that the best empirical Hartree-Fock dispersion (HFD) potentials of the noble gases satisfy extensively the theorem. Further, Bich et al. demonstrated in Fig. 5 of Ref. [19] that for argon at room temperature the viscosity datum of Kestin et al. [17] agrees within ±0.1 % with the values of the HFD potential and hence of the improved corresponding states principle. But at higher temperatures systematic deviations up to +0.8 % occur for the Kestin et al. data, whereas the values of Vogel [15] agree within their experimental uncertainties with the HFD corresponding states values. In addition, the direct comparison between the experimental data of Kestin et al. and the KRW corresponding states values, which were derived on the basis of a fit of the KRW formulation to only the data of Kestin et al. for all five monatomic gases, revealed some interesting features. Figure D16 in Ref. [22] showed for argon that the experimental data at room temperature deviate by −0.5 % from the KRW values, whereas the data at higher temperatures are too high by about +0.5 %. This demonstrates that the KRW theorem follows from only a genuine fit without taking into account that at least the room temperature data have to be described correctly.

All these findings clarify that the experimental data by Kestin et al. are affected in a systematic manner associated with the thermal conductivity of the considered gas. An error of the temperature measurement device, applied in the high-temperature oscillating-disk viscometer [16] used in Kestin's experiments, was assumed in our group to be the reason for the differences. But Professor Kestin denied this possibility in a private discussion in 1985. Nevertheless, the possible error was discussed by Vogel et al. [23] in a report on reference viscosity values for propane, since all experimental data by Kestin et al. measured with this viscometer would have been concerned, if the error is actually true. In 1985 we agreed with Professor Kestin to leave the decision open, until we would be able to calculate the transport properties of argon from first principles. Now, we are approaching this state with our calculations of the thermophysical properties of argon [14]. The value calculated theoretically for the zero-density viscosity of argon at 298.15 K is used to calibrate an all-quartz oscillating-disk viscometer newly built for the present measurements, whereas the theoretical values are compared finally with the experimental data measured at higher temperatures to prove the performance of the viscometer and to establish the temperature function of the viscosity coefficient in the limit of zero density including the NIST reference values.

2 Experimental Equipment

The measurements were performed using an all-quartz oscillating-disk viscometer with small gaps newly constructed for measurements on argon and on some other gases like nitrogen, carbon monoxide, methane, and hydrogen sulfide. Principles concerning the construction of the viscometer were described in a previous paper [24]. Some details of the building design were changed over the years to facilitate the assembly of the instrument. Thus, the construction drawing of the new viscometer is illustrated in Fig. 1. The use of quartz glass is advantageous to enable measurements in a large temperature range without virtual changes in the dimensions of the instrument due to the small thermal expansion coefficient of fused quartz. Further, the internal logarithmic decrement of the quartz-glass suspension strand is very small compared with metal filaments and increases remarkably not until 550 K [25]. In addition, quartz glass has a high chemical stability and does not support the catalytic decomposition of

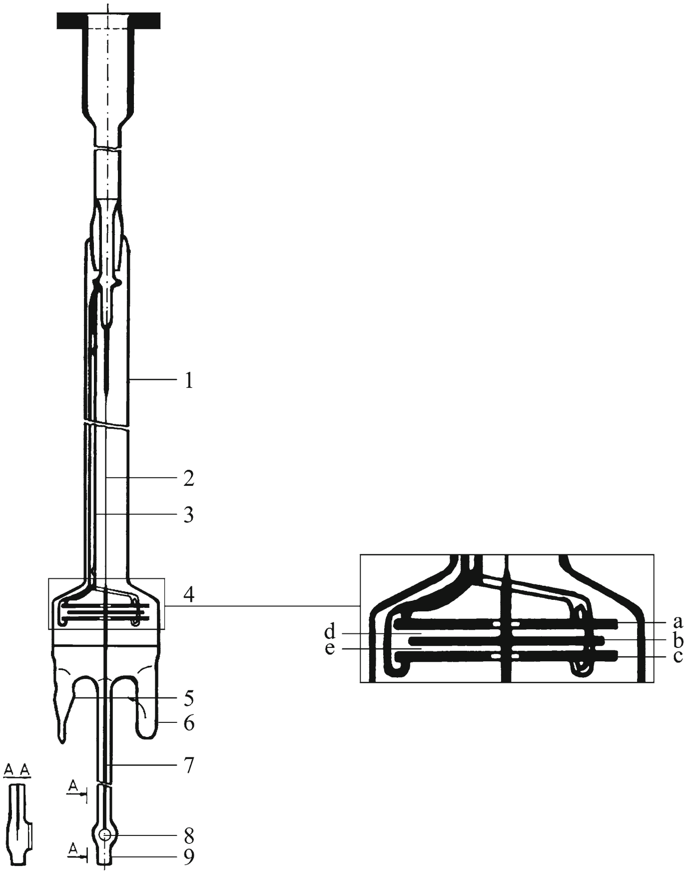

Fig. 1 Construction of the all-quartz oscillating-disk viscometer: *1* body of viscometer; *2* suspension wire; *3* suspension tubing; *4* disk system including, **a** upper fixed disk, **b** oscillating disk, **c** lower fixed disk, **d** upper gap, **e** lower gap; *5* vent pipe; *6* filling pipe; *7* long thin rod; *8* silicon-coated mirror; *9* space for condensable substance

most substances under discussion. It should be noted that the surfaces of the oscillating and fixed disks are optically polished. But due to the fact that all connections between the individual parts of the oscillating-disk viscometer have to be accomplished by fusing, the dimensions of the viscometer cannot be determined with an accuracy needed for absolute measurements. Some characteristics of the oscillating-disk system are summarized in Table 1.

The upper part of the oscillating-disk viscometer is mounted in a rotatable mechanical device. The oscillation of the disk is externally started by turning the device through a small angle of rotation forward and reverse to the basic position. The fixed disks are spaced at the same small gaps by means of three connecting pieces which are attached via a suspension tubing to the mounting part of the suspension strand. A short small rod 1 mm in diameter is fused upside and in the center of the oscillating disk, whereas a long small rod is fused underside carrying at its lower end a small silicon-coated

Table 1 Characteristics of the oscillating-disk system

Suspension strand:	Length		160 mm
	Diameter		35 μm
Upper gap		b_1	1.1 mm
Lower gap		b_2	1.1 mm
Oscillating disk:	Thickness	d	1.55 mm
	Radius	R	17.48 mm
Inertia moment of oscillating system		I	5.03 g · cm^2
Period in vacuo at 25 °C		τ_0	25.540 s

mirror 4 mm in diameter. This mirror is needed for determining the parameters of the damped harmonic oscillation. The suspension strand is drawn in the gravitational field of the earth from a cylindrical rod of fused quartz 1 mm in diameter. For that purpose the rod is mounted vertically with one end gripped in the chuck of a bench drilling machine, whereas the bottom end is loaded by a carefully chosen weight. During slow rotation of the chuck, a flame is applied to the middle of the rod so that the weight pulls a sturdy strand. The strand is not of uniform cross-sectional area, but this is not of importance. The upper and lower ends of the drawn suspension wire are fused between the mounting part at the top and the short small rod upside the disk. It is to be stressed that each of the fusing operations is accomplished by means of specially designed adjusting and auxiliary devices representing the key for the construction of the viscometer. In this way the horizontal position of the oscillating and fixed disks and nearly the same upper and lower gaps are ensured. Further, the centricity of the small rods upside and underside the oscillating disk is assured. Finally, the alignment of the axes of the rotatable mechanical device, of the suspension strand, and of the small rod carrying the mirror is guaranteed so that the axis of oscillation coincides with the rotational axis of the mechanical device.

An opto-electronic system is used for determining the period τ and the decrement Δ of the damped harmonic oscillation by time measurements instead of any length measurements [26]. The arrangement consists of a 1 mW helium–neon laser and two photoreceivers bolted down onto an optical bench at a distance of 2 m from the axis of the viscometer. The laser beam is aimed through the window of the viscometer to the mirror rigidly affixed to the oscillating disk. After the oscillation has been started, the mirror responds to the oscillation and the laser spot travels over the stationary photoreceivers. Each of them consists of two silicon photodiodes as well as a transimpedance amplifier and a comparator. The photodiodes are used as a differential detector so that the triggering is initiated when a zero crossing of the voltage output occurs. In this way it is ensured that the position is practically the same when the beam travels forward and reverse through the fixed, but unknown angular deflection of the oscillation. The trigger signal is fed via an additional logic unit to a personal computer equipped with a counter/timer card, which is characterized by a temporal resolution of 10 μs related to a period of oscillation of about 25 s. The logic unit gathers information about the respective receiver and the direction of the beam motion. After initiating an oscillation run and passing some periods for the decay of perturbations, the time counter is started by hand and the crossing times are registered for 5 to 11 individual oscillations (four crossing times for two receivers and two directions each). The procedure and the working equation to derive the period τ and the decrement Δ of the damped harmonic oscillation from these time measurements were described by Strehlow et al. [26]. The relative uncertainty in Δ is 0.05 %, whereas that in τ is 0.005 %.

The temperature of the oscillating-disk viscometer is regulated by a specially designed air-bath thermostat consisting of three heating zones operated separately using three 100 Ω platinum resistance thermometers and a custom-built three-channel temperature controller. The thermostat generates a vertical temperature profile, increasing slightly from the windows of the viscometer and thermostat to the top of the viscometer body, to create a stable density stratification and to avoid convection inside the viscometer. In doing so, the temperature gradient in the vicinity of the disk system is reduced to a very small value. The temperature is determined with a 10 Ω platinum resistance thermometer and a resistance measuring bridge, each calibrated. The uncertainty of the temperature measurements is 50 mK at 300 K and 150 mK at 700 K.

The viscometer is filled with gases to a pressure less than atmospheric at room temperature. The density of the isochoric series of measurements follows from pressure and temperature measurements during the filling process and from the volume of the viscometer body. The uncertainty of the density determination is 1 % due to the procedure to close the viscometer by fusing its filling pipe.

3 Calibration and Error Analysis

Although the implementation of the relative measurements was described in a previous paper [27], it should be discussed here in conjunction with a completely changed calibration and with an error analysis related to the aim of determining reference values for argon in a large temperature range. In principle, the measuring theory of Newell [28] for an oscillating-disk viscometer with small gaps enables absolute measurements. For that purpose the Newell constant C_N has to be calculated from the dimensions of the viscometer to be known with high accuracy:

$$C_\mathrm{N} = 1 + \frac{8p}{\pi}\left\{(1+u)\ln(2+u) - \frac{1}{2}u\ln\left[(1+u)^2 - 1\right]\right\} + 2p^2\left[1 + 3u - N(u)\right] \tag{1}$$

with

$$p = \frac{b}{R}, \quad u = \frac{d}{2b}, \quad b = \frac{2b_1 b_2}{b_1 + b_2}.$$

Here $N(u)$ is a constant value for a given viscometer [29]. The underlying working equation of the Newell procedure is given as

$$C_\mathrm{N} = \left[\frac{2I}{\pi\rho b R^4}\left(\frac{\Delta}{\theta} - \Delta_0\right) + a\frac{\Delta}{\theta}\right]\beta^2 + f\frac{3\Delta^2 - 1}{\theta^2}\beta^4 + h\frac{\Delta\left(\Delta^2 - 1\right)}{\theta}\beta^6$$

$$\text{with } \beta = \frac{b}{\delta}, \quad \delta = \left(\frac{\eta\tau_0}{2\pi\rho}\right)^{1/2}, \quad \theta = \frac{\tau}{\tau_0}, \quad k = \frac{b_1}{b_2}, \qquad (2)$$
$$\text{and } a = \frac{2}{3}, \quad f = \frac{1}{45}, \quad h = \frac{8}{945} \quad \text{for} \quad k = 1.$$

The experimentally known density of the fluid ρ and the measuring quantities Δ and τ (including Δ_0 and τ_0 in vacuo) result in the viscosity η by means of Eq. 2, when the Newell constant is available from calculation. To this end, β is iteratively calculated and the boundary-layer thickness δ, which is related to η and ρ, yields η.

As already mentioned, the dimensions of our viscometer are not known with an accuracy needed for absolute measurements on the basis of a calculation of C_N according to Eq. 1. In this conjunction it is to be noted that ρ is comparably small for our measurements on argon, so that the contributions of the terms with f and h in Eq. 2 are completely negligible and even the term with a amounts to less than 0.1 % of the main contribution [27]. Consequently, the characteristics of the all-quartz oscillating-disk viscometer, approximately known and given above, and the complete Eq. 2 are applied to determine C_N, using only one reference viscosity value at room temperature and low densities, and to calibrate the apparatus in this way. For that purpose Vogel et al. [27] based their calibration on reference values by Kestin et al. [17,30] for the five noble gases and nitrogen and averaged the C_N values obtained. In our discussion of the theoretically calculated viscosity coefficients for helium [12] and very recently for argon [14], we have shown that the recommended reference values by Kestin et al. [17] were not derived from absolute measurements and do not possess the claimed uncertainty of 0.1 % at room temperature, but that they are slightly too high, for both gases by about +0.2 %. Therefore, the zero-density viscosity coefficient $\eta^{(0)}$, resulting from the new *ab initio* argon–argon interatomic potential and using the kinetic theory of dilute gases [14], is adopted as the reference value together with its temperature derivative near room temperature in this article. The following information on the reference values for argon makes clear that the difference in the calibration consists mainly in the zero-density viscosity coefficient.

Paper	$\eta^{(0)}_{298.15}$ (μPa · s)	$(\partial\eta/\partial T)_\rho$ (μPa · s · K^{-1})	$(\partial\eta/\partial\rho)_T$ (nPa · s · m^3 · kg^{-1})
Vogel et al. [27] using Ref. [17]	22.601 ± 0.02	0.0640	11.099
This article using Ref. [14]	22.552 ± 0.02	0.0635	11.099

The values used for the calibration follow from

$$\eta(T, \rho) = \eta^{(0)}_{298.15} + (T - 298.15)(\partial\eta/\partial T)_\rho + \rho(\partial\eta/\partial\rho)_T \qquad (3)$$

Neglecting the contributions of the terms with a, f, and h in comparison with the main contribution, Eq. 2 can be simplified to perform a thorough error analysis:

$$\eta = C_{\text{cal}}\left(\frac{\Delta}{\tau} - \frac{\Delta_0}{\tau_0}\right) \quad \text{with} \quad C_{\text{cal}} = \frac{4Ib}{C_N R^4} \qquad (4)$$

Considering that Δ_0 is four orders of magnitude smaller than Δ at room temperature and three orders at the highest temperature, the relative uncertainty of the viscosity measurements is estimated by

$$\frac{\Delta\eta}{\eta} = \frac{\Delta C_{\text{cal}}}{C_{\text{cal}}} + \frac{\Delta\Delta}{\Delta} + \frac{\Delta\tau}{\tau} \tag{5}$$

The relative uncertainty of C_{cal} amounts to 0.1 % and is determined by that of the reference value used for the calibration, whereas the uncertainties of Δ and τ have already been given as 0.05 % and 0.005 %. Hence, the relative uncertainty of the viscosity measurements is conservatively estimated to be 0.15 % at room temperature and up to 0.2 % at higher temperatures, assuming that the uncertainties could be slightly increasing with temperature. The reproducibility does not exceed ±0.1 % in the complete temperature range.

The total uncertainty in the viscosity consists of the uncertainty in the viscosity measurements according to Eq. 5 as well as of the allocation errors of the temperature and density measurements considering the temperature and density dependencies of the viscosity:

$$\left(\frac{\Delta\eta}{\eta}\right)_{\text{tot}} = \left[\left(\frac{\Delta\eta}{\eta}\right)^2 + \left(\frac{\partial\eta}{\partial T}\right)_\rho^2 \frac{\Delta T^2}{\eta^2} + \left(\frac{\partial\eta}{\partial\rho}\right)_T^2 \frac{\Delta\rho^2}{\eta^2}\right]^{1/2} \tag{6}$$

Using the values of the applied density (see below), of the viscosity and its temperature and density derivatives, and of the uncertainties of the temperature and density measurements given above, the contributions of the allocation errors to $(\Delta\eta/\eta)_{\text{tot}}$ near room temperature are represented by:

$$\begin{aligned}\left(\frac{\Delta\eta}{\eta}\right)_{\text{tot}} &= \left|\left[0.0015^2 + 0.0635^2\frac{0.05^2}{22.5^2} + (11.0\cdot 10^{-3})^2\frac{(0.01\cdot 1.1)^2}{22.5^2}\right]^{1/2}\right| \\ &= \left|(2.25\cdot 10^{-6} + 2.0\cdot 10^{-8} + 2.9\cdot 10^{-11})^{1/2}\right| = 0.00151.\end{aligned} \tag{7}$$

Consequently, the uncertainties of the temperature and of the density measurements are practically without influence on the total uncertainty of the viscosity.

4 Measurements and Results

Whereas the temperature function of the period $\tau_0(T)$ in vacuo was determined in separate measurements, the values for the logarithmic decrement in vacuo were taken from Whitelaw [25].

Argon with a certified purity of 99.999 % was used for the measurements. Three series were carried out at temperatures between 291 K and 682 K at practically the same density of $1.10\,\text{kg}\cdot\text{m}^{-3}$. The series comprised at least 15 temperatures, for which five oscillation runs were carried out in each case. The measured values of

Table 2 Viscosity of argon at low density ($\rho = 1.10\ \text{kg} \cdot \text{m}^{-3}$)

Series 1			Series 2			Series 3		
T (K)	η (μPa $\cdot$ s)	$\eta^{(0)}$ (μPa $\cdot$ s)	T (K)	η (μPa $\cdot$ s)	$\eta^{(0)}$ (μPa $\cdot$ s)	T (K)	η (μPa $\cdot$ s)	$\eta^{(0)}$ (μPa $\cdot$ s)
293.53	22.263	22.252				291.09	22.116	22.106
296.63	22.457	22.447	296.87	22.475	22.464	296.80	22.490	22.480
322.92	24.128	24.117	323.25	24.146	24.135	323.48	24.151	24.140
350.34	25.760	25.749	350.34	25.768	25.757	350.45	25.777	25.766
377.66	27.358	27.347	377.95	27.386	27.374	378.10	27.389	27.377
405.29	28.922	28.911	405.68	28.951	28.940	405.85	28.954	28.943
433.11	30.450	30.439	433.64	30.479	30.468	433.85	30.490	30.479
461.11	31.939	31.928	461.75	31.975	31.964	462.03	31.992	31.981
489.25	33.390	33.379	490.08	33.443	33.432	490.39	33.456	33.445
517.61	34.823	34.812	518.36	34.861	34.850	518.75	34.886	34.875
540.94	35.975	35.964	542.18	36.024	36.013	542.58	36.068	36.057
561.10	36.957	36.947	564.91	37.153	37.142	565.36	37.177	37.167
589.42	38.300	38.290	593.80	38.501	38.491	594.12	38.525	38.514
618.99	39.668	39.658	623.19	39.878	39.868	623.22	39.869	39.859
649.34	41.068	41.058	652.35	41.192	41.182	652.30	41.179	41.169
678.33	42.350	42.341	681.96	42.510	42.501	681.82	42.496	42.487
295.93	22.432	22.422						
297.39	22.521	22.510						

these runs for temperature, logarithmic decrement, and period were averaged. The averaged data for the room temperature measurements (four for the first, one for the second, and two for the third series) were used to derive one value each for the Newell constant C_{N} using Eqs. 2 and 3 and the *ab initio* viscosity values from Bich et al. [14]. These seven values were averaged, and the mean value ($C_{\text{N}} = 1.34858$) was applied to calculate iteratively via Eq. 2 the viscosity for these temperatures as well as for all other temperatures of the three series of measurements. The results are summarized in Table 2.

All experimental $\eta(T, \rho)$ data of this article were recalculated to the limit of zero density to compare them in the complete temperature range with the values derived theoretically for the *ab initio* potential of argon. Whereas the theoretical values correspond to this limit, experimental data are not directly accessible for it. For the moderately low density under discussion, the correction is based on a first-order expansion for the viscosity, in terms of density:

$$\eta(T, \rho) = \eta^{(0)}(T) \left[1 + B_{\eta}(T)\rho\right]. \tag{8}$$

Here B_{η} is the second viscosity virial coefficient. In the end $\eta^{(0)}$ was computed by means of the Rainwater–Friend theory [31,32] which models the second viscosity virial coefficient in reduced form using the Lennard–Jones (12-6) potential for the interactions in the moderately dense gas.

$$\eta^{(0)}(T) = \frac{\eta(T,\rho)}{1 + N_A \sigma^3 B_\eta^*(T^*)\rho},$$
$$\text{with} \quad B_\eta^*(T^*) = \frac{B_\eta(T)}{N_A\sigma^3}, \quad T^* = \frac{k_B T}{\varepsilon}. \tag{9}$$

Here σ and ε/k_B are the Lennard-Jones 12-6 potential parameters, in the case of argon $\sigma = 0.341$ nm and $\varepsilon/k_B = 125.0$ K. N_A and k_B are Avogadro's and Boltzmann's constants, respectively. T^* is the reduced temperature, whereas B_η^* is the reduced second viscosity virial coefficient. Bich and Vogel [33,34] presented tables of B_η^* as a function of T^*, for which they fitted the theoretical expressions to selected experimental second transport virial coefficients including some for molecular gases. In addition, Vogel et al. [23] recommended an improved empirical expression between $0.5 \leq T^* \leq 100$, which can be extrapolated down to $T^* \approx 0.3$ and for which the coefficients b_i are listed in that paper:

$$B_\eta^*(T^*) = \sum_{i=0}^{6} b_i\, T^{*-0.25i} + b_7\, T^{*-2.5} + b_8\, T^{*-5.5}. \tag{10}$$

The zero-density viscosities $\eta^{(0)}$ resulting via Eqs. 9 and 10 for the experimental points of the three series of measurements are also listed in Table 2. The correction is very small, but reduces the measured values systematically by about 0.05 %.

In Fig. 2 the deviations of the zero-density viscosities $\eta^{(0)}$ of the three series of measurements (symbolized by unequally marked circles) from the theoretical values calculated for the *ab initio* argon potential [14] are illustrated. Note that the experimental room temperature data of the three series correspond to the theoretical values, but also to a unique value of the Newell constant used for the evaluation of the measuring quantities. The deviations of the room temperature data make evident that the changes of the viscometer, after performing measurements up to high temperatures and refilling with argon or other gases for different series of measurements, are small. The deviations at temperatures up to 680 K do not exceed ±0.1 %, approving our conservative error analysis and the performance of the viscometer.

These findings encouraged us to investigate what would happen if we would have based our earlier argon measurements on a calibration with the theoretically calculated room temperature value for the zero-density viscosity of argon [14]. The viscosity coefficients obtained after recalibration and converting the temperatures to the ITS-90 temperature scale are given in Table 3 for the measurements by Vogel in 1972 [24] and in 1984 [15] using all-quartz oscillating-disk viscometers, too. The effect of the changed calibration is demonstrated for these measurements in Fig. 2, but also for those by Wilhelm and Vogel in 2000 [35] applying a vibrating-wire viscometer. The deviations of the original experimental data are indicated by filled symbols, they are (0.25 to 0.4) % higher than the theoretical values. The analogous open symbols represent the

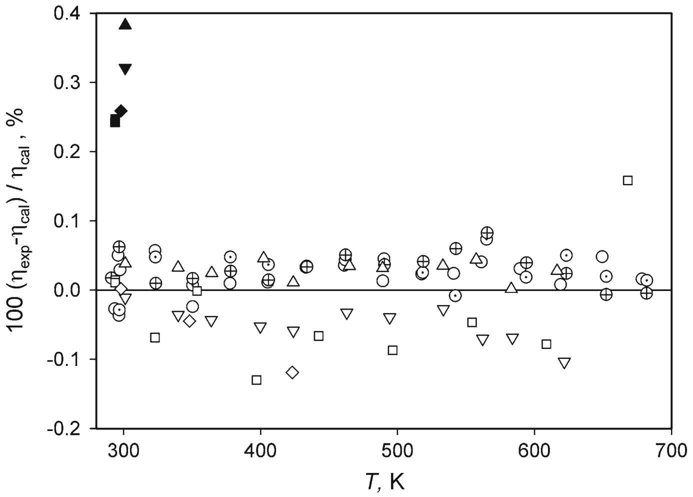

Fig. 2 Deviations of experimental zero-density viscosity coefficients from values η_{cal} calculated with the new interatomic potential for Ar [14] at low and medium temperatures. Experimental data: ○ present paper, 1st series of measurements; ⊙ present paper, 2nd series of measurements; ⊕ present paper, 3rd series of measurements; △ Vogel [24], 1st series of measurements, re-evaluated with the new argon standard; ▲ Vogel [24], 1st series of measurements, uncorrected datum at room temperature; ▽ Vogel [24], 2nd series of measurements, re-evaluated with the new argon standard; ▼ Vogel [24], 2nd series of measurements, uncorrected datum at room temperature; □ Vogel [15], re-evaluated with the new argon standard; ■ Vogel [15], uncorrected datum at room temperature; ◇ Wilhelm and Vogel [35], re-evaluated with the new argon standard; ♦ Wilhelm and Vogel [35], uncorrected datum at room temperature

Table 3 Viscosity of argon at low density corrected with new theoretical argon standard—measurements in 1972 [24] and 1984 [15] with oscillating-disk viscometers at Rostock University

Series 1 ($\rho = 1.2\ \mathrm{kg \cdot m^{-3}}$) [24]			Series 2 ($\rho = 0.8\ \mathrm{kg \cdot m^{-3}}$) [24]			($\rho = 1.183\ \mathrm{kg \cdot m^{-3}}$) [15]		
T (K)	η (μPa · s)	$\eta^{(0)}$ (μPa · s)	T (K)	η (μPa · s)	$\eta^{(0)}$ (μPa · s)	T (K)	η (μPa · s)	$\eta^{(0)}$ (μPa · s)
301.22	22.766	22.755	301.16	22.747	22.740	293.91	22.297	22.286
364.31	26.594	26.582	364.00	26.554	26.546	322.98	24.103	24.091
423.94	29.950	29.938	423.90	29.923	29.915	353.61	25.961	25.949
489.11	33.392	33.380	494.23	33.625	33.617	397.02	28.423	28.411
557.40	36.783	36.772	562.06	36.961	36.954	442.37	30.919	30.907
616.48	39.563	39.552	621.74	39.749	39.742	496.44	33.724	33.713
582.98	37.989	37.977	583.82	37.997	37.990	554.40	36.605	36.594
533.09	35.595	35.584	533.38	35.584	35.576	608.71	39.162	39.151
464.90	32.140	32.128	462.90	32.010	32.002	668.03	41.955	41.945
402.26	28.766	28.754	399.79	28.596	28.588	293.89	22.295	22.284
339.77	25.147	25.135	339.89	25.133	25.125			

deviations of the experimental data in the corresponding complete temperature range after changing the reference values used for the calibration.

Note that the measurements with oscillating-disk viscometers at Rostock University reported in 1972, 1984, and 2010 represent virtually independent studies. In each case the viscometer was completely reestablished using new prefabricated parts of quartz glass. In 2010 an opto-electronic system and time measurements were used for determining the period τ and the logarithmic decrement Δ of the damped harmonic oscillation. On the contrary, in the older studies Δ was derived from length measurements by means of a mirror, telescope, and high-precision scale, whereas τ was obtained by time measurements with a stop watch. The air-bath thermostat and its temperature controller as well as the platinum resistance thermometer and the resistance measuring device were interchanged during this long-lasting investigation. The comparison in Fig. 2 makes evident that the three studies yield the same temperature function for the viscosity in the limit of zero density which is additionally consistent within ±0.1 % with that of the theoretically calculated values in the complete measured temperature range. In principle, the results of all three studies could be included into the primary data sets required for the development of a zero-density viscosity correlation of argon.

5 Comparison and Reference Values

With regard to highly accurate reference values, the comparison is restricted to only a few basic data sets in the temperature range up to 1000 K and to the zero-density viscosity correlation of Lemmon and Jacobsen [1] which is based on the majority of available experimental data, measured until 2004 and included in the comprehensive analysis by these authors. The comparison plotted in Fig. 3 is again based on the temperature function of the theoretically calculated viscosity of argon [14]. The values computed with the equation by Lemmon and Jacobsen are on average by 0.5 % too high above room temperature. But at low temperatures they deviate by more than +1 % exceeding the uncertainty of 0.5 %, assumed for the complete temperature range down to 100 K. Note that in this context the data by Gough et al. [36], determined with a capillary viscometer and also shown in Fig. 3, represent the lowest ones at low temperatures reported until 2004. In 2007 May et al. [3] performed viscosity-ratio measurements with a two-capillary viscometer and based the evaluation in the complete temperature range of their measurements on theoretically calculated viscosity values for helium, as already explained in Sect. 1. The deviations of the data by May et al. make clear that the temperature functions of the viscosity values calculated theoretically for the helium and argon pair potentials are in excellent agreement. These experimental data which are characterized by an uncertainty of 0.084 % [3] exceed the theoretical viscosity values of argon by less than 0.1 %. Further, they are in excellent agreement with the experimental data of this article in the overlapping temperature range from 291 K to 394 K. With regard to the present data, it is to point out once again that they are based on a calibration with only one value at room temperature. In summary, the experimental data of May et al. [3] as well as the present ones are mutually consistent within ±0.1 % with the viscosity values calculated for the pair potential of

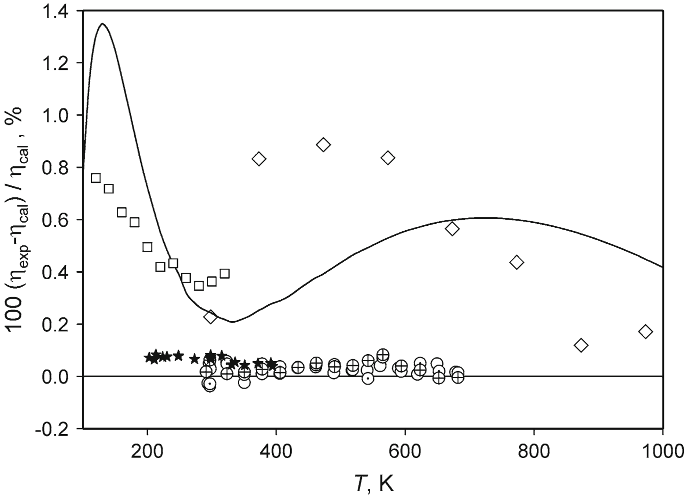

Fig. 3 Deviations of experimental zero-density viscosity coefficients from values η_{cal} calculated with the new interatomic potential for Ar [14] at low and medium temperatures. Experimental data: ○ present paper, 1st series of measurements; ⊙ present paper, 2nd series of measurements; ⊕ present paper, 3rd series of measurements; ◇ Kestin et al. [17]; □ Gough et al. [36]; ★ May et al. [3]; ——— Lemmon and Jacobsen [1]

argon so that they should be assessed as reference values. Such state-of-the-art data are needed in order to develop appropriate viscosity surface correlations. In principle, suitable data sets should be obtained from measurements with a high-precision instrument for which a full working equation is available and all necessary corrections and calibrations can be applied.

Figure 3 shows, as expected due to the now accepted theoretical calibration value at room temperature, that the experimental datum at 298.15 K by Kestin et al. [17] is 0.23 % too high. But the deviations increase to >+0.8 % between 373 K and 573 K combined with again decreasing positive differences at the highest temperatures. These deviations are distinctly larger than the uncertainty of 0.15 % claimed by Kestin et al. Similar results have already been found for helium [12] and neon [13] with a tendency that the deviations decrease with increasing thermal conductivity of the gas. These findings confirm the assumption that the deviations were caused by the construction of the thermostat and the temperature measurement device of the high-temperature oscillating-disk viscometer of Kestin and co-workers [16]. On p. 950 in Ref. [23], we demonstrated in a speculative estimation that, if thermocouples with conventional asymmetric hot junctions are employed for temperature measurements with their leads arranged along a strong temperature gradient ($20\,\mathrm{K} \cdot \mathrm{m}^{-1}$ to $50\,\mathrm{K} \cdot \mathrm{m}^{-1}$ in Kestin's experiments), the heat loss due to the heat conduction of the wires cannot completely be compensated by the heat conduction of the gas and by radiation (see also [37]). Consequently the temperatures in the measuring gap could have been determined too low by 1 K to 5 K depending above all on the thermal conductivity of the gas. Although the estimation cannot exactly explain the deviations, the assumed temperature measurement error is plausible because the sizes of the deviations for helium, neon, and argon have the opposite order as their thermal conductivity coefficients. The data by Kestin et al. [17] are not appropriate to be included into the primary data sets for the development of a new viscosity correlation of argon. Unfortunately, the viscometer developed by Di Pippo et al. [16] was used for further gases and also for gas mixtures. Thus, the results of all these measurements suffer from the same temperature measurement error.

6 Conclusions

The relative measurements on argon with an all-quartz oscillating-disk viscometer, based on a calibration with only one theoretically calculated zero-density viscosity value for argon at 298.15 K, are characterized by an uncertainty of 0.15 % at room temperature increasing up to 0.2 % at 680 K. The new results were compared with data obtained many years ago in our laboratory with two earlier versions of the viscometer. For the sake of a reasonable comparison the older data were corrected with respect to the calibration at 298.15 K. The results of the three studies yield the same temperature function for the zero-density viscosity, which is consistent within ±0.1 % with that of the theoretically calculated values in the complete measured temperature range.

The data of this article and reference zero-density viscosity values of argon, obtained with a capillary viscometer between 200 K and 400 K by May et al. [3] at NIST, are mutually consistent within ±0.1 % in the overlapping temperature range of 291 K to 394 K. In addition, both data sets agree excellently with the theoretical temperature function of the zero-density viscosity of argon so that they are qualified for reference values. Since the NIST data were based on a calibration with zero-density viscosity values deduced theoretically for helium in the complete temperature range of the measurements, it is concluded that the temperature functions of the viscosity values calculated theoretically for the helium and argon pair potentials are in excellent agreement.

The data of Kestin et al. [17] are not appropriate to be included into the primary data sets for the development of a new viscosity correlation of argon due to deviations >+0.8 % between 373 K and 573 K, which are distinctly larger than the uncertainty of 0.15 % claimed by those authors. With regard to the systematic change of the differences and of the thermal conductivity coefficients for the noble gases, a temperature measurement error seems to be a plausible reason for the deviations.

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