

New International Formulation for the Viscosity of H₂O

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New International Formulation for the Viscosity of H₂O

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The International Association for the Properties of Water and Steam (IAPWS) encouraged an extensive research effort to update the IAPWS Formulation 1985 for the Viscosity of Ordinary Water Substance, leading to the adoption of a Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance. This manuscript describes the development and evaluation of the 2008 formulation, which provides a correlating equation for the viscosity of water for fluid states up to 1173 K and 1000 MPa with uncertainties from less than 1% to 7% depending on the state point. © 2009 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.

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Key words: IAPWS; kinematic viscosity; steam; viscosity; water.

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1. Introduction

The viscosity of water over broad ranges of pressure and temperature is often needed for scientific and industrial applications. Water is often used as a calibration or reference fluid for various instruments to measure the viscosity of other substances.¹ Accurate consensus values for the viscosity of water are desirable for a variety of research and practical efforts including reservoir engineering, electric power generation, and industrial process design to optimally size equipment. Additionally, there are other applications including quality control and for dimensionless parameters in heat transfer. The formulation described in this paper provides an internationally agreed-upon equation to describe the viscosity of water up to 1173 K and 1 GPa with state-dependent uncertainties commensurate with the experimental and theoretical information currently available.

Starting with the first International Conference on the Properties of Steam in London in 1929, there have been ef-

forts to arrive at recommendations for calculating the thermophysical properties of water and steam ("water substance"). Since 1972, research and standardization of the properties of water substance have been coordinated by the International Association for the Properties of Steam (IAPS), which in 1989 became the International Association for the Properties of Water and Steam (IAPWS).² While the original emphasis was on the thermodynamic properties of water and steam, the first set of skeleton tables for the transport properties of water substance, together with some recommended interpolation equations, was issued in 1964 upon the instruction of the sixth International Conference on the Properties of Steam.^{3,4} However, the eighth International Conference on the Properties of Steam, held in Giens, France, in 1974, decided that the 1964 skeleton tables for the transport properties were not sufficiently accurate, a decision that led IAPS to issue a Release on the Dynamic Viscosity of Water Substance in 1975 (Refs. 5–9) and a Release on the Thermal Conductivity of Water Substance in 1977.^{9–12} The present paper is concerned with updated recommendations for the calculation of the viscosity of water and steam.

The 1975 release on the dynamic viscosity contained a table of critically evaluated experimental data and a recommended interpolating equation for the viscosity as a function of temperature and density, originally developed by Aleksandrov *et al.*¹³ for temperatures from 0 to 800 °C and densities from 0 to 1050 kg m⁻³. To obtain the viscosity as a function of pressure, it was recommended that the pressures be converted to densities with the aid of the 1968 International Formulation Committee (IFC) Formulation for Scientific and General Use.^{14,15} However, the 1968 IFC Formulation was seldom used in actual practice. Another problem was that the 1968 IFC Formulation was a composite of separate equations for a number of subregions. Hence, the ninth International Conference held in Munich in 1979 empowered IAPS to develop a new formulation for the thermodynamic properties to replace the 1968 IFC Formulation for General and Scientific Use. This led to the adoption of a Provisional IAPS Formulation in 1982, which was subsequently recast in dimensionless form as the IAPS 1984 Formulation for the Thermodynamic Properties of Ordinary Water Substance¹⁶ based on an equation of state developed by Haar *et al.*¹⁷ The interpolating correlation equation for the viscosity adopted in 1975 was based on the International Practical Temperature Scale of 1948 (IPTS-48), while the new IAPS Formulation was based on IPTS-68. It was verified that the earlier viscosity equation could also be used in conjunction with the new IAPS Formulation for the thermodynamic properties and the Release on the Dynamic Viscosity was amended accordingly.¹⁸ Nevertheless, it became desirable to reconsider the correlating equation for the viscosity for a number of reasons. First, the 1975 equation for viscosity was restricted to the range of validity of the IFC 1968 Formulation, namely, up to 800 °C in temperature and up to 100 MPa in pressure. Since the IAPS Formulation 1984 for the thermodynamic properties was valid over a wider range of temperatures and densities, it became possible to check to what ex-

tent the equation for the viscosity could be extrapolated outside the range for which it was originally developed. Second, using improved methods for statistical analysis, Watson *et al.* noticed that the number of terms in the viscosity equation could be reduced significantly while at the same time obtaining improved agreement with the experimental data.¹⁹

Finally, it had become possible to estimate the asymptotic divergent behavior of the viscosity near the critical point,^{19,20} a phenomenon that had not been incorporated in the earlier viscosity equation. Accordingly, IAPS subsequently issued an IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance incorporating the features mentioned above.²¹

While the IAPS Formulation 1984, in contrast to the 1968 IFC Formulation, provided a single fundamental equation in the form of a Helmholtz function as a function of density and temperature for the thermodynamic properties of water substance, it had some less satisfactory features requiring further research.²² Moreover, the International Practical Temperature Scale of 1968 was replaced by the International Temperature Scale of 1990 (ITS-90),²³ making it desirable to have a thermodynamic property formulation consistent with the new temperature standard. This led IAPWS to issue the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use (IAPWS-95).^{24–26} For the viscosity, one continued to use the IAPS Formulation 1985, issued by IAPS in September 1984, except for some minor revisions to make the viscosity formulation consistent with the IAPWS-95 formulation for the thermodynamic properties and with the international temperature scale of 1990.^{26,27} Hence, this most recent historical formulation (Revised Release on the IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance²⁷) will be the basis for some of the comparisons shown below.

A problem was that the IAPWS formulations for the transport properties^{26,27} do not cover the higher temperatures and pressures included in the IAPWS-95 formulation for the thermodynamic properties. Hence, IAPWS encouraged an extensive research effort to develop updated releases for the transport properties, leading to the adoption of a Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance.^{26,28} The goal of the present paper is to provide the scientific and technical documentation for the IAPWS Formulation 2008 on the viscosity. Work on a new release on the thermal conductivity of water substance is in progress.

We shall proceed as follows. The correlating equation recommended by the IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance was originally developed by Watson *et al.* based on experimental data for the viscosity of H₂O available prior to 1980.¹⁹ An update on the available experimental data for water and steam is presented in Sec. 2. An analysis of the temperature dependence of the viscosity of water vapor and of steam in the limit of zero density is presented in Sec. 3.1. Section 3.2 deals with the temperature and density dependence of the viscosity at elevated pressures. The theoretical and experimental information for the singular behavior of the viscosity in the region near the critical point is reviewed in Sec. 3.3. A simplified version for use

outside the critical region is presented in Sec. 3.4. Information for computer-program verification is provided in Sec. 3.5, and recommendations for industrial applications are given in Sec. 3.6. The special case of liquid water at atmospheric pressure is treated in Sec. 3.7. Section 4 presents comparisons of the new viscosity formulation with experimental data, as well as a comparative evaluation of the previous IAPWS formulation for viscosity,²⁷ and discusses the range of validity and uncertainties of the new correlating equation.

2. Experimental Data

As part of a joint project between IAPWS and the International Association for Transport Properties [formerly the Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry (IUPAC) Commission I.2 on Thermodynamics], experimental data on the viscosity and thermal conductivity of water and steam were collected, converted to the ITS-90 temperature scale and a common set of units, and evaluated.²⁹ Unless the temperature scale was explicitly stated in a publication or additional information was available, the year of publication was used to determine the appropriate temperature scale for the conversion. This work resulted in a database for the viscosity of water that contained 4090 points covering the range of temperatures from 238 to 1346 K with pressures to 346 MPa, described in detail in Ref. 29. This database contains data collected through bibliographic efforts under the auspices of IAPWS and documented in unpublished reports to 1988, as well as later data to the year 2000. In addition, it includes some earlier data that were not considered in previous compilations. In the work reported here, we used the database described in Ref. 29 as a starting point.

To the database, we added several data sets^{30–36} published after the compilation of Ref. 29. In addition, we included selected experimental data for viscosity^{37–43} at higher pressures than were considered in the previous formulation for viscosity, since the IAPWS-95 equation of state is valid to pressures of 1 GPa. There are two additional very recent publications^{44,45} that present data at high pressures, which are not included in our compilation. Table 1 gives a compilation of all experimental data sources^{30–113} used in the development of the viscosity formulation, including an estimate of the uncertainty, the temperature and pressure ranges of the data, the experimental method, and the number of individual data points. It is difficult to assess the uncertainty of some of these data; often the value claimed by the original authors is quite optimistic. The viscosity data of Rivkin *et al.*⁴⁶ for water in the critical region have been re-evaluated. The computer database contains the original⁴⁶ as well as re-evaluated data, although only the re-evaluated data have been used in the development of the correlation. This will be discussed further in Sec. 3.3. The resulting data set used for regression comprises 5006 individual points covering temperatures from 238 to 1346 K and pressures up to 1 GPa, providing coverage over a wider range of temperatures and

pressures than the formulation developed in 1980,¹⁹ as shown in Fig. 1. All densities in the database were calculated from the experimental pressures and temperatures with IAPWS-95.

3. Development of the Correlation

In order to provide consistency with the conventions adopted by IAPWS in their releases on the transport properties of water, we use the following dimensionless variables for temperature T , mass density ρ , pressure p , and viscosity μ :

$$\bar{T} = \frac{T}{T^*}, \quad \bar{\rho} = \frac{\rho}{\rho^*}, \quad \bar{p} = \frac{p}{p^*}, \quad \bar{\mu} = \frac{\mu}{\mu^*}, \quad (1)$$

where the reference constants are $T^* = 647.096$ K, $\rho^* = 322.0$ kg m⁻³, $p^* = 22.064$ MPa, and $\mu^* = 1 \times 10^{-6}$ Pa s. The reference values for temperature, pressure, and density are in agreement with the presently accepted critical parameters recommended by IAPWS.¹¹⁴ All temperatures are expressed in terms of the ITS-90 temperature scale.

The formulation for the viscosity of water has the same general form as the previous formulations,^{19,21,27} namely,

$$\bar{\mu} = \bar{\mu}_0(\bar{T}) \times \bar{\mu}_1(\bar{T}, \bar{\rho}) \times \bar{\mu}_2(\bar{T}, \bar{\rho}). \quad (2)$$

The first factor $\bar{\mu}_0$ of the product represents the viscosity in the zero-density limit and is a function of temperature only. The second factor $\bar{\mu}_1$ represents the contribution to viscosity due to increasing density, while the third factor $\bar{\mu}_2$ represents an enhancement of the viscosity near the critical point. The determination of each of these contributions will be considered in the following sections.

3.1. Viscosity in the Limit of Zero Density

Because measurements at zero pressure, i.e., the dilute-gas limit, are not feasible, the data considered for the estimation of the viscosity of water vapor and steam in the limit of zero density include all data in the experimental database at all available temperatures up to a maximum density of 50 kg m⁻³. This maximizes the number of data to be examined while staying within the low-density region. Since the publication of the manuscript on the database for the transport properties of water,²⁹ there has been one significant new set of measurements in the dilute-gas region³⁶ that we have included in our analysis. The resulting data set includes experimental viscosity measurements from 14 individual sources (indicated by italics in Table 1),^{36,55,56,58,61,62,64,68,69,76,77,84,87,90} thus increasing significantly the number of data considered for the generation of an equation for the viscosity in the limit of zero density compared to the development of the previous IAPWS formulation for the viscosity.²⁷ The ranges of all the data used for $\mu_0(T)$ are as follows. Temperature, 279.88–1346.24 K; pressure, 0.0008–15.779 MPa; and density, 0.006–50 kg m⁻³.

In order to use the data to derive a new equation for $\mu_0(T)$, it was necessary to group them according to temperature. To

TABLE 1. Summary of experimental data for the viscosity of water

First author ^a	Year	Method ^b	Uncertainty ^c (%)	Temperature range, K	Pressure range, MPa	Number of data
White ⁴⁷	1914	CAP	0.5	264–293	atm ^e	11
Coc ⁴⁸	1944	CAP	0.3	298–313	atm	3
Hardy ⁴⁹	1949	CAP	0.5	278–398	0.3	10
Swindells ⁵⁰	1952	CAP	0.1	293	atm	1
Weber ⁵¹	1955	CAP	0.3	273–313	atm	9
Roscoe ⁵²	1958	OSC	0.1	293	atm	1
Ravikovich ⁵³	1958	CAP	2	299–356	atm	7
Malyarov ⁵⁴	1959	CAP	0.1	293	atm	1
Shifrin ⁵⁵	1959	CAP	3 ^d	422–1140	atm	114
Kestin ⁵⁶	1960	OSD	2 ^d	411–511	atm	19
Whitelaw ⁵⁷	1960	CAP	4 ^d	294–927	0.1–78.5	56
Moszynski ⁵⁸	1961	OSS	2	293–540	0.2–34.7	66
Mayinger ⁵⁹	1962	CAP	2–3 ^d	352–980	5.6–76.5	84
Hallett ⁶⁰	1963	CAP	0.3	254–273	atm	20
Kestin ⁶¹	1963	OSD	0.8	421–548	0.1–5.2	39
Latto ⁶²	1965	CAP	3 ^d	383–1346	atm	555
Tanaka ⁶³	1965	CAP	2–3 ^d	285–1181	0.1–98.2	152
Dudziak ³⁷	1966	OSD	5	433–833	100–346	91
Rivkin ⁶⁴	1966	CAP	1.5	323–573	0.3–5	41
Horne ³⁸	1966	ROB	2	275–293	6.9–206.8	141
Agae ⁶⁵	1967	CAP	1	273–373	0.1–117.8	598
Harlow ³⁹ (also Bett ⁶⁶)	1967	Fcyl	2	275–373	0.1–988.2	125
Korosi ⁶⁷	1968	CAP	0.3	298–423	0.1–0.5	9
Rivkin ⁶⁸	1968	CAP	1	548–723	0.6–35.4	127
Sato ⁶⁹	1968	CAP	1.5 ^d	430–473	0.2–0.9	17
Kerimov ⁷⁰	1969	CAP	1	373–548	0.1–117.8	224
Korson ⁷¹	1969	CUb	0.3	283–343	atm	13
Nagashima ⁷²	1969	CAP	2–3 ^d	323–1179	5.8–100.4	251
Stanley ⁴⁰	1969	ROB	4	275–293	17.3–137.9	93
Dumas ⁷³	1970	OSD	1	289–294	atm	4
Rivkin ⁷⁴	1970	CAP	1	585–668	10–22	68
Rivkin ⁷⁵	1970	CAP	1	497–648	2.5–50	94
Sato ⁷⁶	1970	CAP	1.5 ^d	433–778	0.2–2.5	79
Yasumoto ⁷⁷	1970	CAP	0.5	280–302	0.0008–0.003	15
Eicher ⁷⁸	1971	CAP	0.3	265–313	atm	13
Mashovets ⁷⁹	1971	CAP	2	365–548	0.1–5.9	11
Penkina ⁸⁰	1971	RIV	3	373–523	15.2	7
Rivkin ⁸¹	1972	CAP	1	523–648	40–100	38
Rivkin ⁸²	1972	CAP	1	497–668	2.5–22	119
Rivkin ⁸³	1973	CAP	1	649–773	22.5–50	59
Timrot ⁸⁴	1973	OSD	0.4 ^d	326–772	0.001–0.14	46
Kingham ⁸⁵	1974	CUb	0.05	274–283	atm	20
Kudish ⁸⁶	1974	CUb	0.05	288–308	atm	5
Nagashima ⁸⁷	1974	CAP	1.5	523–874	0.5–20.8	53
Rivkin ⁴⁶	1975	CAP	1	647–663	22.1–30	78
Rivkin ⁸⁸	1975	CAP	1	497–668	2.5–22	119
Isdale ⁴¹	1975	FBd	2	298–323	0.1–1000	22
Kestin ⁸⁹	1977	OSD	0.3	284–312	0.1–31.1	70
Oltermann ⁹⁰	1977	OSD	4	614–656	0.1–23.9	96
DeFries ⁴²	1977	ROB	2	258–283	0.1–600	46
Osipov ⁹¹	1977	CAP	3	238–273	atm	28
Kestin ⁹²	1978	OSD	0.7 ^d	313–423	0.1–30.8	111
Kubota ⁹³	1979	CAP	2	283–348	0.1–68.8	32
Agayev ⁹⁴	1980	CAP	1.5	263–473	0.1–196.2	166
Goncalves ⁹⁵	1980	CAP	0.2	293–333	atm	6
Kestin ⁹⁶	1981	OSD	0.3	299–424	0.1–2.4	78
Baldauf ⁹⁷	1983	CAP	3	283–303	atm	3

TABLE 1. Summary of experimental data for the viscosity of water—Continued

First author ^a	Year	Method ^b	Uncertainty ^c (%)	Temperature range, K	Pressure range, MPa	Number of data
Collings ⁹⁸	1983	CAP	0.2	274–343	atm	12
James ⁹⁹	1984	CAP	1	273–333	atm	8
Naake ¹⁰⁰	1984	OSD	1	291–479	10–100	18
Kestin ¹⁰¹	1985	OSD	0.5	298–492	0.003–30	74
Kozlov ¹⁰²	1985	NMR	n.p.	283–338	atm	6
Tanaka ¹⁰³	1987	FBd	2	283–348	0.1–117.8	47
Berstad ¹⁰⁴	1988	OSC	0.05	293–299	atm	18
Melzer ¹⁰⁵	1989	CAP	1	283–303	atm	3
Ramkumar ¹⁰⁶	1989	CUB	0.1	303–343	atm	5
Mazurkiewicz ¹⁰⁷	1990	ROT	1	298	atm	1
Lee ¹⁰⁸	1992	FBd	1	303–323	atm	3
Rosenberger ¹⁰⁹	1992	CAP	1	297	atm	1
Assael ¹¹⁰	1994	VbW	0.5	293–328	0.1–32.0	19
Olive ¹¹¹	1994	CUB	0.5	303	atm	1
Wode ¹¹²	1994	CUB	0.5	293–313	atm	5
Lee ¹¹³	1995	FBd	1.5	303–323	atm	3
Först ⁴³	2000	ROB	2	260–313	0.1–700	95
Abdulagatov ³⁰	2003	CAP	1.5	298–574	10–30	27
Abdulagatov ³³	2004	CAP	1.5	294–598	1–50	25
Harris ^{31,32}	2004	FBd	1	256–298	0.1–389	109
Abdulagatov ³⁴	2005	CAP	1.5	297–574	5–40	28
Abdulagatov ³⁵	2005	CAP	1.5	295–598	1–50	25
Teske ³⁶	2005	OSD	0.2–0.3	297–440	0.003–0.05	109
Deguchi ⁴⁵	2006 ^f	DLS	n.p.	301–656	0.1–35	46
Abramson ⁴⁴	2007 ^f	ROB	n.p.	294–573	220–5650	69

^aPrimary data sources used in the analysis of the zero-density function are indicated by italic font.

^bCAP: capillary; CUB: Cannon-Ubbelohde; DLS: dynamic light scattering; FBd: falling body; Fcyl: falling cylinder; NMR: NMR method; OSC: oscillating cylinder; OSD: oscillating disk; OSS: oscillating sphere; OSV: oscillating vessel; RIV: radioisotope; ROB: rolling ball; ROT: rotary; VbW: vibrating wire.

^cn.p.: uncertainty not provided in the source reference.

^dUncertainty as recommended by Watson *et al.*¹⁹

^eDenotes atmospheric pressure, approximately 0.1 MPa.

^fNot included in the development of the correlation.

obtain isothermal data, 103 approximate isotherms having a temperature range of 5 K were organized. This range is flexible (the maximum used was 6.91 K), so that the number of grouped data is as large as possible when there are no other data for a particular temperature region. The data forming these nominal isotherms (T_{nom}) can then be extrapolated to the dilute-gas limit. Furthermore, the data were arranged into nearly isothermal groups in such a way that for each group there was not more than one measured isotherm of the raw data included in the group. It should be noted that in order to consider a “measured isotherm,” we required at least three viscosity values. Additionally, the data must include the lower-density region; this means that all nominal isotherms include data with at least one point having a density of less than 12 kg m⁻³.

The experimental viscosity values must first be corrected to the nominal temperature of the isotherm. Note that the nominal temperature is the mean temperature of all points within the grouping. The correction involved two stages. The first stage incorporated a density correction. The density was recalculated at T_{nom} , p_{exp} with the IAPWS-95 thermodynamic formulation^{24,115} (T_{nom} =nominal temperature of the approximate isotherm, p_{exp} =experimental pressure, as in the

data bank). It should be emphasized that the density values of the experimental points are those calculated at T_{exp} , p_{exp} , in accordance with the IAPWS-95 formulation, since density is rarely measured in a viscosity experiment. The second stage consisted of applying a temperature correction for the viscosity, which was approximated by applying the currently available information for the temperature dependence of the viscosity.¹¹⁶ Thus, we first calculated $\mu_{\text{calc}}(T_{\text{exp}}, p_{\text{exp}})$ using the previous IAPWS formulation for the viscosity.²⁷ We then also calculated with the same formulation $\mu_{\text{calc}}(T_{\text{nom}}, p_{\text{exp}})$. The value of the viscosity $\mu_{\text{corr}}(T_{\text{nom}}, p_{\text{exp}})$ was then adjusted into a nominal isotherm by use of the following formula:

$$\mu_{\text{corr}}(T_{\text{nom}}, p_{\text{exp}}) = \mu_{\text{exp}}(T_{\text{exp}}, p_{\text{exp}}) + \mu_{\text{calc}}(T_{\text{nom}}, p_{\text{exp}}) - \mu_{\text{calc}}(T_{\text{exp}}, p_{\text{exp}}). \quad (3)$$

The temperature correction was always less than 1% of the experimental viscosity for all data points considered in this analysis.

In some cases, the nominal isotherms consisted of points only at a single (constant) pressure. This was the case for isotherms containing data from the following sources: Latto⁶² and Shifrin.⁵⁵ After the correction, the density for all

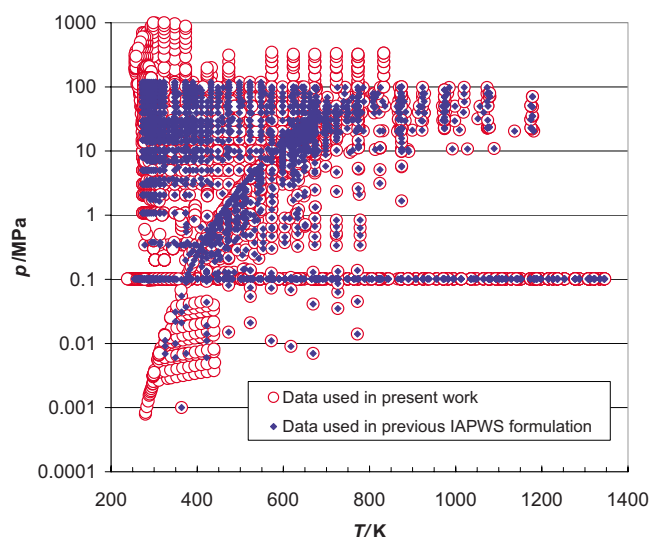


FIG. 1. (Color online) Distribution of experimental viscosity data in the temperature-pressure plane.

points was identical, making it impossible to extrapolate to the dilute-gas limit. Thus, these nominal isotherms were treated in a different way. Data with pressures up to 0.1 MPa (as is the case for the two sources involved) were used to obtain the $\mu_0(T)$ as follows. The corrected viscosity values were extrapolated to the zero-density limit by subtracting the initial density dependence $\mu^{(1)}\rho = B_\eta(k_B T/\varepsilon)\rho$. The functional form of B_η was taken from Eq. (11) in Ref. 117. The value of ε/k_B was taken as 471.53 K. In all cases, the correction for the initial density dependence was less than 0.2% of the $\mu(T, \rho)$ value. The initial uncertainty estimate for the values of $\mu_0(T)$ established this way is the sum of the quoted uncertainty of the experimental data plus the value of the correction. This is essentially equivalent to simply using the experimental uncertainty of the data. In addition, the original experimental data of Yasumoto⁷⁷ were at sufficiently low densities to allow them to be approximated as zero-density points, and the only correction necessary was a temperature correction to the nominal isotherm.

After the corrections, the nominal isotherms were formed. Figure 2 shows the distribution of the data as a function of density and temperature, and Fig. 3 emphasizes the lowest-density region. The symbols represent each of the 103 nominal isotherms covering the nominal temperature range 281.2–1345.1 K. Although there was not a uniform spread of data at all densities, we had enough data for the generation of reliable μ_0 values. It should be noted that there are fewer data at the lower and higher temperatures than at moderate temperatures due to the relative difficulty of performing experiments in these regions.

The next step involved the estimation of a value for the viscosity in the dilute-gas limit, μ_0 , for each of the 103 nominal isotherms. Both linear and quadratic density fits were tested for the isotherms with multiple distinct values of density. Weighted linear least-squares regression was found to be the most suitable procedure to account for the experimental uncertainties of the data points. In the case where the

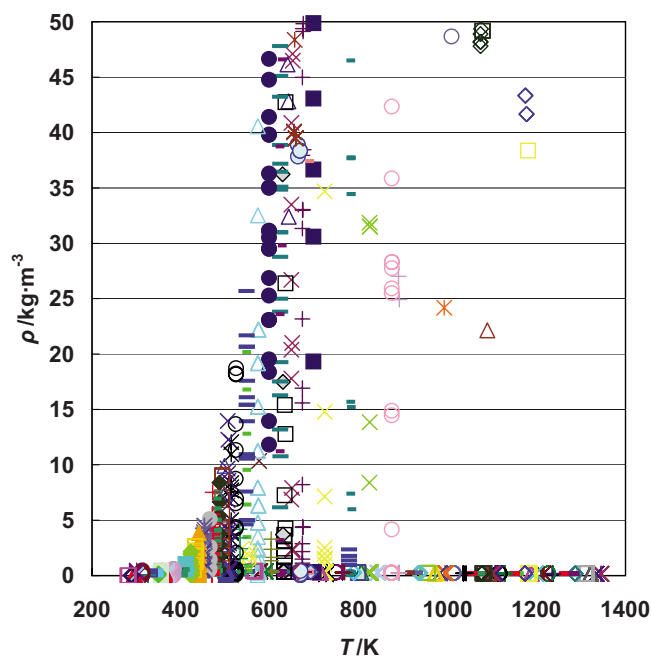


FIG. 2. (Color online) Distribution of density for nominal temperature isotherms.

density values were not separable (Latto⁶² and Shifrin⁵⁵), the viscosity values were extrapolated to the zero-density limit, as described earlier; the μ_0 values for these isotherms were obtained by means of a weighted average based on the uncertainties of the measurements.

In addition to obtaining values for the viscosity in the limit of zero density, μ_0 , we also analyzed the experimental data to obtain the initial density dependence of the viscosity, $\mu^{(1)}$, defined as

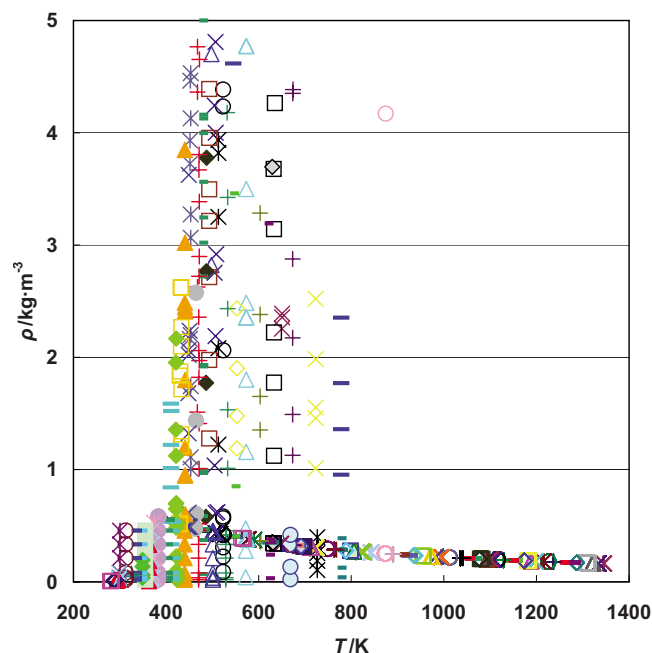


FIG. 3. (Color online) Distribution of density for nominal temperature isotherms, low-density region.

$$\mu^{(1)} = \lim_{\rho \rightarrow 0} \left. \frac{\partial \mu}{\partial \rho} \right|_T. \quad (4)$$

This function changes sign with temperature; at some temperatures the viscosity decreases with increasing density. For the data reported by Latto⁶² and Shiffrin,⁵⁵ values for $\mu^{(1)}$ were obtained with the aforementioned calculation steps. In the case where the data were structured in isotherms with multiple distinct density values, a different procedure was adopted. The corrected, nominal temperatures T_{nom} and viscosities μ_{nom} along with the experimental uncertainties were used. For each isotherm, a statistical-analysis code¹¹⁸ was executed to perform a weighted linear least-squares analysis, and the generated slope was obtained as the $\mu^{(1)}$ value, along with its standard deviation. Finally, when an isotherm contained more than one individual set, the Key Comparison Reference Value¹¹⁹ (KCRV) procedure was adopted to get the weighted mean of the $\mu^{(1)}$ value along with its standard deviation. The data for $\mu^{(1)}$ were used in the development of the dense-fluid contribution to viscosity and will be considered later in Secs. 3.2 and 4.1.

A set of equations that expresses the relations that exist between the measured (“observed”) values and the unknown parameters is a set of observational equations. For the straight-line case, the form is

$$y_i = \alpha + \beta x_i + \varepsilon_i, \quad (5)$$

where y_i is the dependent variable, x_i is the independent variable, α and β are the unknown parameters, and ε_i is the error (because the measurements are subject to experimental error). Hence, the assumption is made that the errors ε_i belong to statistical populations of zero mean and with standard deviations σ_i . If we assume that we have succeeded in deriving estimates $\bar{\alpha}$ and $\bar{\beta}$ for the unknown parameters α and β , then the equations are written in the form

$$\bar{y}_i = \bar{\alpha} + \bar{\beta} x_i. \quad (6)$$

The values defined by these equations may be considered as the “theoretical estimates,” corresponding to the observed values y_i . We can consider the weighted sum of squares of the residuals,

$$S = \sum_{i=1}^n w_i d_i^2, \quad (7)$$

where each weight w_i is defined as the reciprocal of the corresponding variance: $w_i = 1/\sigma_i^2$ and the residuals d_i are the differences between the observed and the estimated values:

$$d_i = y_i - \bar{y}_i = y_i - (\bar{\alpha} + \bar{\beta} x_i). \quad (8)$$

The principle by which we obtain the estimates of $\bar{\alpha}$ and $\bar{\beta}$ is that of minimizing the sum of squares of the residuals.¹²⁰

The weighted linear least-squares regression has been used in order to account for the different experimental uncertainties of the data. Furthermore, statistical tests show that our data are better described by a linear rather than a quadratic

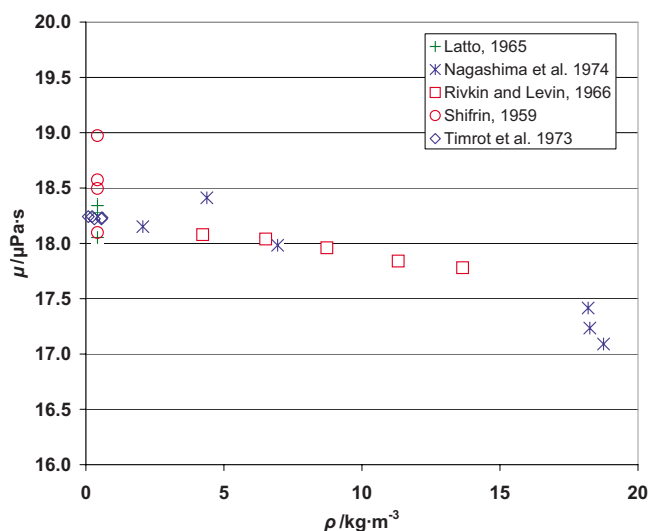


FIG. 4. (Color online) Nominal isotherm at 523.6 K.

fit. This method provides as many μ_0 values for each isotherm as the number of different primary data sources used.

A typical, representative isotherm is shown in Fig. 4. It consists of data from five different sources at a nominal temperature of 523 K, each of which can be extrapolated to a μ_0 value, so that five individual μ_0 values are derived. There are two ways of generating the dilute-gas value for every source depending on whether the data are at different pressures or at a single pressure. For different pressures, the weighted linear least-squares regression was used. In the case of data at a constant pressure,^{55,62} the dilute-gas values were determined by subtracting the initial density dependence. All the dilute-gas values derived were consistent if one takes into account the experimental uncertainties of the data. At this point, several μ_0 values had been calculated for each nominal isotherm. Nevertheless, there was a need for a single consensus value, associated with all the data. In order to get this value, the KCRV was considered.

The KCRV procedure is applicable only when the following conditions are met.¹¹⁹ First, each source must provide a measurement, or a series of measurements in our case, having good stability and with an associated standard uncertainty. Second, the measurement(s) of each source is (are) realized independently of the other sources' measurements in the key comparison. Finally, for each source a Gaussian distribution can be assigned to the measurand, of which the sources' measurement is an estimate.

In this analysis, these conditions were assumed to apply. The participating sources are the individual data points $i = 1, \dots, N$. The input values to the evaluation are the μ_0 viscosity values x_i , $i = 1, \dots, N$, and the standard uncertainties associated with these values $u(x_i)$, $i = 1, \dots, N$ are the experimental uncertainties of the measurements of the primary data points.

The weighted mean y of the sources' measurements, i.e., the weighted mean of the μ_0 viscosity values in our analysis, is

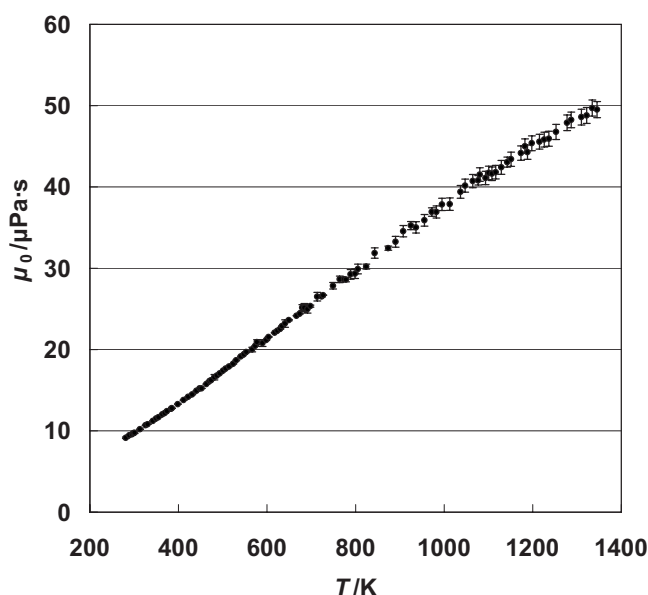


FIG. 5. Values of μ_0 for the 103 nominal isotherms as a function of temperature.

$$y = \frac{x_1/u^2(x_1) + \cdots + x_N/u^2(x_N)}{1/u^2(x_1) + \cdots + 1/u^2(x_N)}, \quad (9)$$

and the standard deviation $u(y)$ associated with y is

$$\frac{1}{u^2(y)} = \frac{1}{u^2(x_1)} + \cdots + \frac{1}{u^2(x_N)}. \quad (10)$$

This procedure generates an individual μ_0 viscosity value for each considered isotherm regardless of the way it was calculated (single or multiple pressures). Each value has an error associated with it. The resulting viscosities at the dilute-gas limit are shown in Fig. 5. We note that, as the temperature increases, the error bars are larger. This fact is in accordance with the larger experimental uncertainties (2%) at higher temperatures.

Several different forms of equations for $\mu_0(T)$ were tested, such as the previous IAPWS formulation for the viscosity,²⁷ modified expressions of the Chapman-Enskog equation, and several standard mathematical formulations. Moreover, different optimization techniques were examined. The functional form chosen for this study is the same as the previous IAPWS formulation for the viscosity:^{19,21,27}

$$\bar{\mu}_0(\bar{T}) = \frac{100\sqrt{\bar{T}}}{\sum_{i=0}^3 \frac{H_i}{\bar{T}^i}}, \quad (11)$$

where $\bar{\mu}_0 = \mu/\mu^*$ is the dimensionless viscosity and $\bar{T} = T/T^*$ the dimensionless temperature. We use the critical temperature as the reference temperature, $T^* = T_c = 647.096$ K, and the reference value for the viscosity was set to $\mu^* = 1 \times 10^{-6}$ Pa s. The form of the equation was discussed within the Working Group on Thermophysical Properties of Water and Steam of IAPWS. Equation (11) was

TABLE 2. Coefficients H_i in Eq. (11) for $\bar{\mu}_0(\bar{T})$

i	H_i
0	1.677 52
1	2.204 62
2	0.636 656 4
3	-0.241 605

obtained from a general expression for the viscosity given by the kinetic theory of gases by replacing the collision integrals with an empirical power-series expansion in inverse temperature for the collision integrals.

The coefficients in Eq. (11) were estimated by orthogonal distance regression with the aid of the statistical package ODRPACK,¹²¹ and they are given in Table 2. The objective function was minimized with weights according to the uncertainty estimates. Due to the scarcity of data at the lowest temperatures, additional weight was given to the data of Teske *et al.*³⁶ Comparisons with the zero-density viscosities obtained with the KCRV procedure are presented in Fig. 6. The fit represents the nominal isotherm data shown in Fig. 5 with an average absolute percentage deviation (AAD) of 0.59% and a standard deviation of 0.54%.

3.2. Residual Contribution

The second factor $\bar{\mu}_1$ in Eq. (2) is the residual viscosity and represents the contribution to viscosity due to increasing density. This term is frequently referred to in the literature as the excess viscosity,¹⁹ but here we follow the alternative nomenclature of residual viscosity.¹²² The critical region is not considered here; it will be treated separately in Sec. 3.3. We adopt the same general form for $\bar{\mu}_1$ as in the previous formulations:^{19,21,27}

$$\bar{\mu}_1(\bar{T}, \bar{\rho}) = \exp \left[\bar{\rho} \sum_{i=0}^5 \left(\frac{1}{\bar{T}} - 1 \right)^i \sum_{j=0}^6 H_{ij} (\bar{\rho} - 1)^j \right], \quad (12)$$

with coefficients H_{ij} to be determined by regression of experimental data.

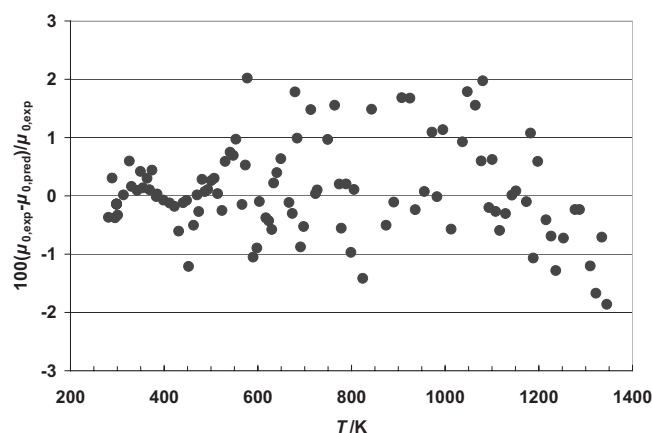


FIG. 6. Percentage deviations of the zero-density viscosity for each isotherm from predicted values obtained with Eq. (11).

All points were assigned weights $1/u^2$, where u is the estimated experimental uncertainty, with a few exceptions as discussed here. The uncertainties are given in Table 1; they are those given by Assael *et al.*,²⁹ the original author's recommendation, or the recommendations by Watson *et al.*¹⁹ Also, following the recommendations given in the previous formulation of Watson *et al.*,¹⁹ the first five points at 380 °C in Ref. 57 were assigned a weight of zero due to their large uncertainties. Eighteen points of Nagashima⁷² between 300 °C and the critical temperature were given a weight of zero to ensure consistency in the near-critical region. Furthermore, seven additional points as identified by Watson *et al.*¹⁹ were also given zero weight (Ref. 63, $T=172.3$ °C, $p=49.749$ MPa; Ref. 68, $T=375.0$ °C, $p=22.658$ MPa; $T=400$ °C, $p=35.436$ MPa; $T=425.0$ °C, $p=30.498$ MPa; $T=425$ °C, $p=33.417$ MPa; $T=450$ °C, $p=35.406$ MPa, and in Ref. 72, $T=402.83$ °C, $p=40.060$ MPa). Again, following the recommendations of Watson *et al.*¹⁹ for the experimental measurements of Korson *et al.*⁷¹ and of Eicher and Zwolinski,⁷⁸ we adopted the re-evaluated values of Kestin *et al.*,¹²³ except that relative values were scaled with the presently accepted¹²⁴ value of 1001.6 $\mu\text{Pa s}$ for the viscosity of water at 20 °C and 0.101 325 MPa. As discussed earlier in Sec. 2, all densities were computed with IAPWS-95. Similarly, manuscripts that presented viscosity as a relative value with respect to the viscosity at 20 °C (Refs. 48, 49, and 51) were recomputed by adopting the presently recommended value at 20 °C and 0.101 325 MPa. Also, any points that exhibited differences of more than three standard deviations from preliminary regressions were considered outliers and were not used in further regression analysis. Furthermore, data at temperatures below 255 K (this applies to the data of Osipov⁹¹) in the metastable liquid-solid region were assigned a weight of zero for the regression but are included for comparison purposes. Finally, six recommended values for the viscosity of water at atmospheric pressure for the temperature range 15–40 °C from Ref. 124 were added to the set of data used in the regression with an assigned uncertainty of 0.17%. Additional discussion on the viscosity of water at atmospheric pressure can be found in Sec. 2.1.1 of Ref. 29.

There are two sets of experimental data that contain data in the critical region: the data of Oltermann⁹⁰ and the data of Rivkin *et al.*⁴⁶ The data of Oltermann outside the critical region were used in the regression of $\bar{\mu}_1(\bar{T}, \bar{p})$ and weighted according to the author's uncertainty estimate, 1.6%. Data of Oltermann within the region bounded by $640.50 \text{ K} \leq T \leq 650.95 \text{ K}$, $254.1 \text{ kg m}^{-3} \leq \rho \leq 393.4 \text{ kg m}^{-3}$ were given a weight of zero¹⁹ as discussed in Sec. 3.2.2 and were not used. The data of Rivkin were reanalyzed with a procedure to be discussed in the next section and the data with the critical enhancement removed (based on preliminary estimates of the enhancement term) were used in the generation of $\bar{\mu}_1(\bar{T}, \bar{p})$.

Equation (12) contains a maximum of 42 empirical terms; there is no theoretical motivation for the form or the total number of terms necessary or which terms will best represent

the experimental data. To determine the statistically significant terms, we used a simulated annealing procedure¹²⁵ along with the orthogonal distance regression package ODRPACK (Ref. 121) to arrive at our final formulation. Simulated annealing¹²⁵ is an optimization technique that can be used in complex problems where there may be multiple local minima. It is a combinatorial method that does not require derivatives and does not depend upon "traveling downhill;" it also is relatively easy to implement. In this work, the search space contained a bank of terms corresponding to the terms in Eq. (12). The total number of terms was fixed in each optimization experiment, and the simulated annealing algorithm was used to determine the optimal terms from the bank of terms. As in earlier work,¹²⁶ we implemented an annealing schedule recommended by Lundy and Mees.¹²⁷ Successive runs were made with different total numbers of terms, from 18 to 25. For the regression, the data were weighted according to their estimated uncertainty (u) with weights of $1/u^2$. Points that deviated by more than three standard deviations from preliminary fits were considered outliers and were not included in the statistics and final regression.

Several conditions were imposed on the regression. First, the equation was constrained to reproduce the recommended value¹²⁴ of the viscosity of water at 20 °C and atmospheric pressure (0.101 325 MPa), $\mu=1001.6 \mu\text{Pa s}$. Second, the first density correction to the viscosity in the gas phase, $\mu^{(1)}$, was forced to approach zero for very large T and to be negative at low temperatures. This is consistent with theoretical approaches.¹²⁸ One can represent the initial density dependence of the viscosity in the gas phase as

$$\mu = \mu_0 + \mu^{(1)}\rho, \quad (13)$$

where the coefficient $\mu^{(1)}$ is the first density correction defined previously in Eq. (4).

From Eqs. (12) and (4) we obtain

$$\mu^{(1)} = \frac{\mu_0(T)}{\bar{p}} \sum_{i=0}^5 H_{i0} \left(\frac{1}{\bar{T}} - 1 \right)^i. \quad (14)$$

We fitted the experimental viscosities from the data bank and the first density correction data simultaneously. The objective function was the weighted sum of the squared difference between the experimental and calculated values. The relative weight of the first density correction was adjusted until $\mu^{(1)}$ had the desired behavior but did not degrade the fit of the viscosity data. The formulation with a total of 21 terms provided the best representation of the data with the fewest number of terms. Increasing the total number of terms above 21 provided marginally better representations of the data but with increased uncertainty in the coefficients. The quality of the fits degraded for formulations with fewer than 21 terms; thus we chose 21 as the optimal formulation. The final values of the coefficients for the residual function are given in Table 3. A detailed comparison of the correlation with experimental data will be presented in Sec. 4.

TABLE 3. Coefficients H_{ij} in Eq. (12) for $\bar{\mu}_1(\bar{T}, \bar{\rho})$. Coefficients H_{ij} omitted from the table are identically equal to zero

i	j	H_{ij}
0	0	$5.200\,94 \times 10^{-1}$
1	0	$8.508\,95 \times 10^{-2}$
2	0	$-1.083\,74$
3	0	$-2.895\,55 \times 10^{-1}$
0	1	$2.225\,31 \times 10^{-1}$
1	1	$9.991\,15 \times 10^{-1}$
2	1	$1.887\,97$
3	1	$1.266\,13$
5	1	$1.205\,73 \times 10^{-1}$
0	2	$-2.813\,78 \times 10^{-1}$
1	2	$-9.068\,51 \times 10^{-1}$
2	2	$-7.724\,79 \times 10^{-1}$
3	2	$-4.898\,37 \times 10^{-1}$
4	2	$-2.570\,40 \times 10^{-1}$
0	3	$1.619\,13 \times 10^{-1}$
1	3	$2.573\,99 \times 10^{-1}$
0	4	$-3.253\,72 \times 10^{-2}$
3	4	$6.984\,52 \times 10^{-2}$
4	5	$8.721\,02 \times 10^{-3}$
3	6	$-4.356\,73 \times 10^{-3}$
5	6	$-5.932\,64 \times 10^{-4}$

3.3. Critical Region

3.3.1. Theory

The critical region is a region where reliable theoretical predictions are available for the thermodynamic and transport properties of H₂O.¹²⁹ In the vicinity of a critical point, fluids exhibit large fluctuations in the order parameter associated with the critical phase transition. For fluids near the vapor-liquid critical point, the order parameter can be asymptotically identified with the density ρ . The corresponding susceptibility χ , defined as the derivative of the order parameter with respect to the ordering field (chemical potential), is related to the isothermal compressibility such that $\chi \equiv \rho(\partial\rho/\partial p)_T$.¹²⁹ The spatial extent of the density fluctuations is characterized by a correlation length ξ . Along the critical isochore, $\rho = \rho_c = \rho^*$, the correlation length ξ and the dimensionless susceptibility $\bar{\chi} \equiv \bar{\rho}(\partial\bar{\rho}/\partial\bar{p})_{\bar{T}}$ diverge as a function of $t = (\bar{T} - 1)/\bar{T}$ asymptotically close to the critical point according to power laws of the form

$$\xi \approx \xi_0 t^{-\nu} \quad \text{and} \quad \bar{\chi} \approx \Gamma_0 t^{-\gamma}. \quad (15)$$

The reference temperature T^* equals the critical temperature T_c , so that $\bar{T} = T/T_c$. In these power laws, ξ_0 and Γ_0 are system-dependent amplitudes and ν and γ are universal critical exponents. Fluids belong to the universality class of Ising-like systems for which $\nu = 0.630$ and $\gamma = 1.239$.¹³⁰ From Eq. (15), it follows that

$$\xi \approx \xi_0 (\bar{\chi}/\Gamma_0)^{\nu/\gamma}. \quad (16)$$

Although Eq. (16) is strictly valid only for $\rho = \rho_c$, it is also used as an approximation for $\rho \neq \rho_c$.^{20,131}

It has been well established that both the thermal conductivity and the viscosity of fluids diverge at the critical point.¹³² Two theoretical approaches have been developed to account for the divergent behavior of the transport properties: the mode-coupling theory of critical dynamics and the dynamic renormalization-group theory.¹³³ The viscosity exhibits a weak divergence that affects this transport property only in a small range of temperatures and densities around the critical point. For a theoretical description, the viscosity is separated into a background contribution $\bar{\mu}_b$ and a critical enhancement $\Delta\bar{\mu}$. The idea is that $\bar{\mu}_b$ represents the viscosity in the absence of critical fluctuations and that $\Delta\bar{\mu}$ accounts for an enhancement of the viscosity due to the critical fluctuations, so that $\bar{\mu} = \bar{\mu}_b + \Delta\bar{\mu}$. In practice, $\bar{\mu}_b$ is estimated by extrapolating the viscosity data outside the critical region into the critical region. The viscosity is predicted to diverge as¹³⁴

$$\bar{\mu} \approx \bar{\mu}_b (Q_0 \xi)^{x_\mu}, \quad (17)$$

where Q_0 is an effective wave number that determines the amplitude of the power-law divergence of the viscosity, while x_μ is a universal dynamic critical exponent.¹³³ In this paper, we have adopted the most recent theoretical prediction $x_\mu = 0.068$.¹³⁵ We note that the viscosity exhibits a so-called multiplicative anomaly, that is, the critical enhancement $\Delta\bar{\mu}$ is proportional to the background viscosity $\bar{\mu}_b$.¹³⁶

Equation (17) represents the divergent behavior of the viscosity asymptotically close to the critical point. To apply the theory to experimental data, one needs a ‘‘crossover’’ equation that incorporates the theoretical power law asymptotically close to the critical point and reduces to the normal background viscosity $\bar{\mu}_b$ away from the critical point. In the viscosity correlation previously recommended by IAPWS, this problem was solved empirically by adopting a crossover equation of the form^{19,20}

$$\ln(\bar{\mu}/\bar{\mu}_b) = x_\mu \ln(Q_0 \xi) \Theta(Q_0 \xi - 1), \quad (18)$$

where $\Theta(z)$ is a Heaviside step function such that $\Theta(z) = 1$ for $z > 1$ and $\Theta(z) = 0$ for $z \leq 1$. A weakness of such an empirical crossover function is that the slope of the viscosity will exhibit a discontinuity at $Q_0 \xi = 1$. This problem has been solved theoretically by Bhattacharjee and co-workers,^{134,137} who derived the following crossover equation for the critical behavior of the viscosity:

$$\bar{\mu} = \bar{\mu}_b \exp(x_\mu Y). \quad (19)$$

The function Y is defined by

$$Y = \frac{1}{12} \sin(3\psi_D) - \frac{1}{4q_C \xi} \sin(2\psi_D) + \frac{1}{(q_C \xi)^2} \left[1 - \frac{5}{4}(q_C \xi)^2 \right] \sin(\psi_D) - \frac{1}{(q_C \xi)^3} \left\{ \left[1 - \frac{3}{2}(q_C \xi)^2 \right] \psi_D - |(q_C \xi)^2 - 1|^{3/2} L(w) \right\}, \quad (20)$$

with

$$\psi_D = \arccos(1 + q_D^2 \xi^2)^{-1/2} \quad (21)$$

and with the function $L(w)$ given by

$$L(w) = \begin{cases} \ln \frac{1+w}{1-w} & \text{for } q_C \xi > 1 \\ 2 \arctan|w| & \text{for } q_C \xi \leq 1. \end{cases} \quad (22)$$

The variable w is defined by

$$w = \left| \frac{q_C \xi - 1}{q_C \xi + 1} \right|^{1/2} \tan\left(\frac{\psi_D}{2}\right). \quad (23)$$

The function Y contains two system-dependent constants, namely, the wave numbers q_C and q_D . Asymptotically close to the critical point, i.e., in the limit of large ξ , Eq. (19) reproduces Eq. (17) with an amplitude Q_0 that is related to q_C and q_D such that^{134,137}

$$Q_0^{-1} = (q_C^{-1} + q_D^{-1})e^{4/3}/2. \quad (24)$$

The wave number q_C is related to a background contribution to the decay rate of the critical fluctuations and is given by

$$q_C = \frac{k_B T_c^2}{16 \mu_b^c \lambda_b^c \rho_c^2} \frac{\Gamma_0}{\xi_0^2} \left(\frac{\partial p}{\partial T} \right)_{\rho=\rho_c}^2, \quad (25)$$

where k_B is Boltzmann's constant, μ_b^c and λ_b^c are the values of the background viscosity and background thermal conductivity, respectively, at the critical point, while $(\partial p / \partial T)_{\rho=\rho_c}$ is the slope of the critical isochore at the critical temperature. The wave number q_D represents a "Debye" cutoff of the mode-coupling integrals for critical dynamics and is the only adjustable parameter in the theory.

For small ξ , the function Y approaches zero, so that $\bar{\mu}$ approaches $\bar{\mu}_b$ in this limit. Around $\xi=0$, the function Y has a Taylor expansion of the form

$$Y = \frac{1}{5} q_C \xi (q_D \xi)^5 \left(1 - q_C \xi + (q_C \xi)^2 - \frac{765}{504} (q_D \xi)^2 \right). \quad (26)$$

The approximations in the derivation of Eq. (19) for the critical enhancement of the viscosity have been discussed by Luettmmer-Strathmann *et al.*¹³⁸ One of the approximations is that the isobaric specific heat capacity c_p in the mode-coupling integral for the viscosity has been replaced by the difference $c_p - c_v$, where c_v is the isochoric specific heat capacity. The approximations are well justified in the small region around the critical point where a critical viscosity enhancement is observed.

Equation (16) represents the behavior of the correlation length ξ near the critical point. In the theory of critical phenomena, ξ is to be interpreted as that part of the actual correlation length associated with the long-range critical fluctuations. Hence, the correlation length ξ in Eq. (20) should vanish far away from the critical point. To accomplish this goal, we have adopted a procedure proposed by Olchowy and co-workers^{138,139} by generalizing Eq. (16) to

$$\xi = \xi_0 \left(\frac{\Delta \bar{\chi}}{\Gamma_0} \right)^{1/\gamma} \quad (27)$$

in terms of $\Delta \bar{\chi}$ (≥ 0) which is defined by

$$\Delta \bar{\chi} = \bar{\rho} \left[\left(\frac{\partial \bar{\rho}(\bar{T}, \bar{\rho})}{\partial \bar{\rho}} \right)_{\bar{T}} - \left(\frac{\partial \bar{\rho}(\bar{T}_R, \bar{\rho})}{\partial \bar{\rho}} \right)_{\bar{T}} \frac{\bar{T}_R}{\bar{T}} \right]. \quad (28)$$

In Eq. (28), \bar{T}_R is a reference temperature sufficiently high above the critical temperature that the critical fluctuations can be assumed to be small. In practice, one may select $\bar{T}_R = 1.5$.^{138–140} Furthermore, $\Delta \bar{\chi}$ is to be taken to be zero when the left-hand side of Eq. (28) becomes negative. This procedure assures that the correlation length ξ in Eqs. (20) and (26) will vanish far away from the critical point.

An accurate experimental determination of the viscosity close to the critical point is hampered by the presence of gravitationally induced density profiles.¹⁴¹ To avoid this complication, the viscosity of xenon near the critical density and critical temperature has been measured by Berg *et al.* at low-gravity conditions in the Space Shuttle.^{142–144} In the hydrodynamic limit of zero frequency, the experimental viscosity data are well represented by Eq. (19) with an experimental value for the critical exponent x_μ that agrees within its uncertainty with the theoretical value of 0.068.¹³⁵ We conclude that the crossover Eq. (19) for the critical behavior has a sound theoretical basis and has been validated experimentally.

3.3.2. Application to H₂O

Basu and co-workers showed that Eq. (19) yields a satisfactory description of the critical behavior of the viscosity of H₂O.^{134,145} For the present project, we have performed a complete reanalysis of the experimental data for the viscosity of H₂O in the critical region, adopting the IAPWS-95 formulation^{24,25} for the representation of the equilibrium thermodynamic properties.

The background viscosity $\bar{\mu}_b$ is represented by

$$\bar{\mu}_b = \bar{\mu}_0(\bar{T}) \times \bar{\mu}_1(\bar{T}, \bar{\rho}) \quad (29)$$

from Eq. (2), as specified in Secs. 3.1 and 3.2. The amplitudes of the power laws, Eq. (15), for the susceptibility and the correlation length of H₂O are^{129,146,147}

$$\Gamma_0 = 0.06, \quad \xi_0 = 0.13 \text{ nm}. \quad (30)$$

With $(\partial p / \partial T)_{\rho=\rho_c} = 0.267 \text{ MPa K}^{-1}$, with $\mu_b^c = 39.3 \text{ } \mu\text{Pa s}$ as calculated from Eq. (29) at $T=T_c$ and $\rho=\rho_c$ and with $\lambda_b^c = 0.197 \text{ W m}^{-1} \text{ K}^{-1}$ as estimated from the current interpolating equation for the thermal conductivity of H₂O,^{26,148} we find from Eq. (25):

$$q_C^{-1} = 1.9 \text{ nm}. \quad (31)$$

The equation for the critical enhancement of the viscosity of H₂O is now completely specified except for one system-dependent constant, namely, the wave number q_D .

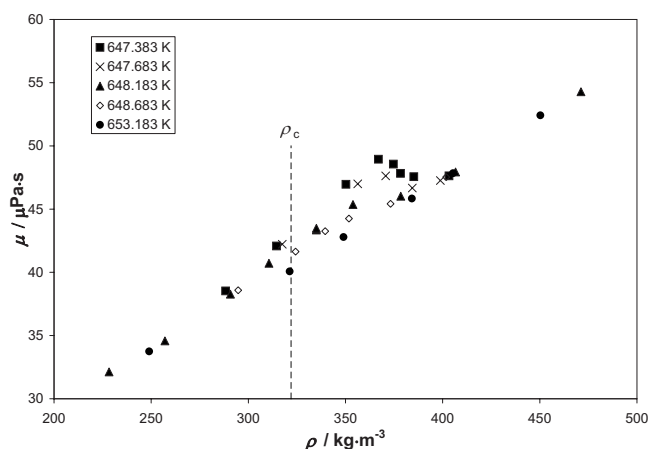


Fig. 7. The viscosity data obtained by Rivkin *et al.*⁴⁶ as a function of density with the density calculated from the IAPWS-95 equation of state and the temperatures converted to ITS-90.

A detailed experimental study of the viscosity of H₂O in the critical region was made by Rivkin *et al.*^{46,149} In these experiments, the kinematic viscosity μ/ρ was determined by measuring the flow rate through a capillary which had an internal diameter of 0.3 mm and a length of 50 cm as a function of the pressure drop over the capillary.¹⁴⁹ In principle, the method can lead to some complications due to the large compressibility near the critical point.^{150–153} However, the investigators made measurements with various pressure differences ranging from 13.3 kPa (100 mm Hg) to 1 kPa (8 mm Hg) and verified that the measured kinematic viscosity became independent of the applied pressure difference below 1.6 kPa (12 mm Hg).¹⁵⁴ The measurements seem to have been executed with great care, and we have adopted the values determined by Rivkin *et al.* for the kinematic viscosity with an uncertainty estimate of 1%, as suggested by the authors. Another attempt to measure the critical-region viscosity of H₂O was made by Oltermann with an oscillating-disk viscometer.⁹⁰ Near the critical density, his data are consistent with those of Rivkin *et al.*, but the agreement is not good at lower and higher densities. We have adopted the data of Rivkin *et al.* as the primary source for characterizing the behavior of the viscosity in the critical region. The same decision was made by Watson *et al.*¹⁹ in developing the previous correlating equation for the viscosity of H₂O in the critical region.

Rivkin *et al.* obtained the kinematic viscosity as a function of temperature in terms of measured pressures and temperatures on the IPTS-48 scale. We have converted the experimental temperatures to ITS-90, calculated the densities from the IAPWS-95 formulation, and converted the experimental values for the kinematic viscosity μ/ρ into values for the dynamic viscosity μ . The viscosities thus obtained are plotted as a function of density in Fig. 7. The figure shows that μ appears to exhibit an enhancement at a density substantially larger than the critical density ρ_c . Watson *et al.*¹⁹ adopted the hypothesis that this apparent shift in the location of the maximum of the viscosity enhancement may be due to an offset

of the temperature or, more precisely, to an inaccurate value of the temperature difference $T - T_c$ attributed to the experimental data. Such an offset can result from a temperature difference between the sample in the cell and the location of the thermometer, mechanical stresses in thermocouple connections, or similar problems, while the critical temperature can depend on the purity of the sample. Adopting the best available value for the critical temperature at that time and a scaled equation of state, Watson *et al.* showed that the data did become consistent with the expected diverging critical behavior of the viscosity if the temperatures reported by Rivkin *et al.* were increased by 0.040 K.¹⁹ We have performed a new statistical analysis to determine the optimum temperature shift using the IAPWS-95 formulation for the equation of state, which assumes a critical temperature $T_c = T^* = 647.096$ K (ITS-90). This analysis yielded a temperature shift of 0.051 K with a standard deviation of 0.002 K; the resulting reanalyzed data are presented in Table 4. In Table 4, the temperatures are derived from the reported temperature of Rivkin *et al.* in IPTS-48, converted to ITS-90, plus the temperature offset of 0.051 K. The densities are calculated with the IAPWS-95 formulation given these temperatures and the experimental pressures as input. The “experimental” viscosities are derived from these IAPWS-95 densities and the reported experimental kinematic viscosities. Figure 8 shows the critical enhancement of the viscosity deduced from the measurements of Rivkin *et al.*, when the temperatures on ITS-90 plus the offset of 0.051 K are used to compute the densities with IAPWS-95. The curves in this figure represent the values calculated from the theoretical equation (19) with

$$q_D^{-1} = 1.1 \text{ nm}. \quad (32)$$

We conclude that, with the temperature correction, the data are consistent with the theoretical prediction for the behavior of the viscosity in the critical region. The reported uncertainty in the experimental temperature is 0.02 K, and the reported uncertainty in the pressure is 0.01 MPa, which is equivalent to a temperature uncertainty of 0.04 K (based on the 0.267 MPa K^{-1} slope of the vapor-pressure curve at the critical point). The uncertainty in the critical temperature in the IAPWS-95 equation of state is 0.100 K.¹¹⁴ The combined uncertainty from these three sources is 0.160 K. Hence, the temperature offset of 0.051 is well within the uncertainty of $T - T_c$ to be attributed to the experimental data of Rivkin *et al.* In principle, the density at which the critical enhancement has a maximum can be shifted to the critical density by applying either a temperature shift or a pressure shift. We have verified that replacing the temperature shift by a pressure shift does not yield a satisfactory agreement between theory and experiments.

One comment should be made concerning the technical application of Eq. (19) for the behavior of the viscosity in the critical region. While the function Y defined by Eq. (20) does become zero in the limit that ξ goes to zero, some individual terms diverge in this limit. Hence, Eq. (20) is no longer suitable for numerical calculations at small values of ξ , and

TABLE 4. Reanalyzed viscosity data in the critical region based on the capillary measurements of kinematic viscosity μ/ρ by Rivkin *et al.*⁴⁶

T (K)	p (MPa)	μ/ρ ($10^{-10} \text{ m}^2 \text{ s}^{-1}$)	ρ (kg m^{-3})	μ ($\mu\text{Pa s}$)
647.434	22.136	1336	265.9	35.5
647.434	22.140	1338	270.4	36.2
647.434	22.144	1341	276.4	37.1
647.434	22.150	1334	292.4	39.0
647.434	22.156	1296	336.6	43.6
647.434	22.160	1264	356.9	45.1
647.434	22.170	1235	373.7	46.1
647.434	22.220	1181	398.8	47.1
647.734	22.220	1330	279.2	37.1
647.734	22.230	1319	302.9	40.0
647.734	22.240	1285	344.7	44.3
647.734	22.260	1214	375.0	45.5
647.734	22.300	1185	394.0	46.7
648.234	22.200	1407	226.4	31.9
648.234	22.300	1345	251.9	33.9
648.234	22.340	1316	275.5	36.3
648.234	22.350	1311	286.6	37.6
648.234	22.360	1294	303.3	39.3
648.234	22.360	1298	303.3	39.4
648.234	22.370	1282	325.9	41.8
648.234	22.400	1216	369.3	44.9
648.234	22.500	1179	403.4	47.6
648.234	23.500	1152	470.5	54.2
648.734	22.470	1309	281.6	36.9
648.734	22.490	1284	303.8	39.0
648.734	22.500	1274	318.6	40.6
648.734	22.510	1258	333.7	42.0
648.734	22.540	1217	364.6	44.4
648.734	22.640	1183	398.6	47.2
649.234	22.600	1297	286.1	37.1
649.234	22.620	1276	304.2	38.8
649.234	22.630	1274	315.0	40.1
649.234	22.650	1238	336.8	41.7
649.234	22.700	1205	370.8	44.7
649.234	22.800	1181	397.8	47.0
650.234	22.300	1503	197.1	29.6
650.234	22.700	1366	240.1	32.8
650.234	22.840	1294	281.3	36.4
650.234	22.890	1256	311.5	39.1
650.234	22.940	1227	344.7	42.3
650.234	23.000	1203	370.2	44.5
650.234	23.200	1175	407.3	47.9
653.234	23.400	1355	247.3	33.5
653.234	23.700	1247	317.1	39.5
653.234	23.800	1226	345.4	42.3
653.234	24.000	1193	382.0	45.6
653.234	24.200	1180	403.8	47.6
653.234	25.000	1164	449.5	52.3
653.234	30.000	1147	533.5	61.2
663.232	25.000	1466	214.4	31.4
663.232	26.100	1289	287.8	37.1
663.232	26.600	1233	333.6	41.1
663.232	27.000	1207	364.5	44.0
663.232	27.500	1188	393.4	46.7
646.935	22.100	1174	409.8	48.1
647.114	22.100	1194	391.7	46.8
647.174	22.100	1213	380.2	46.1

TABLE 4. Reanalyzed viscosity data in the critical region based on the capillary measurements of kinematic viscosity μ/ρ by Rivkin *et al.*⁴⁶—Continued

T (K)	p (MPa)	μ/ρ ($10^{-10} \text{ m}^2 \text{ s}^{-1}$)	ρ (kg m^{-3})	μ ($\mu\text{Pa s}$)
647.204	22.100	1262	369.6	46.6
647.204	22.100	1262	369.6	46.6
647.234	22.100	1346	304.4	41.0
647.234	22.100	1347	304.4	41.0
647.264	22.100	1342	272.6	36.6
647.264	22.100	1342	272.6	36.6
647.234	22.200	1181	409.9	48.4
647.534	22.200	1226	374.2	45.9
647.584	22.200	1299	350.4	45.5
647.634	22.200	1326	289.3	38.4
647.654	22.200	1325	279.0	37.0
647.674	22.200	1327	272.3	36.1
648.234	22.200	1407	226.4	31.9
647.234	22.300	1164	425.3	49.5
647.734	22.300	1185	394.0	46.7
647.934	22.300	1255	354.5	44.5
647.984	22.300	1301	317.6	41.3
648.034	22.300	1315	287.1	37.8
648.084	22.300	1325	272.4	36.1
648.234	22.300	1345	251.9	33.9
650.234	22.300	1503	197.1	29.6

for $\xi \leq 0.381\ 701\ 641\ 6\ \text{nm}$ the function Y should be evaluated by using its truncated Taylor expansion given by Eq. (26).

Figure 9 shows a plot of the logarithm of the multiplicative critical viscosity enhancement μ/μ_b calculated with Eq. (19) and the parameters summarized in Table 5 as a function of the correlation length ξ . The symbols represent the experimental data of Rivkin *et al.*⁴⁶ with densities calculated from the IAPWS-95 equation and the temperatures converted to ITS-90 and shifted by 0.051 K. The curve represents the theoretical expression for this viscosity enhancement. The criti-

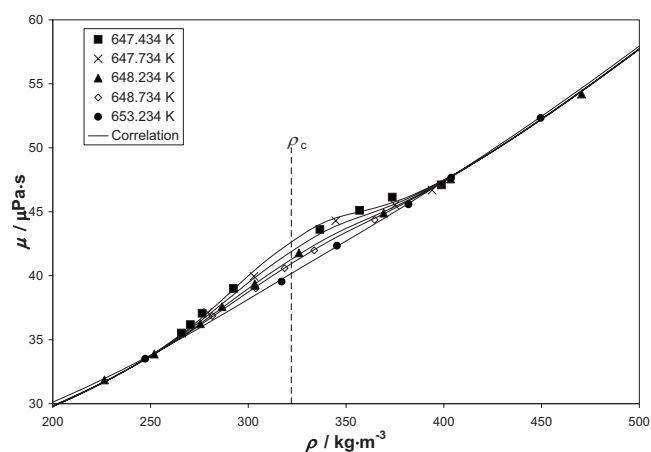


FIG. 8. The viscosity data obtained by Rivkin *et al.*⁴⁶ as a function of density with the density calculated from the IAPWS-95 equation and the temperatures converted to ITS-90 and shifted by 0.051 K. The curves represent the present correlation equation for the viscosity in the critical region.

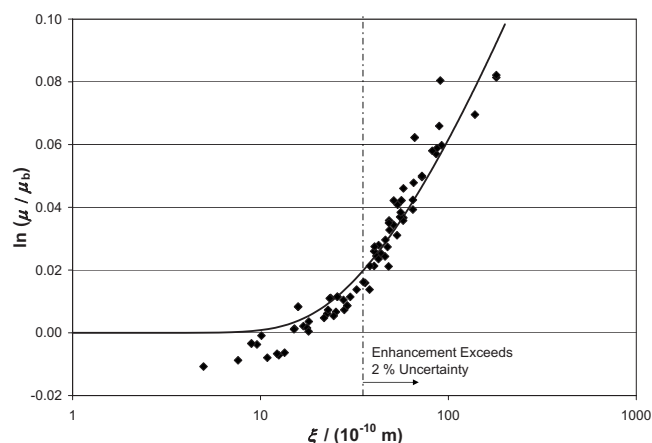


FIG. 9. Logarithm of the multiplicative critical viscosity enhancement μ/μ_b plotted as a function of the correlation length ξ .

cal enhancement of the viscosity is significant only in a very small region of temperatures and densities around the critical point. Although the viscosity is infinite exactly at the critical point, the enhancement term,

$$\bar{\mu}_2 = \exp(x_\mu Y) \quad (33)$$

in Eq. (19), contributes an amount greater than the uncertainty of 2% of our correlating equation only at values of ξ larger than $\xi = 3.51$ nm. This condition is satisfied only at temperatures and densities within the following boundaries:

$$645.91 \text{ K} < T < 650.77 \text{ K},$$

$$245.8 \text{ kg m}^{-3} < \rho < 405.3 \text{ kg m}^{-3}. \quad (34)$$

Both the curve where $\bar{\mu}_2 = 1.02$ and the region given by Eq. (34) are shown in Fig. 10. Note that the function Y is defined for two different ranges of correlation length ξ : for $0 \leq \xi \leq 0.3817016416$ nm, Eq. (26) should be used, while for $\xi > 0.3817016416$ nm, Eq. (20) applies. In addition, when $\Delta\bar{\chi}$ calculated by Eq. (28) is less than zero, it must be set to zero for calculations to proceed. Furthermore, due to the numerical implementation of the equation of state, the calculated singularity in the first derivative in Eq. (28) may not occur exactly at T_c and ρ_c , as it should. Therefore, depending on the software used, calculated values of $\bar{\mu}_2$ may behave unphysically at points extremely close to the critical

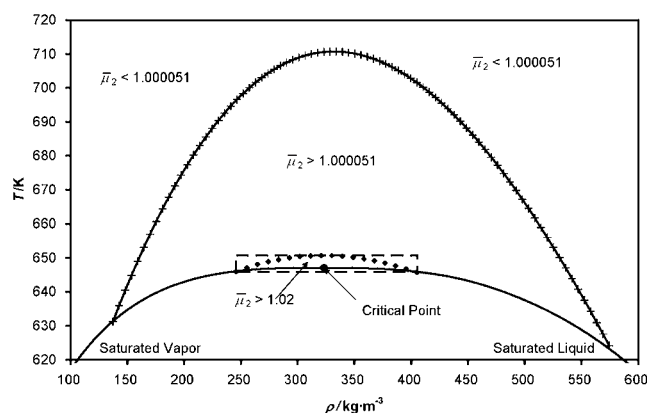


FIG. 10. Temperature and density regions where the viscosity enhancement $\bar{\mu}_2$ exceeds 1.000 051 and 1.02.

point (approximately within 0.01 kg m^{-3} of ρ_c on the critical isotherm). The formulation should be used with caution in this very small region.

3.4. Simplified Correlation

Because the critical enhancement of the viscosity is insignificant except in a small region around the critical point [described approximately by Eq. (34)], complexity and computing time may be reduced by omitting the critical enhancement for applications outside this region. This can be done by setting $\bar{\mu}_2 = 1$. If a calculation is performed that uses the critical enhancement, Eq. (33), near the critical point but uses $\bar{\mu}_2 = 1$ far from the critical point, some discontinuity is inevitable. However, this discontinuity is less than 0.0051% for single-phase states outside a region near the critical point bounded by the equation

$$T/(1 \text{ K}) = \sum_{i=0}^3 a_i [\rho/(1 \text{ kg m}^{-3})]^i, \quad (35)$$

where $a_0 = 457.95895935062$, $a_1 = 1.68077273385305$, $a_2 = -3.24405775203984 \times 10^{-3}$, and $a_3 = 1.43032446173023 \times 10^{-6}$. Equation (35) is also shown in Fig. 10 relative to the location of the critical point.

3.5. Computer-Program Verification

Tables 6 and 7 are provided to assist the user in computer-program verification. The viscosity calculations are based on the tabulated temperatures and densities.

3.6. Recommendation for Industrial Applications

For industrial applications where greater computing speed is needed, it is recommended that the viscosity be calculated from

$$\bar{\mu} = \bar{\mu}_b = \bar{\mu}_0(\bar{T}) \times \bar{\mu}_1(\bar{T}, \bar{\rho}), \quad (36)$$

with $\bar{\mu}_0(\bar{T})$ as specified in Sec. 3.1 and with $\bar{\mu}_1(\bar{T}, \bar{\rho})$ as specified in Sec. 3.2. In addition, the IAPWS Industrial Formulation for the Thermodynamic Properties of Water and

TABLE 5. Critical-region constants

Constant	Value
x_μ	0.068
q_C^{-1}	1.9 nm
q_D^{-1}	1.1 nm
ν	0.630
γ	1.239
ξ_0	0.13 nm
Γ_0	0.06
\bar{T}_R	1.5

TABLE 6. Sample points for computer-program verification of the correlating equation, Eq. (2), with $\bar{\mu}_2=1$

T (K)	ρ (kg m ⁻³)	μ (μPa s)
298.15	998	889.735 100
298.15	1200	1437.649 467
373.15	1000	307.883 622
433.15	1	14.538 324
433.15	1000	217.685 358
873.15	1	32.619 287
873.15	100	35.802 262
873.15	600	77.430 195
1173.15	1	44.217 245
1173.15	100	47.640 433
1173.15	400	64.154 608

Steam,^{155,156} known as IAPWS-IF97, should be used to determine the density for use in Eq. (36) when the state point is defined by the temperature and pressure or other state variables. Physically, this means that for industrial applications the critical viscosity enhancement can be neglected and the viscosity μ can be identified with the background viscosity μ_b , defined by Eq. (29), everywhere including in the near-critical region.

With this recommended industrial formulation for the viscosity of H₂O, the error introduced is smaller than the uncertainty of the full viscosity formulation, given by Eq. (2), provided the point is within the range of validity of IAPWS-IF97, except for points close to and inside the near-critical region described by Eq. (34). Deviations between the viscosities calculated from the industrial viscosity formulation and the complete viscosity formulation are shown in Fig. 11. The region of densities and temperatures where the deviations exceed 2% is very small and may in practice be ignored for industrial applications. Although it would be possible, in principle, to get an estimate for the critical-viscosity-enhancement factor in Eq. (2) by calculating the thermodynamic properties in Eq. (33) for $\bar{\mu}_2$ with IAPWS-IF97, for applications where an accurate estimate of the critical enhancement of the viscosity is needed, it is recommended that the IAPWS-95 formulation for the thermodynamic properties of H₂O be used.

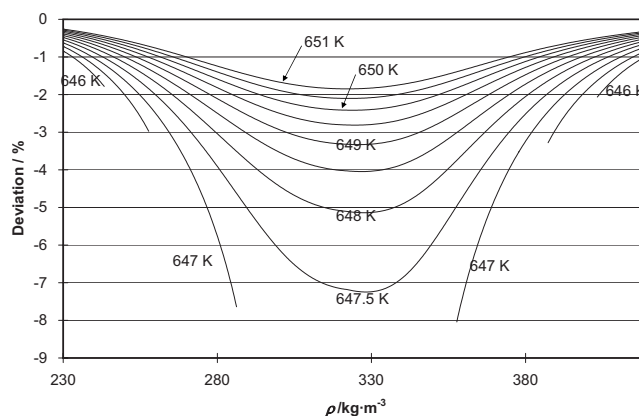
3.7. Liquid H₂O at 0.1 MPa

It is useful to have simplified correlating equations for the properties of liquid water at atmospheric pressure with un-

TABLE 7. Sample points for computer-program verification of the correlating equation, Eq. (2), in the region near the critical point

T (K)	ρ (kg m ⁻³)	ξ (nm)	$\bar{\mu}_2$	μ (μPa s)
647.35	122	0.309 247	1.000 002 89 ^a	25.520 677
647.35	222	1.571 405	1.003 751 20	31.337 589
647.35	272	5.266 522	1.034 167 89	36.228 143
647.35	322	16.590 209	1.091 904 40	42.961 579
647.35	372	5.603 768	1.036 658 71	45.688 204
647.35	422	1.876 244	1.005 963 32	49.436 256

^aCorrelation length $\xi < 0.381\,701\,641\,6$ nm so Y is evaluated from Eq. (26).

FIG. 11. Deviations $(\mu_{\text{Eq. (36)}} - \mu_{\text{Eq. (2)}})/\mu_{\text{Eq. (2)}}$ along selected isotherms.

certainties no greater than those of the more complex formulations that cover wide ranges of temperature and pressure. To this end, Pátek *et al.*^{157,158} provided formulations for the properties, including viscosity, of liquid water as a function of absolute temperature T at a standard pressure of 0.1 MPa. Details on the background, development, and validation of these correlations are presented in Ref. 157; we present only the viscosity correlation here.

The dimensionless viscosity $\bar{\mu}$ of liquid water at 0.1 MPa is described by

$$\bar{\mu} = \sum_{i=1}^4 a_i (\tilde{T})^{b_i}, \quad (37)$$

where $\tilde{T} = T/(300 \text{ K})$ and a_i and b_i are coefficients and exponents given in Table 8. Equation (37) is recommended for use in the following temperature range:

$$253.15 \text{ K} \leq T \leq 383.15 \text{ K}, \quad (38)$$

and should not be extrapolated outside these limits. At some temperatures within this range, the equilibrium phase at 0.1 MPa is a solid or a vapor, and at these conditions Eq. (37) describes the viscosity of the metastable liquid phase. The uncertainty of Eq. (37) is 1% for the stable liquid region. No uncertainty estimate is given for the metastable regions, but the agreement with available data for the subcooled region is within 5% as discussed in Sec 4.2 of this paper. Equation (37) also reproduces the International Organization for Standardization (ISO) recommended value of the viscosity at 20 °C (293.15 K) and standard atmospheric pressure within the number of digits given in Ref. 124; it also agrees

TABLE 8. Coefficients a_i and b_i in Eq. (37) for the viscosity of liquid water at 0.1 MPa

i	a_i	b_i
1	280.68	-1.9
2	511.45	-7.7
3	61.131	-19.6
4	0.459 03	-40.0

with all values from 288.15 K to 313.15 K at atmospheric pressure in Ref. 124 within the stated uncertainty of 0.17% at 293.15 K.

4. Evaluation

In summary, the recommended formulation for the viscosity is given by Eq. (2):

$$\bar{\mu} = \bar{\mu}_0(\bar{T}) \times \bar{\mu}_1(\bar{T}, \bar{\rho}) \times \bar{\mu}_2(\bar{T}, \bar{\rho}).$$

The function $\bar{\mu}_0(\bar{T})$ is given by Eq. (11) with coefficients in Table 2. The function $\bar{\mu}_1(\bar{T}, \bar{\rho})$ is given by Eq. (12) with coefficients in Table 3. The function $\bar{\mu}_2(\bar{T}, \bar{\rho})$ is given by Eq. (33) as a function of $Y(\xi)$ defined by Eq. (26) for $0 \leq \xi \leq 0.381\,701\,641\,6$ nm and by Eq. (23) for $\xi > 0.381\,701\,641\,6$ nm with parameters in Table 5.

4.1. Comparisons with Experimental Data and Previous IAPWS Formulation

In order to evaluate performance, we compare the results of the new formulation, Eq. (2), as well as the previous IAPWS formulation for the viscosity,²⁷ with the experimental database. Comparisons with all sources in the experimental database are presented in Table 9, which gives the number of data points, estimated uncertainty of the data, average percentage deviation, AAD, standard deviation, and the maximum percentage deviation of each data source. Some points are extrapolations of the previous IAPWS correlation,²⁷ because they are outside of the recommended range of temperatures and densities. We define the percentage deviation as $P = 100 \times (\mu_{\text{exp}} - \mu_{\text{calc}}) / \mu_{\text{exp}}$, where μ_{exp} is the experimental value of the viscosity, and μ_{calc} is the value calculated from the present correlation, Eq. (2). The AAD is found with the expression $\text{AAD} = (\sum |P|) / n$, where the summation is over all n points; the average percentage deviation is $\text{AVG} = (\sum P) / n$, and the standard deviation is $\text{STDEV} = ([n \sum P^2 - (\sum P)^2] / n^2)^{1/2}$. As indicated in Table 9, the results of the new formulation and the previous IAPWS formulation for the viscosity²⁷ are in most cases comparable, with significant differences observed in only a few cases.

The first region where there are differences in the performance of the previous IAPWS formulation for the viscosity²⁷ and this work is in the low-density gas phase, especially at densities below 0.25 kg m^{-3} and temperatures below 400 K. This is illustrated in Figs. 12–15. As pointed out by Teske *et al.*,³⁶ the previous IAPWS formulation for the viscosity²⁷ did not include the data set of Yasumoto⁷⁷ in the analysis, and the recent data of Teske *et al.*³⁶ were not available at the time, thus leaving room for improvement in this region. The present correlation was developed with both of these data sets and offers significant improvement in the representation of the data in this region. The availability of new dilute-gas data also allowed for some improvement in the representation of the initial-density viscosity coefficient $\mu^{(1)}$; this is shown in Fig. 16. The experimental values obtained by the

procedure discussed in Sec. 3.1 are shown in Fig. 16 along with the previous IAPWS correlation, the present work, and the correlation of Teske *et al.*³⁶

In both the correlation of Teske *et al.*³⁶ and in the present correlation, $\mu^{(1)}$ approaches zero in the high-temperature limit; the previous IAPWS formulation for the viscosity²⁷ incorrectly yields $\mu^{(1)}$ diverging to negative infinity.

It also is interesting to compare the high-temperature extrapolation behavior of the present equation with other formulations for the viscosity of water substance in the limit of zero density, such as the previous IAPWS formulation for the viscosity,²⁷ the equation proposed by Alexandrov *et al.*,¹⁵⁹ and the recent formulation of Quiñones-Cisneros and Deiters.¹⁶⁰ The correlation of Teske *et al.*³⁶ is not considered here since it is for use in the temperature range 273–1350 K and was not intended for extrapolation. Figure 17 displays the zero-density viscosity from 255 to 2500 K. The empirical equations presented in this work and in the work of Quiñones-Cisneros and Deiters¹⁶⁰ are in close agreement (and are indistinguishable in Fig. 17) and both agree with the high-temperature recommended values of Fokin and Kalashnikov¹⁶¹ to within the estimated uncertainty of the values. However, very recently new calculations have become available¹⁶² based on the potential hypersurface of Bukowski *et al.*¹⁶³ that show somewhat lower viscosities. In the absence of experimental data, we recognize that there is significant uncertainty in the very-high-temperature extrapolation behavior of the correlation.

A second region where differences between the performance of previous IAPWS formulation for the viscosity²⁷ and the present correlation are observed is in the liquid phase at low temperatures and elevated pressures, as shown in Figs. 18 and 19. The previous IAPWS formulation for the viscosity²⁷ shows significant deviations in this region, especially for the data of Harris and Woolf,^{31,32} Harlow,^{39,66} and Isdale and Spence.⁴¹ When the correlation of Watson *et al.*¹⁹ was formulated, data at high pressures were not incorporated into the development of the equation, and the range of validity for temperatures less than 150°C extended only to 500 MPa. In this work, we included data up to 1 GPa in our analysis, allowing an improvement over the previous formulation in this region, as shown in Fig. 19. We note here that we became aware of new measurements at very high pressures,^{44,45} up to 25 GPa, after the development of our equation, and comparisons indicate that the present work is not applicable to pressures above 1 GPa. Future work on this region is needed.

The viscosity of liquid water at ambient conditions is of significant interest. The ISO (Ref. 124) has published recommended values for the viscosity of liquid water at reference temperatures from 15 to 40°C . Figures 20 and 21 show comparisons of the two formulations for water at atmospheric pressure. ISO (Ref. 124) gives an estimated relative uncertainty for the viscosity of water at 20°C and 0.101 325 MPa (1.0016 mPa s) of 0.17%. Both the previous IAPWS formulation for the viscosity²⁷ and the present correlation represent the reference value to within this uncer-

TABLE 9. Summary of comparisons of Eq. (2) with experimental data and of the previous IAPWS formulation for the viscosity with experimental data

First author	Uncertainty ^a (%)	Number of data	Present work				Previous IAPWS formulation ²⁷			
			AAD	AVG	STDEV ^c	MAX	AAD	AVG	STDEV ^c	MAX
White ⁴⁷	0.5	11	0.33	−0.17	0.39	−0.86	0.31	−0.13	0.36	−0.76
Coe ⁴⁸	0.3	3	0.03	−0.03	0.009	−0.04	0.05	−0.05	0.005	−0.06
Hardy ⁴⁹	0.5	10	0.07	0.03	0.07	0.13	0.04	−0.01	0.05	−0.09
Swindells ⁵⁰	0.1	1	0.00	0.00	n.a.	0.00	0.00	0.00	n.a.	0.00
Weber ⁵¹	0.3	9	0.03	−0.01	0.04	0.07	0.04	−0.02	0.04	−0.08
Roscoe ⁵²	0.1	1	0.06	0.06	n.a.	0.06	0.06	0.06	n.a.	0.06
Ravikovich ⁵³	2	7	1.21	0.82	0.91	1.50	1.18	0.77	0.92	1.47
Malyarov ⁵⁴	0.1	1	0.16	0.16	n.a.	0.16	0.16	0.16	n.a.	0.16
Shifrin ⁵⁵	3 ^b	114	1.23	−0.81	1.34	−3.95	1.22	−0.76	1.36	−3.99
Kestin ⁵⁶	2 ^b	19	0.47	0.43	0.46	1.33	0.46	0.42	0.46	1.34
Whitelaw ⁵⁷	4 ^b	56	3.16	−1.78	10.44	−76.80	3.23	−1.51	10.54	−77.08
Moszynski ⁵⁸	2	66	1.35	−0.21	1.43	3.10	1.31	−0.18	1.39	2.89
Mayinger ⁵⁹	2–3 ^b	84	2.87	2.06	3.36	12.21	3.05	2.33	3.40	12.33
Hallett ⁶⁰	0.3	20	0.55	−0.02	0.69	1.77	0.47	0.17	0.53	−1.17
Kestin ⁶¹	0.8	39	0.49	0.37	0.68	2.04	0.49	0.35	0.66	1.77
Latto ⁶²	3 ^b	555	1.12	0.12	1.41	6.41	1.08	0.26	1.35	6.43
Tanaka ⁶³	2–3 ^b	152	2.00	1.44	2.26	10.73	1.98	1.52	2.27	10.42
Dudziak ³⁷	5	91	3.99	0.62	4.73	12.80	4.31	1.69	4.74	12.47
Rivkin ⁶⁴	1.5	41	0.42	0.09	0.60	1.99	0.42	0.09	0.59	1.92
Horne ³⁸	2	141	1.17	0.55	1.32	3.38	1.32	0.94	1.34	3.70
Agae ⁶⁵	1	598	0.33	0.03	0.41	−2.05	0.32	0.18	0.35	−1.48
Harlow ³⁹ (also Bett ⁶⁶)	2	125	0.57	0.09	0.77	3.15	3.10	2.93	5.58	23.90
Korosi ⁶⁷	0.3	9	0.22	−0.13	0.27	−0.62	0.18	−0.14	0.22	−0.54
Rivkin ⁶⁸	1	127	0.63	0.03	0.97	4.82	0.67	0.21	1.04	5.64
Sato ⁶⁹	1.5 ^b	17	0.29	−0.06	0.37	−0.76	0.30	−0.11	0.37	−0.77
Kerimov ⁷⁰	1	224	0.29	0.11	0.36	−1.23	0.32	0.24	0.32	1.50
Korson ⁷¹	0.3	13	0.11	0.01	0.14	0.31	0.11	−0.03	0.13	0.22
Nagashima ⁷²	2–3 ^b	251	1.87	0.81	2.19	6.09	1.86	0.82	2.19	6.06
Stanley ⁴⁰	4	93	1.60	−1.08	1.79	−4.68	1.49	−0.78	1.76	−4.33
Dumas ⁷³	1	4	0.84	0.84	0.28	1.29	0.84	0.84	0.28	1.29
Rivkin ⁷⁴	1	68	0.47	−0.36	0.42	−1.23	0.53	−0.40	0.49	−1.33
Rivkin ⁷⁵	1	94	0.34	−0.07	0.64	−3.84	0.35	−0.03	0.65	−3.94
Sato ⁷⁶	1.5 ^b	79	0.33	0.16	0.38	−0.94	0.36	0.17	0.41	1.02
Yasumoto ⁷⁷	0.5	15	0.35	−0.12	0.46	−1.16	2.12	−2.12	0.55	−3.76
Eicher ⁷⁸	0.3	13	0.05	0.01	0.05	0.09	0.05	0.02	0.05	0.09
Mashovets ⁷⁹	2	11	0.41	0.07	0.52	1.11	0.41	0.17	0.51	1.17
Penkina ⁸⁰	3	7	1.22	1.17	1.20	3.78	1.33	1.30	1.23	4.02
Rivkin ⁸¹	1	38	0.39	−0.33	0.40	−1.33	0.26	−0.18	0.30	−0.81
Rivkin ⁸²	1	119	0.46	−0.37	0.44	−1.81	0.53	−0.40	0.52	−2.13
Rivkin ⁸³	1	59	1.12	−1.06	0.65	−2.26	0.68	−0.53	0.65	−2.50
Timrot ⁸⁴	0.4 ^b	46	0.23	0.11	0.25	0.56	0.14	0.03	0.20	−0.58
Kingham ⁸⁵	0.05	20	0.02	−0.02	0.02	−0.06	0.02	−0.01	0.02	−0.05
Kudish ⁸⁶	0.05	5	0.04	0.04	0.04	0.11	0.04	0.03	0.04	0.11
Nagashima ⁸⁷	1.5	53	1.35	−0.64	1.46	−3.05	1.33	−0.55	1.48	3.00
Rivkin ⁴⁶	1	78	0.50	−0.04	0.65	−2.3	0.54	−0.14	0.69	−2.15
Rivkin ⁸⁸	1	119	0.47	−0.38	0.44	−1.81	0.54	−0.41	0.52	−2.13
Isdale ⁴¹	2	22	0.70	−0.64	0.69	−1.91	4.73	4.48	6.75	21.74
Kestin ⁸⁹	0.3	70	0.13	−0.04	0.16	−0.56	0.09	0.07	0.08	0.36
Oltmann ⁹⁰	4	96	1.08	0.95	1.51	6.48	1.10	1.02	1.47	6.48
DeFries ⁴²	2	46	0.98	−0.39	1.21	3.85	1.05	−0.71	1.13	−3.44
Osipov ⁹¹	3	28	6.44	5.01	7.83	23.01	7.46	6.22	9.00	26.99
Kestin ⁹²	0.7 ^b	111	0.19	−0.04	0.25	0.91	0.19	−0.05	0.24	0.86
Kubota ⁹³	2	32	0.12	0.00	0.15	0.38	0.19	0.12	0.20	0.45
Agayev ⁹⁴	1.5	166	0.59	0.02	0.84	3.90	0.58	0.24	0.85	4.81
Goncalves ⁹⁵	0.2	6	0.03	0.03	0.02	0.07	0.01	0.00	0.02	−0.03
Kestin ⁹⁶	0.3	78	0.20	0.03	0.27	−0.78	0.16	0.01	0.22	−0.70

TABLE 9. Summary of comparisons of Eq. (2) with experimental data and of the previous IAPWS formulation for the viscosity with experimental data—Continued

First author	Uncertainty ^a (%)	Number of data	Present work				Previous IAPWS formulation ²⁷			
			AAD	AVG	STDEV ^c	MAX	AAD	AVG	STDEV ^c	MAX
Baldauf ⁹⁷	3	3	1.53	0.64	1.48	2.25	1.52	0.63	1.48	2.23
Collings ⁹⁸	0.2	12	0.05	0.05	0.03	0.14	0.03	0.02	0.03	0.06
James ⁹⁹	1	8	0.07	0.01	0.11	0.21	0.06	−0.01	0.08	−0.18
Naake ¹⁰⁰	1	18	0.38	−0.38	0.34	−0.83	0.39	−0.19	0.43	−0.84
Kestin ¹⁰¹	0.5	74	0.20	−0.10	0.24	−0.79	0.16	−0.04	0.21	−0.72
Kozlov ¹⁰²	n.p.	6	5.08	1.93	6.54	11.40	5.10	1.89	6.57	11.39
Tanaka ¹⁰³	2	47	0.19	−0.10	0.22	−0.48	0.07	0.06	0.07	0.31
Berstad ¹⁰⁴	0.05	18	0.13	−0.13	0.02	−0.16	0.13	−0.13	0.02	−0.17
Melzer ¹⁰⁵	1	3	1.96	1.96	1.06	2.92	1.95	1.95	1.07	2.91
Ramkumar ¹⁰⁶	0.1	5	0.46	0.39	0.60	1.48	0.43	0.33	0.58	1.39
Mazurkiewicz ¹⁰⁷	1	1	0.02	−0.02	n.a.	−0.02	0.02	−0.02	n.a.	−0.02
Lee ¹⁰⁸	1	3	0.46	0.46	0.13	0.65	0.43	0.43	0.11	0.59
Rosenberger ¹⁰⁹	1	1	0.80	−0.80	n.a.	0.80	0.81	−0.81	n.a.	−0.81
Assael ¹¹⁰	0.5	19	0.23	−0.09	0.26	−0.55	0.21	−0.05	0.24	−0.49
Olive ¹¹¹	0.5	1	0.19	0.19	n.a.	0.19	0.17	0.17	n.a.	0.17
Wode ¹¹²	0.5	5	0.08	0.08	0.04	0.14	0.06	0.06	0.05	0.14
Lee ¹¹³	1.5	3	0.38	0.38	0.05	0.45	0.34	0.34	0.04	0.39
Först ⁴³	2	95	2.82	−2.34	4.04	−16.60	2.65	−2.15	3.36	−14.34
Abdulagatov ³⁰	1.5	27	0.55	0.26	0.59	−1.10	0.51	0.35	0.52	1.09
Abdulagatov ³³	1.5	25	0.28	−0.15	0.32	−0.82	0.27	−0.04	0.32	0.57
Harris ^{31,32}	1	109	0.45	0.08	0.56	−1.53	0.92	−0.52	1.23	−4.04
Abdulagatov ³⁴	1.5	28	0.44	−0.33	0.40	−1.03	0.40	−0.24	0.42	0.90
Abdulagatov ³⁵	1.5	25	0.27	−0.18	0.31	−0.82	0.24	−0.08	0.29	−0.54
Teske ³⁶	0.2–0.3	109	0.12	0.03	0.14	−0.44	0.46	−0.41	0.62	−2.17

^an.p.: uncertainty not provided in the source reference.

^bUncertainty as recommended in by Watson *et al.*¹⁹

^cn.a.: not applicable.

tainty. In addition to liquid water, the two formulations also are in excellent agreement for steam over a wide range of densities, as shown in Figs. 22 and 23.

4.2. Range and Uncertainty Estimates for the Correlation

The domain of validity of the correlation encompasses all thermodynamically stable fluid states in the following ranges of pressure p and temperature T :

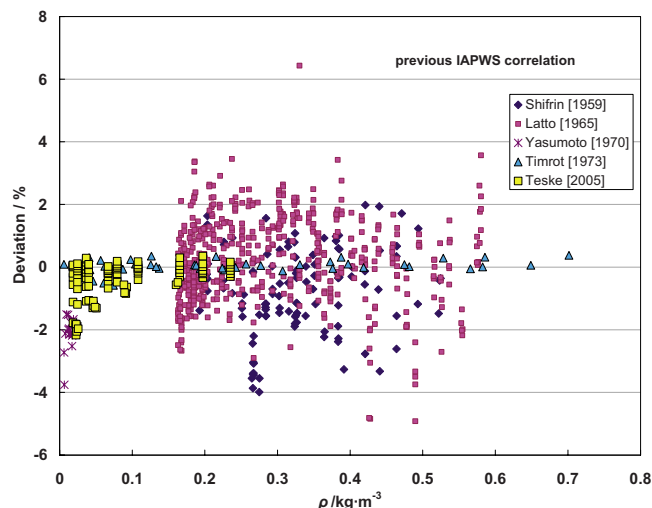


FIG. 12. (Color online) Percentage deviations of the experimental data from the previous IAPWS formulation for the viscosity²⁷ for low-density water vapor as a function of density.

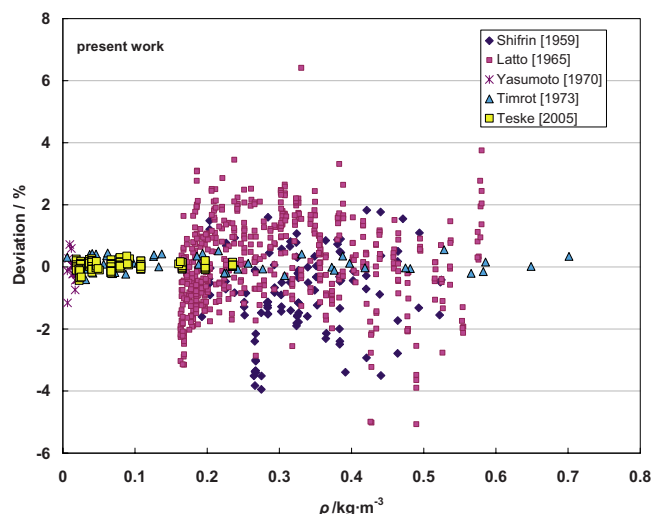


FIG. 13. (Color online) Percentage deviations of the experimental data from the present correlation for low-density water vapor as a function of density.

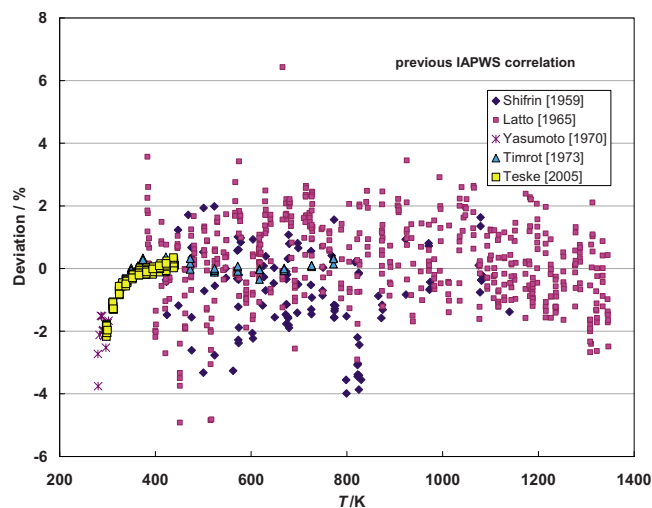


FIG. 14. (Color online) Percentage deviations of the experimental data from the previous IAPWS formulation for the viscosity²⁷ for low-density water vapor as a function of temperature.

$$\begin{aligned}
 0 < p < p_t \quad \text{and} \quad 273.16 \text{ K} \leq T \leq 1173.15 \text{ K}, \\
 p_t \leq p \leq 300 \text{ MPa} \quad \text{and} \quad T_m(p) \leq T \leq 1173.15 \text{ K}, \\
 300 \text{ MPa} < p \leq 350 \text{ MPa} \quad \text{and} \quad T_m(p) \leq T \\
 \leq 873.15 \text{ K}, \\
 350 \text{ MPa} < p \leq 500 \text{ MPa} \quad \text{and} \quad T_m(p) \leq T \\
 \leq 433.15 \text{ K}, \\
 500 \text{ MPa} < p \leq 1000 \text{ MPa} \quad \text{and} \quad T_m(p) \leq T \\
 \leq 373.15 \text{ K}.
 \end{aligned} \tag{39}$$

In Eq. (39), T_m is the pressure-dependent melting temperature and p_t is the triple-point pressure; both are given in Refs. 164 and 165. For general and scientific applications, the

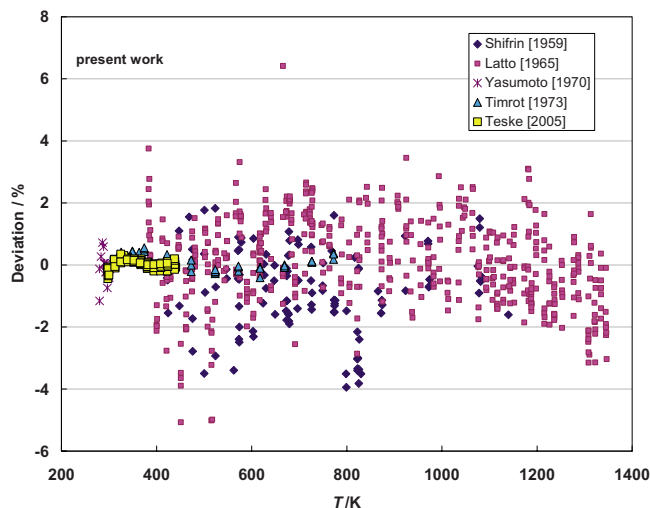


FIG. 15. (Color online) Percentage deviations of the experimental data from the present correlation for low-density water vapor as a function of temperature.

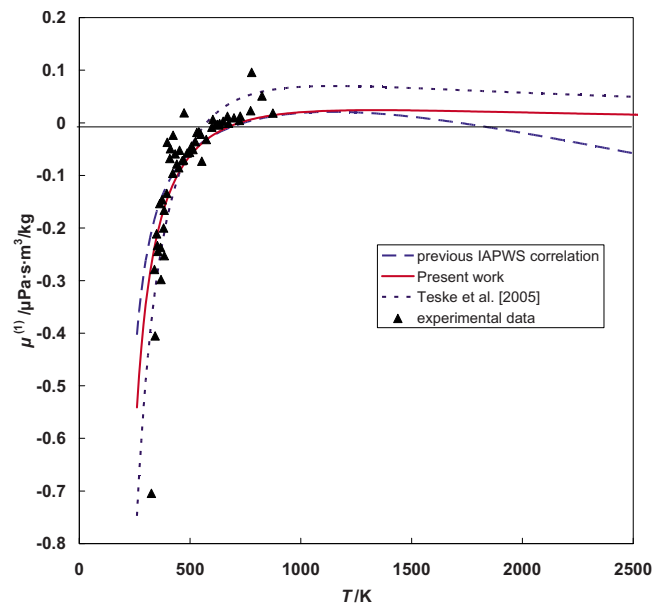


FIG. 16. (Color online) Temperature dependence of the initial-density viscosity coefficient $\mu^{(1)}$, Eq. (4).

IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use^{24,115} should be used to determine the densities used as input to Eq. (2) when the state point under consideration is defined by pressure and temperature or by other thermodynamic variables instead of density and temperature.

In addition, we can state the following about extrapolation of Eq. (2) outside the range of validity given above: (1) For vapor states at temperatures below the triple-point temperature of 273.16 K and pressures less than or equal to the sublimation pressure, the viscosity calculation is dominated by the dilute-gas term, and this behaves in a physically reasonable manner down to at least 250 K. (2) For stable fluid states outside the range of validity of Eq. (2) but within the range of validity of the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for

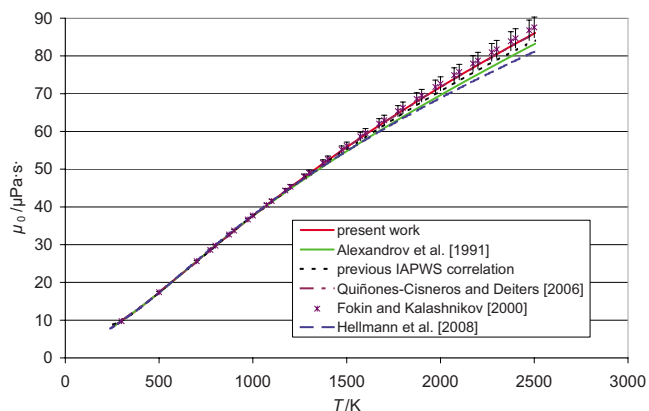


FIG. 17. (Color online) Comparison of extrapolation behavior at high temperatures of the proposed equation, of the previous IAPWS formulation for the viscosity,²⁷ and of the correlations of Alexandrov *et al.*,¹⁵⁹ and Quiñones-Cisneros and Deiters¹⁶⁰ with the recommended data of Fokin and Kalashnikov¹⁶¹ and with new calculations of Hellmann *et al.*¹⁶²

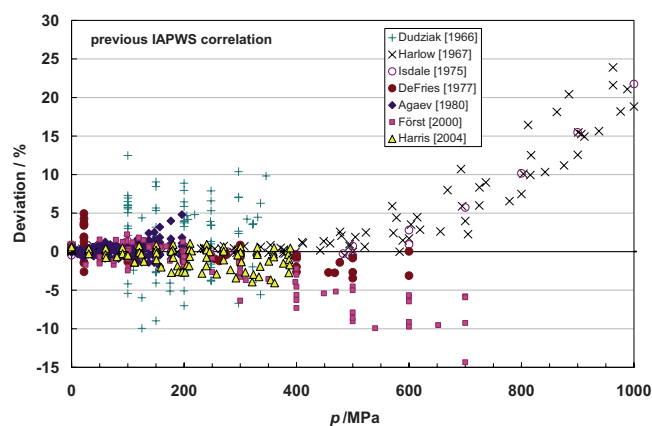


Fig. 18. (Color online) Percentage deviations of the experimental data from the previous IAPWS formulation for the viscosity²⁷ for elevated pressures as a function of pressure.

General and Scientific Use,^{24,115} the extrapolation behavior of Eq. (2) is physically reasonable. (3) At pressures above 1 GPa, the equation may not behave in a physically reasonable manner and the equation is not recommended for this region. (4) At high temperatures, the extrapolation of the dilute-gas portion of Eq. (2) is in agreement with the high-temperature recommended values of Fokin and Kalashnikov¹⁶¹ up to 2500 K. However, experimental data in this region are unavailable and there exists significant uncertainty in the very-high-temperature extrapolation behavior of the correlation. (5) For the metastable, subcooled liquid at atmospheric pressure, Eq. (2) is in fair agreement (within 5%) with available data^{47,60,78,91} down to 250 K.

For development of the estimates of uncertainty, we relied upon comparisons with the previous IAPWS formulation for the viscosity²⁷ and with a subset of the experimental database used to develop the correlation. The subset contained the data with the lowest uncertainties for specific regions in the phase diagram. When attempting to define an uncertainty band of, for example, 1%, it is appropriate to use only data that have been evaluated and found to have an uncertainty of no larger than 1%. Including data with an uncertainty of 4% in an attempt to establish a 1% uncertainty band is not mean-

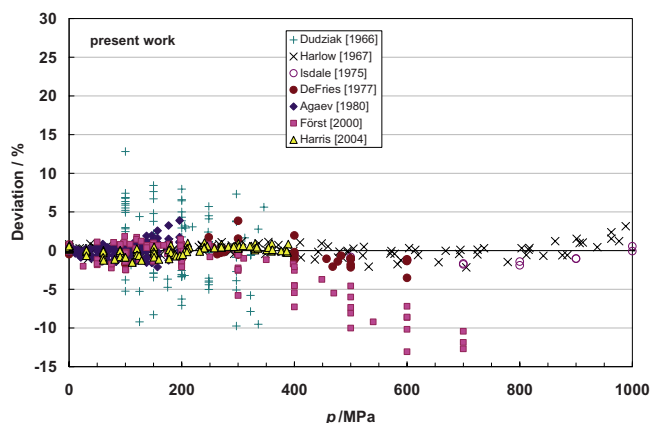


Fig. 19. (Color online) Percentage deviations of the experimental data from the present correlation for elevated pressures as a function of pressure.

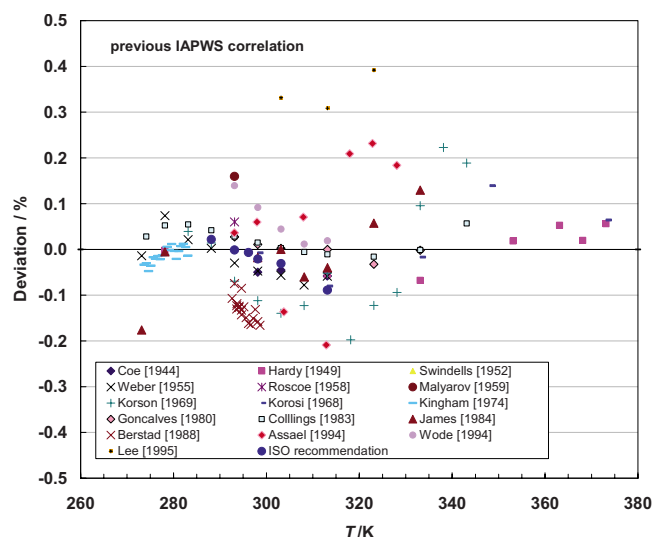


Fig. 20. (Color online) Percentage deviations of the experimental data from the previous IAPWS formulation for the viscosity²⁷ for liquid water at atmospheric pressure as a function of density.

ingful. However, one must be careful, since sets with large amounts of scatter may still provide useful information about mean trends. In addition, if a particular data set has a systematic offset, it was not used for the determination of the uncertainty, and outliers were removed as well to avoid skewing the results.

The uncertainties in this formulation are summarized in Fig. 24. The uncertainty estimates can be considered as estimates of a combined expanded uncertainty with a coverage factor $k=2$. Thus, the viscosity at any state point can be expressed as $\mu \pm \delta$, where δ is the applicable value in Fig. 24. The formulation reproduces the ISO recommended value of the viscosity at 20 °C (293.15 K) and standard atmospheric pressure (0.101 325 MPa) within the number of digits given in Ref. 124; it also agrees with all values from

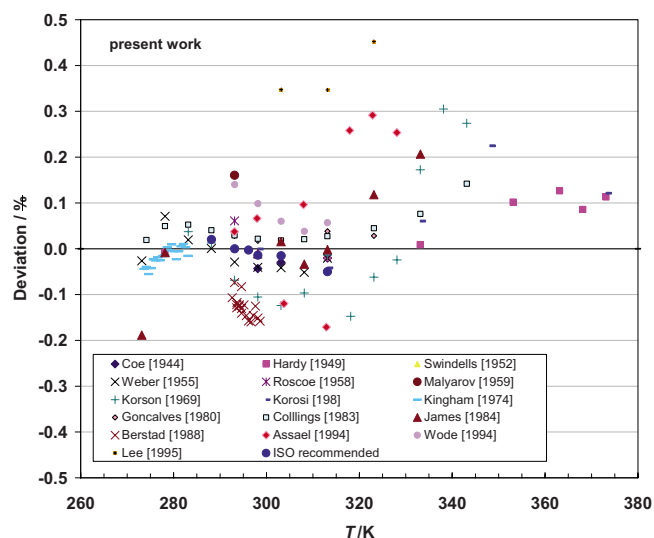


Fig. 21. (Color online) Percentage deviations of the experimental data from the present correlation for liquid water at atmospheric pressure as a function of density.

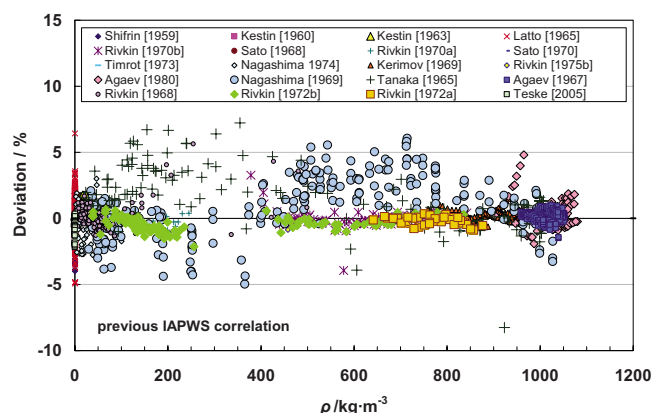


FIG. 22. (Color online) Percentage deviations of the experimental data from the previous IAPWS formulation for the viscosity²⁷ for steam, as a function of density.

288.15 to 313.15 K at atmospheric pressure in Ref. 124 within the stated uncertainty of 0.17% at 293.15 K.

For subregion 1 in Fig. 24, the highest pressures and temperatures below 373 K, with an estimated uncertainty of 3%, we considered the data from nine sources in this region^{31,38,39,41,42,65,94,100,103} that had estimated uncertainties of 3% or less. We did not consider the data of Först *et al.*,⁴³ because they appear to have unexplained systematic deviations from other data in this region. The data set for region 1 contained 443 points with a standard deviation of 1.07%, thus establishing that 3% as an uncertainty band at a 95% confidence level (1.96σ) is conservative. Additional details, in the form of box-and-whisker diagrams¹⁶⁶ of the data sets used for uncertainty analysis can be found in the supplementary information.¹⁶⁷

For subregion 2, the highest pressures and temperatures above 373 K, with an estimated uncertainty of 7%, we considered the data from six sources^{37,70,72,81,94,100} with estimated experimental uncertainties of less than 7%. The work of Dudziak and Franck³⁷ contains both raw experimental data and a table of smoothed values. For our uncertainty analysis, we used the smoothed data rather than the raw data, which exhibit a very large scatter. The resulting data for the

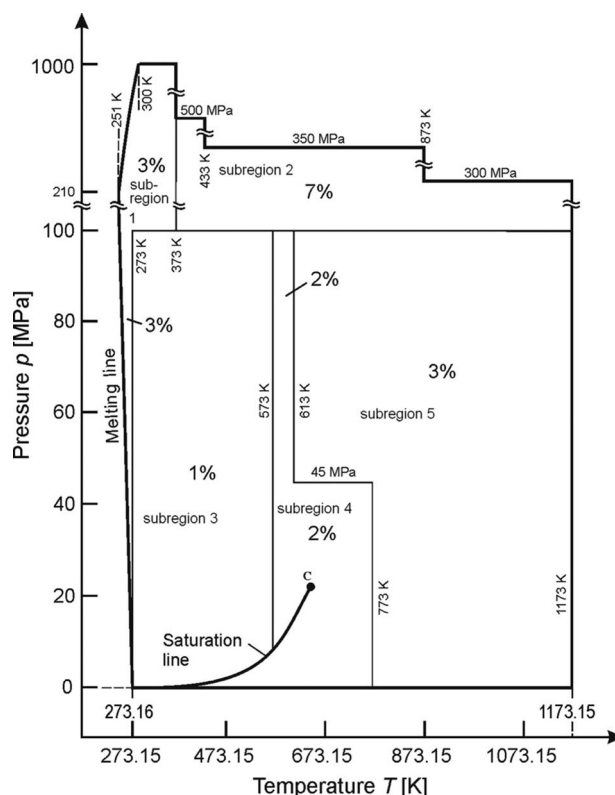


FIG. 24. Estimated uncertainties for Eq. (2).

region 2 set contained 131 data points and a standard deviation of 2.42%; thus at a 95% confidence level, the uncertainty band is 5%. To be conservative, we increased this to 7%, because the analysis with raw data resulted in higher uncertainties. Additional experimental data in this region would be helpful in further improving the correlation and establishing smaller uncertainty estimates.

For subregion 3, the liquid region with temperatures to 573 K and pressures to 100 MPa, with an estimated uncertainty of 1%, we considered the data from 41 sources^{31,47–52,54,64,65,67,70,71,73,75,78,81,82,85,86,88,89,92,94–101,104–113} with estimated uncertainties of less than 1%. The set comprised 1419 points with a standard deviation of 0.38%. We conservatively estimated the uncertainty level to be 1% at a 95% confidence level.

For subregion 4, which includes the critical point, with an estimated uncertainty of 2%, we considered data from 20 sources^{30,33–36,46,56,61,64,68,69,74,75,77,81–84,88} with uncertainties of 2% or less. The data of Nagashima and Tanishita⁷² between 300 °C and the critical point were rejected in favor of the measurements of Rivkin, based on comments by Watson *et al.*¹⁹ In the immediate critical region, the re-evaluated data of Rivkin presented in Table 4 were used instead of the original values. The resulting set contains 1014 data points with a standard deviation of 0.68%, and our estimated uncertainty at a 95% confidence level is 2%.

For subregion 5, temperatures above 613 K for pressures from 45 to 100 MPa and all pressures up to 100 MPa for the temperature range from 773 to 1173 K, with an estimated

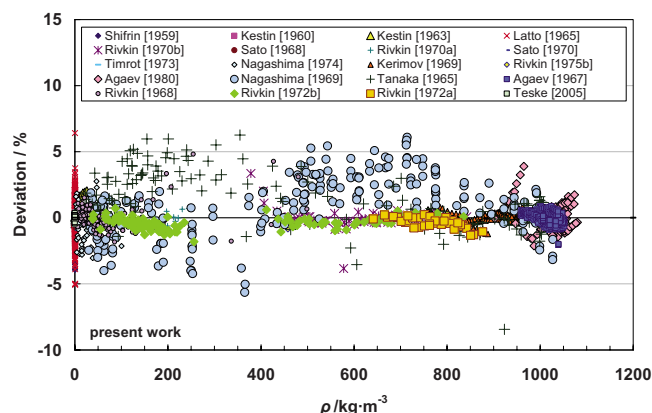


FIG. 23. (Color online) Percentage deviations of the experimental data from the present correlation for steam as a function of density.

uncertainty of 3%, we considered data from eight sources^{55,62,72,75,76,81,83,87} with uncertainties of 3% or less. The data of Mayinger⁵⁹ and Tanaka *et al.*⁶³ both have systematic deviations from the other sets—as the pressure increases, in particular, above 30 MPa, the data of Tanaka *et al.*⁶³ and of Mayinger⁵⁹ are systematically higher than those of Nagashima and Tanishita.⁷² Nagashima⁶ noted that some of this could be caused by unfavorable flow conditions, when the kinematic viscosity is low and the flow could be turbulent, especially in the metal capillaries used, because the internal walls cannot be made satisfactorily smooth. We therefore removed the data of both Tanaka *et al.*⁶³ and Mayinger⁵⁹ from consideration for the uncertainty estimate. With this set of data (a total of 377 points), the standard deviation was found to be 1.5%, and thus for a 95% confidence level (1.96σ), we obtain a 3% estimated uncertainty, which agrees with that given by Watson *et al.*¹⁹ for the previous IAPWS formulation for the viscosity.²⁷

5. Discussion

The international task group, consisting of members affiliated with IAPWS and the IUPAC transport properties committee (now established as the International Association for Transport Properties), has completed its examination of the data, theory, and models most appropriate for describing the viscosity of water over broad ranges of temperature and pressure. The resulting Eq. (2), with subsidiary equations and the accompanying tables of coefficients and parameters, should allow calculation of the viscosity of water for most purposes according to international consensus and within uncertainty bounds achievable with current information. As is evident in Fig. 24, there still are regions (especially subregion 2) where the availability of new experimental data with low uncertainties could lead to improvements in future representations of the viscosity surface of water. Furthermore, improvements in theory may better elucidate the high-temperature extrapolation behavior.

The form of Eq. (2) and the general forms of the constituent factors are very similar to those established in the earlier standard formulation described in Ref. 27. However, the new equation provides an improved theoretical description of the critical region, allows calculations in a broader range of state variables, considers an expanded set of experimental data, and is consistent with the most recent consensus formulation for the thermodynamic properties of water. The comparisons of Sec. 4 provide support for the uncertainty estimates over the full range of applicability of the correlation.

The current IAPWS Release on the Viscosity of Ordinary Water Substance (available at <http://www.iapws.org>) provides a concise description of the correlating equations for potential users. This paper provides a detailed explanation of the formulation.

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