Reference Correlations for Thermophysical Properties of Liquid Water at 0.1 MPa

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Simple but highly accurate correlations have been developed for the thermodynamic properties (including density, heat capacity, and speed of sound), viscosity, thermal conductivity, and static dielectric constant of liquid water as a function of temperature at a pressure of 0.1 MPa. The calculations may be simply extended to a pressure range from the saturation pressure to 0.3 MPa. The temperature range covered in most cases is from 253.15 to 383.15 K; this includes some temperatures where liquid water is metastable. These correlations are designed to reproduce the best available data, which in most cases are described by formulations issued by the International Association for the Properties of Water and Steam (IAPWS). The equations presented here are simple enough to be used in applications such as spreadsheets. They provide a convenient alternative to the more complicated IAPWS formulations in cases where only liquid properties at near-atmospheric pressure are of interest without increasing the uncertainty beyond that of the more complex formulations. © *2009 American Institute of Physics.*
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CONTENTS

List of Tables

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1. Introduction

Water is probably the most important chemical substance in science and industry. International efforts to produce standardized, high-accuracy values of water's thermophysical properties began in the 1920s; these efforts are now organized by the International Association for the Properties of Water and Steam (IAPWS).

IAPWS has produced comprehensive formulations for general and scientific uses for a variety of properties, including the thermodynamic properties,[1,2] the viscosity,[3,4] the thermal conductivity,[5,6] and the static dielectric constant.[7,8] These formulations are designed to describe (within the uncertainty of available experimental data) the behavior of vapor, liquid, and supercritical water over wide ranges of temperature and pressure.

However, the comprehensive IAPWS formulations are not simple to use (unless one obtains software where someone else has done the work of implementation). For example, the formulation for thermodynamic properties,[1,2] commonly known as IAPWS-95, is a fundamental equation for the Helmholtz energy as a function of temperature and density, containing eight terms in the ideal-gas part and 56 terms, some rather complicated, in the residual part. Differentiation and iterative solution are required to obtain common properties such as density and heat capacity as a function of temperature and pressure. For other properties such as the viscosity, obtaining a property as a function of temperature and pressure requires first solving the IAPWS-95 thermodynamic formulation to obtain the density to be input to the formulation for the property of interest.

For many purposes, a simpler option would be desirable. For example, water is widely used as a calibration fluid, and many of these calibrations use liquid water at atmospheric pressure. A one-dimensional correlation of the relevant property as a function of temperature would be suitable for these purposes. The desire for simplicity has led people to use tabulated numbers from handbooks (which may not represent the best current knowledge) or obsolete and less accurate equations such as the density correlation of Kell,[9] in preference to the official IAPWS formulations.

In this work, we provide simple formulas as a function of temperature for properties of liquid water at 0.1 MPa pressure. They are designed to reproduce the more comprehensive IAPWS standards to a precision at least a factor of 10 smaller than the uncertainty of the original IAPWS formulation, so that the correlations developed here contribute negligibly to the overall uncertainty of the property calculation. The formulas can be programmed easily in common applications such as spreadsheets, allowing users to obtain properties of the best accuracy with relatively little effort.

The temperature range covered by these correlations is (with exceptions to be noted below) 253.15–383.15 K. This exceeds the range in which liquid water is the thermodynamically stable phase at 0.1 MPa by approximately 20 K at the low-temperature end and 10 K at the high-temperature end. Properties in this extended range are useful for the study of metastable water and for the study of aqueous solutions that are stable over a wider temperature range than the pure solvent.

The formulas presented here were adopted as a Supplementary Release by IAPWS at its meeting in Berlin, Germany, in September 2008.[10]

In this paper, we begin by discussing thermodynamic properties in Sec. 2. Sections 3 and 4 present the viscosity and thermal conductivity, respectively. Section 5 describes the static dielectric constant, for which the publication of more accurate data subsequent to the IAPWS release required a different approach. Application at different pressures (particularly the commonly used standard atmospheric pressure of 0.101 325 MPa) is discussed in Sec. 6.

Before we present our correlations, we mention three details. First, we use "water" to refer to what is often called "ordinary water substance" in IAPWS formulations. This means chemically pure H_2O with the standard isotopic composition for hydrogen and oxygen given by Vienna Standard Mean Ocean Water (VSMOW).[11] Most water in nature or in the laboratory will have isotopic composition differing slightly from that of VSMOW, but the difference is negligible for all properties considered here, with the exception of the density, where isotopic composition could affect the most precise measurements. Second, these formulations are for pure, air-free water. In some applications, the interest may be in water in contact with the atmosphere and therefore fully or partially saturated with air. Dissolved air at atmospheric

TABLE 1. Coefficients and exponents of Eqs. (2)–(4) (the notation $y E \pm n$ should be interpreted as $y \times 10^{\pm n}$)

Eq.	i	n_i	m_i	a_i	b_i	c_i
(2)	1	4	2	$-1.661\,470\,539\text{E}+5$	$-8.237\,426\,256\text{E}-1$	$-2.452\,093\,414\text{E}+2$
	2	5	3	$2.708\,781\,640\text{E}+6$	$1.908\,956\,353$	$3.869\,269\,598\text{E}+1$
	3	7	4	$-1.557\,191\,544\text{E}+8$	$-2.017\,597\,384$	$-8.983\,025\,854$
	4	n/a	5	n/a	$8.546\,361\,348\text{E}-1$	
(3)	5	n/a	1	$1.937\,631\,57\text{E}-2$	$5.785\,452\,92\text{E}-3$	
	6	4	2	$6.744\,584\,46\text{E}+3$	$-1.531\,956\,65\text{E}-2$	
	7	5	3	$-2.225\,216\,04\text{E}+5$	$3.113\,378\,59\text{E}-2$	
	8	7	4	$1.002\,312\,47\text{E}+8$	$-4.235\,462\,41\text{E}-2$	
	9	8	5	$-1.635\,521\,18\text{E}+9$	$3.387\,135\,07\text{E}-2$	
	10	9	6	$8.322\,996\,58\text{E}+9$	$-1.199\,467\,61\text{E}-2$	
(4)	11	1	1	$-7.524\,587\,8\text{E}-6$	$-3.109\,147\,0\text{E}-6$	
	12	3	3	$-1.376\,741\,8\text{E}-2$	$2.896\,491\,9\text{E}-5$	
	13	5	4	$1.062\,729\,3\text{E}+1$	$-1.311\,276\,3\text{E}-4$	
	14	6	5	$-2.045\,779\,5\text{E}+2$	$3.041\,045\,3\text{E}-4$	
	15	7	6	$1.203\,741\,4\text{E}+3$	$-3.903\,459\,4\text{E}-4$	
	16		7		$2.340\,311\,7\text{E}-4$	
	17		9		$-4.851\,010\,1\text{E}-5$	

pressure has a negligible effect on the properties considered here, again with the exception of very precise density measurements. The small effect of dissolved atmospheric air on the density (and refractive index) of water has been discussed by Harvey et al.[12] Third, we do not consider the "industrial" formulation for thermodynamic properties[13,14] (commonly known as IAPWS-IF97), which IAPWS developed primarily for the steam power industry. While IAPWS-IF97 closely approximates thermodynamic properties from IAPWS-95, it does not provide the simple one-dimensional correlations that we seek here.

2. Thermodynamic Properties

2.1. Input Data

The correlation of thermodynamic properties was designed to reproduce values from the *Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use*,[1,2] referred to in this paper as IAPWS-95 or simply as 95 when

used in subscripts. Values of the dependent variables were generated from IAPWS-95 for liquid water at 0.1 MPa at 1 K intervals from 253.15 to 383.15 K, and the fitting procedure was constrained to fit the input data to a precision at least a factor of 10 smaller than the uncertainty of the IAPWS formulation.

2.2. Correlation Results

Thermodynamic properties are related by thermodynamic identities. Correlation of each property separately would inevitably lead to inconsistency, i.e., the thermodynamic identities would not be satisfied exactly. Moreover, the number of equations would be large. One approach to ensure thermodynamic consistency is to employ a thermodynamic potential such as the Helmholtz energy or Gibbs energy depending on the natural independent variables. All thermodynamic properties are then obtained from thermodynamic identities as combinations of derivatives of the potential. For the present purpose of a formulation restricted to a fixed pressure p_0 =0.1 MPa, this approach is not suitable. To ensure thermo-

TABLE 2. Thermodynamic properties of liquid water at 0.1 MPa obtained by differentiating Eqs. (2)–(4)

Property[a]	Relation
Entropy [derived from Eq. (2)]	$s_0 = -\dfrac{dg_0}{dT} = -R[c_2 + c_3(1 + \ln\tau) + \sum_{i=1}^{3} n_i a_i \alpha^{n_i+1} - \sum_{i=1}^{4} m_i b_i \beta^{m_i+1}]$
Isobaric heat capacity [derived from Eq. (2)]	$c_{p0} = -T\dfrac{d^2 g_0}{dT^2} = -R[c_3 + \tau\sum_{i=1}^{3} n_i(n_i+1)a_i \alpha^{n_i+2} + \tau\sum_{i=1}^{4} m_i(m_i+1)b_i \beta^{m_i+2}]$
$v_T \equiv (\partial v / \partial T)_p$ [derived from Eq. (3)]	$v_{T0} = \dfrac{dv_0}{dT} = \dfrac{R}{p_0}\left(\sum_{i=6}^{10} n_i a_i \alpha^{n_i+1} - \sum_{i=5}^{10} m_i b_i \beta^{m_i+1}\right)$
$v_{TT} \equiv (\partial^2 v / \partial T^2)_p$ [derived from Eq. (3)]	$v_{TT0} = \dfrac{d^2 v_0}{dT^2} = \dfrac{R}{p_0 T_R}\left(\sum_{i=6}^{10} n_i(n_i+1)a_i \alpha^{n_i+2} + \sum_{i=5}^{10} m_i(m_i+1)b_i \beta^{m_i+2}\right)$
$v_{pT} \equiv \partial^2 v / \partial p \partial T$ [derived from Eq. (4)]	$v_{pT0} = \dfrac{dv_{p0}}{dT} = \dfrac{R}{p_0^2}\left(\sum_{i=11}^{15} n_i a_i \alpha^{n_i+1} - \sum_{i=11}^{17} m_i b_i \beta^{m_i+1}\right)$

[a]Derivatives v_{TT0} and v_{pT0} are only needed for computing thermodynamic properties at pressures different from 0.1 MPa (Table 4).

TABLE 3. Thermodynamic properties of liquid water at 0.1 MPa given by algebraic combinations of Eqs. (2)–(4) and their derivatives

Property		Relation
Enthalpy		$h_0 = g_0 + T s_0$
Internal energy		$u_0 = g_0 + T s_0 - p_0 v_0$
Helmholtz energy		$f_0 = g_0 - p_0 v_0$
Isochoric heat capacity		$c_{v0} = c_{p0} + T v_{T0}^2 / v_{p0}$
Isothermal compressibility	$\kappa_T \equiv -\dfrac{1}{v}\left(\dfrac{\partial v}{\partial p}\right)_T$	$\kappa_{T0} = -v_{p0}/v_0$
Thermal expansivity	$\alpha \equiv \dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_p$	$\alpha_0 = v_{T0}/v_0$
Isentropic compressibility	$\kappa_s \equiv -\dfrac{1}{v}\left(\dfrac{\partial v}{\partial p}\right)_s$	$\kappa_{s0} = -(T v_{T0}^2/c_{p0} + v_{p0})/v_0$
Speed of sound		$w_0 = [-v_0^2/(v_{p0} + T v_{T0}^2/c_{p0})]^{1/2}$

dynamic consistency and to avoid redundant equations, the formulation is based on three temperature-dependent functions: the Gibbs energy g, the specific volume v, and the isothermal derivative of specific volume with respect to pressure $v_p \equiv (\partial v / \partial p)_T$. The remaining properties are obtained from thermodynamic identities.

For easy programming and speed of computation, polynomial equations are employed in this work. However, the isobar 0.1 MPa given by IAPWS-95 has two singular points: one in the region of superheated water, corresponding to the liquid-vapor spinodal, and one in the region of supercooled water, corresponding to the so-called re-entrant spinodal. Although these singular points are well beyond the range of validity of the present formulation, it proved efficient to include terms imitating these singular behaviors at high and low temperatures. Consequently, the equations were designed as mixed polynomials in terms of dimensionless temperature parameters,

$$\tau = \frac{T}{T_R}, \quad \alpha = \frac{T_R}{T_a - T}, \quad \beta = \frac{T_R}{T - T_b}, \tag{1}$$

where T is the temperature in K, $T_R = 10$ K, $T_a = 593$ K, and $T_b = 232$ K. The particular values of T_R, T_a, and T_b have no physical significance. The temperature-dependent thermodynamic functions at $p_0 = 0.1$ MPa are represented by

$$g_0(T) \equiv g(p_0, T) = RT_R\left(c_1 + c_2\tau + c_3\tau\ln\tau + \sum_{i=1}^{3} a_i\alpha^{n_i}\right.$$
$$\left. + \sum_{i=1}^{4} b_i\beta^{m_i}\right), \tag{2}$$

$$v_0(T) \equiv v(p_0, T) = \frac{RT_R}{p_0}\left(a_5 + \sum_{i=6}^{10} a_i\alpha^{n_i} + \sum_{i=5}^{10} b_i\beta^{m_i}\right), \tag{3}$$
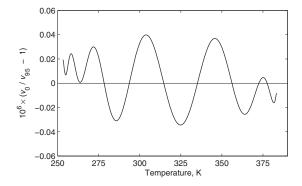
FIG. 1. Relative deviation of the specific volume at 0.1 MPa given by the present formulation from the IAPWS-95 formulation.[1,2]

$$v_{p0}(T) \equiv v_p(p_0, T) = \frac{RT_R}{p_0^2}\left(\sum_{i=11}^{15} a_i\alpha^{n_i} + \sum_{i=11}^{17} b_i\beta^{m_i}\right), \tag{4}$$

where $R = 461.518\ 05$ J kg^{-1} K^{-1},[1] and the dimensionless coefficients a_i, b_i, and c_i and integer exponents n_i and m_i are given in Table 1. The coefficients were rounded such that the ignored digits have negligible effect on the computed thermodynamic properties.

Further properties are derived from Eqs. (2)–(4) by use of thermodynamic identities. Quantities obtained by differentiating Eqs. (2)–(4) are given in Table 2. Table 3 shows relations for properties obtained by algebraic combinations of quantities given by Eqs. (2)–(4) and quantities given in Table 2.

The performance of the correlation in reproducing IAPWS-95 results at $p_0 = 0.1$ MPa for specific volume, isobaric heat capacity, and speed of sound may be seen in Figs. 1–3, respectively. In each case, the deviations from IAPWS-95 are smaller than the uncertainties for the corresponding properties of IAPWS-95 itself by more than an order of magnitude through the entire range of correlation.

2.3. Range of Validity and Uncertainty

The correlation of thermodynamic properties at $p_0 = 0.1$ MPa given by Eqs. (2)–(4) is recommended for use in the following temperature range:
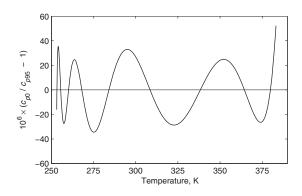

FIG. 2. Relative deviation of the specific isobaric heat capacity at 0.1 MPa given by the present formulation from the IAPWS-95 formulation.[1,2]
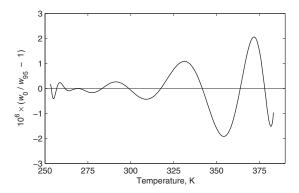
FIG. 3. Relative deviation of the speed of sound at 0.1 MPa given by the present formulation from the IAPWS-95 formulation.[1,2]

FIG. 4. Relative deviation of the density at 0.101 325 MPa given by the present formulation [reciprocal of v_{atm} from Eq. (6)] and by the IAPWS-95 formulation[1,2] from the CIPM recommended values for the density of water between 0 and 40 °C.[15]

$$253.15 \text{ K} \leqslant T \leqslant 383.15 \text{ K}. \quad (5)$$

It should not be extrapolated outside these limits. At some temperatures within this range, the equilibrium phase at 0.1 MPa is a solid (below approximately 273.15 K) or a vapor (above approximately 372.76 K); at these conditions Eqs. (2)–(4) describe only the properties of the metastable liquid phase.

The uncertainty of Eqs. (2)–(4) (which can be considered as an estimate of the expanded uncertainty with coverage factor $k=2$) is that of the underlying IAPWS-95 formulation.[1,2] In most of the stable region, this is a relative uncertainty of 0.0001% for specific volume (or density), 0.005% for the speed of sound, and 0.1% for isobaric heat capacity. No uncertainty estimate is given for the metastable regions, but the agreement with available data for the supercooled region is within about 0.01% in density, 1% in speed of sound, and 1% in isobaric heat capacity.

2.4. Application at Standard Atmospheric Pressure

The specific volume of liquid water at standard atmospheric pressure $p_{atm}=0.101\ 325$ MPa, computed as

$$v_{atm} = v_0 + v_{p0}(p_{atm} - p_0), \quad (6)$$

agrees in relative terms within 0.04×10^{-6} with the IAPWS-95 formulation[1,2] over the whole temperature interval given by Eq. (5). The speed of sound and isobaric heat capacity at standard atmospheric pressure can be taken equal to their values at 0.1 MPa, w_0 and c_{p0}, respectively, with no appreciable effect on the uncertainty.

Comparison may also be made with the standard correlation for the density of liquid water from 273.15 to 313.15 K adopted for use in metrology by the International Committee for Weights and Measures (known by its French acronym as the CIPM).[15] The CIPM formulation and IAPWS-95 are mutually consistent, within their respective uncertainties, in the range in which the CIPM formulation is valid.[16] Figure 4 shows that the density from this work is similarly consistent with the CIPM formulation.
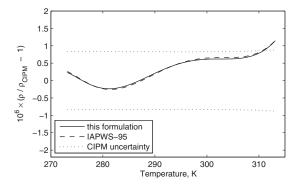
2.5. Application in a Limited Pressure Range

Thermodynamic properties of liquid water at other pressures can be obtained based on Eqs. (2)–(4) and thermodynamic identities; e.g., the Gibbs energy can be approximated as $g(T,p) \approx g_0(T) + v_0(T)(p - p_0)$. This approach is applicable to all thermodynamic properties except for the isothermal compressibility and related properties, particularly isentropic compressibility and speed of sound. For these properties, a linear correction was applied: $(\partial v / \partial p)_T \approx v_{p0}(T) + v_{pp0}(p - p_0)$, where the linear coefficient v_{pp0} is a constant (independent of temperature). Unlike v_{p0}, the coefficient v_{pp0} does not closely approximate the corresponding derivative of the specific volume $(\partial^2 v / \partial p^2)_T$. Relations for computing the thermodynamic properties of liquid water at pressures different from 0.1 MPa are given in Table 4. The uncertainties of the properties are essentially identical with the uncertainties of the IAPWS-95 formulation[1,2] in the pressure range from the vapor-liquid saturation pressure up to 0.3 MPa.

The present formulation can also be used for phase-equilibrium computations. Saturation vapor pressure com-

TABLE 4. Relations for thermodynamic properties of liquid water at pressure p different from 0.1 MPa

Property	Relation
Gibbs energy	$g \approx g_0 + v_0(p - p_0)$
Entropy	$s \approx s_0 - v_{T0}(p - p_0)$
Isobaric heat capacity	$c_p \approx c_{p0} - Tv_{TT0}(p - p_0)$
Specific volume	$v \approx v_0 + v_{p0}(p - p_0)$
$v_T \equiv (\partial v / \partial T)_p$	$v_T \approx v_{T0} + v_{pT0}(p - p_0)$
$v_p \equiv (\partial v / \partial p)_T$	$v_p \approx v_{p0} + v_{pp0}(p - p_0)$
	where $v_{pp0} \equiv 3.24 \times 10^{-10} RT_R / p_0^3$
Enthalpy	$h = g + Ts$
Internal energy	$u = g + Ts - pv$
Helmholtz energy	$f = g - pv$
Isochoric heat capacity	$c_v = c_p + Tv_T^2 / v_p$
Isothermal compressibility	$\kappa_T = -v_p / v$
Thermal expansivity	$\alpha = v_T / v$
Isentropic compressibility	$\kappa_s = -(Tv_T^2 / c_p + v_p) / v$
Speed of sound	$w = [-v^2 / (v_p + Tv_T^2 / c_p)]^{1/2}$

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

puted by equating the Gibbs energy of liquid water (as given in Table 4) to the Gibbs energy of vapor (as given by IAPWS-95) deviates negligibly over the entire temperature range given by Eq. (5) from the saturation pressure computed by using IAPWS-95 for both vapor and liquid phases.

3. Viscosity

3.1. Input Data

The viscosity correlation was designed to reproduce values computed from the *Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance*.[3,4] Points were generated from this formulation for liquid water at 0.1 MPa pressure at 1 K intervals from 253.15 to 383.15 K, and the fitting procedure was constrained to fit the input data to a precision at least a factor of 10 smaller than the uncertainty of the IAPWS formulation.

3.2. Correlation Results

The viscosity μ of liquid water at a pressure of 0.1 MPa is described as a function of absolute temperature T by the following equation:

$$\mu/(10^{-6} \text{ Pa s}) = \sum_{i=1}^{4} a_i (T^*)^{b_i}, \tag{7}$$

where $T^* = T/(300 \text{ K})$ and the coefficients and exponents a_i and b_i are given in Table 5.

Figure 5 shows the percentage deviation of Eq. (7) from the full IAPWS viscosity formulation. The deviations in Fig. 5 are at least two orders of magnitude smaller than the un-
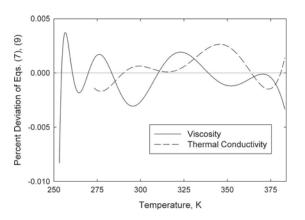
FIG. 5. Relative deviation of correlations for viscosity [Eq. (7)] and thermal conductivity [Eq. (9)] from the corresponding IAPWS standards.

certainty of the underlying IAPWS formulation (see below), meaning that approximating the viscosity by Eq. (7) adds negligible additional uncertainty to the viscosity calculation at these conditions.

Equation (7) also reproduces the ISO recommended[17] value of the viscosity at 20 °C (293.15 K) and standard atmospheric pressure within the number of digits given in Ref. 17; it also agrees with all values from 288.15 to 313.15 K at atmospheric pressure in Ref. 17 within the stated uncertainty of 0.17% at 293.15 K.

3.3. Range of Validity and Uncertainty

Equation (7) is recommended for use in the following temperature range:

$$253.15 \text{ K} \leqslant T \leqslant 383.15 \text{ K}. \tag{8}$$

It should not be extrapolated outside these limits. At some temperatures within this range, the equilibrium phase at 0.1 MPa is a solid (below approximately 273.15 K) or a vapor (above approximately 372.76 K); at these conditions Eq. (7) describes the viscosity of the metastable liquid phase.

The uncertainty of Eq. (7) (which can be considered as an estimate of the expanded uncertainty with coverage factor $k=2$) is that of the underlying IAPWS formulation.[3,4] This is 1% for the stable liquid region. No uncertainty estimate is given for the metastable regions, but the agreement with available data for the supercooled region is within 5%.

4. Thermal Conductivity

4.1. Input Data

The thermal conductivity correlation was designed to reproduce values computed from the *Revised Release on the IAPS Formulation 1985 for the Thermal Conductivity of Ordinary Water Substance*.[5,6] Points were generated from this formulation for liquid water at 0.1 MPa pressure at 1 K intervals from 273.15 to 383.15 K, and the fitting procedure was constrained to fit the input data to a precision at least a factor of 10 smaller than the uncertainty of the IAPWS formulation. For this property, the supercooled liquid below 273.15 K was not included because those conditions are outside the range of validity of the underlying IAPWS formulation.[5,6]

4.2. Correlation Results

The thermal conductivity λ of liquid water at a pressure of 0.1 MPa is described as a function of absolute temperature T by the following equation:

$$\lambda/(1 \text{ W m}^{-1} \text{ K}^{-1}) = \sum_{i=1}^{4} c_i (T^*)^{d_i}, \tag{9}$$

where $T^* = T/(300 \text{ K})$, and the coefficients and exponents c_i and d_i are given in Table 6.

Figure 5 shows the percentage deviation of Eq. (9) from the full IAPWS thermal conductivity formulation. The devia-

TABLE 6. Parameters for calculation of thermal conductivity with Eq. (9)

i	c_i	d_i
1	0.802 01	−0.32
2	−0.259 92	−5.7
3	0.100 24	−12.0
4	−0.032 005	−15.0

tions in Fig. 5 are at least two orders of magnitude smaller than the uncertainty of the underlying IAPWS formulation (see below), meaning that approximating the thermal conductivity by Eq. (9) adds negligible additional uncertainty to the thermal conductivity calculation at these conditions.

4.3. Range of Validity and Uncertainty

Equation (9) is recommended for use in the following temperature range:

$$273.15 \text{ K} \le T \le 383.15 \text{ K}. \tag{10}$$

It should not be extrapolated outside these limits. At some temperatures within this range, the equilibrium phase at 0.1 MPa is a vapor (above approximately 372.76 K); at these conditions Eq. (9) describes the thermal conductivity of the metastable liquid phase.

The uncertainty of Eq. (9) (which can be considered as an estimate of the expanded uncertainty with coverage factor $k=2$) is that of the underlying IAPWS formulation.[5,6] This is given approximately by the tolerances stated in Table A.1 of the IAPWS release,[5] which are between 1.5% and 2% in relative terms.

5. Static Dielectric Constant

5.1. Input Data

The static dielectric constant is different from the other properties considered here, in that experimental data of superior accuracy have become available since the production of the current IAPWS formulation.[7,8] In particular, the radio-frequency resonance measurements of Hamelin et al.[18] determine the dielectric constant of the liquid to much greater accuracy than it was previously known, with an expanded ($k=2$) uncertainty of approximately 0.01 in the dielectric constant ε.

We therefore use the data of Hamelin et al.[18] as the primary basis for our correlation. These data cover the liquid over the approximate temperature range from 274 to 418 K; we used their data up to our temperature limit of 383.15 K. Because the pressure associated with these data is not always 0.1 MPa, a small adjustment is required to produce values corresponding to 0.1 MPa. This adjustment was computed with values of $(\partial \varepsilon / \partial p)_T$ from the current IAPWS formulation[7,8] as implemented in the database of Harvey et al.[19] The adjustment was no larger than 0.005 in ε for any of the points used in our work.
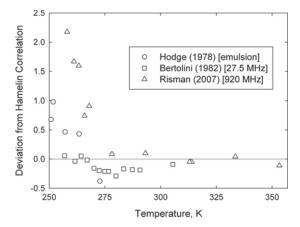

FIG. 6. Deviation from the correlation of Hamelin et al.[18] of dielectric-constant data from studies that measured data for supercooled water.

For the supercooled liquid over our temperature range of interest, three experimental sources are available, and their data are not mutually consistent. Hodge and Angell[20] used an emulsion polarization technique to obtain an indirect estimate of the static dielectric constant of liquid water down to 238 K. Bertolini et al.[21] measured the dielectric properties of supercooled liquid water down to 257 K, reporting static values extrapolated from measurements at 27.5 MHz. Risman and Wäppling-Raaholt[22] derived static values from resonance measurements at 920 MHz; their lowest temperature was near 258 K.

In order to see the differences among these data, we plot them in Fig. 6 as the differences between the experimental values and the smoothing equation of Hamelin et al.[18] While that smoothing equation is not valid below 274 K, it gives us a convenient means of comparing the data with one another and with the more precise data of Hamelin et al.[18] at temperatures where they overlap.

All three of the data sources are in fair agreement with the data of Hamelin et al. for the normal liquid. However, their supercooled liquid behavior differs significantly by more than the claimed uncertainties of the experiments. The low-temperature data of Bertolini et al.[21] are in better agreement with the equation of Hamelin et al.,[18] but that is not decisive because the equation of Hamelin et al. is empirical and its extrapolation to lower temperatures may not be correct.

While there is no definitive reason to prefer any of these three data sets, we chose to use the data of Bertolini et al.[21] because their work most closely approximated a measurement of the static dielectric constant. The extrapolation from the measurement frequency to zero frequency is much further for the data of Risman and Wäppling-Raaholt,[22] with correspondingly greater opportunity for error. Hodge and Angell[20] did not use pure water, and their data require various manipulations in order to obtain a value for ε. Because of the scatter of the data sources, it must be recognized that there is an inherent uncertainty in our knowledge of the dielectric constant of supercooled liquid water; that uncertainty is indicated by the scatter in Fig. 6.

We observed that the data of Bertolini et al.[21] were sys-

TABLE 7. Parameters for calculation of static dielectric constant with Eq. (11)

i	e_i	f_i
1	−43.7527	−0.05
2	299.504	−1.47
3	−399.364	−2.11
4	221.327	−2.31

tematically below the definitive data of Hamelin *et al.*[18] for liquid water above 274 K. A shift of their data upward by 0.18 in ε produced excellent agreement with the data of Hamelin *et al.* in the region where the sources overlap, so we applied this same shift to the supercooled data of Bertolini *et al.*[21] before fitting the correlation to the data. In the fitting process, greater weight was given to the data of Hamelin *et al.*[18] due to their much smaller uncertainty.

5.2. Correlation Results

The static dielectric constant ε of liquid water at a pressure of 0.1 MPa is described as a function of absolute temperature T by the following equation:

$$\varepsilon = \sum_{i=1}^{4} e_i (T^*)^{f_i}, \tag{11}$$

where $T^* = T/(300\ \mathrm{K})$ and the coefficients and exponents e_i and f_i are given in Table 7.

Figure 7 shows the deviation of our two accepted data sources from Eq. (11). In addition, the current IAPWS formulation[7,8] is plotted for comparison. The data of Hamelin *et al.*[18] are fitted well within their uncertainty of 0.01. We were unable to fit Eq. (11) closely through the data of Bertolini *et al.*[21] in the supercooled region without distorting the rest of the fit, so we are left with a small systematic deviation for these data (the points shown are shifted as discussed in Sec. 5.1). However, this deviation is well within the overall uncertainty of the dielectric constant in this supercooled region.

5.3. Range of Validity and Uncertainty

Equation (11) is recommended for use in the following temperature range:

$$257\ \mathrm{K} \leqslant T \leqslant 383.15\ \mathrm{K}. \tag{12}$$

It should not be extrapolated outside these limits. At some temperatures within this range, the equilibrium phase at 0.1 MPa is a solid (below approximately 273.15 K) or a vapor (above approximately 372.76 K); at these conditions Eq. (11) describes the dielectric constant of the metastable liquid phase.

The uncertainty of Eq. (11) (which can be considered as an estimate of the expanded uncertainty with coverage factor $k=2$) is that of the underlying experimental data. As discussed in Sec. 5.1, this is approximately 0.01 for the stable
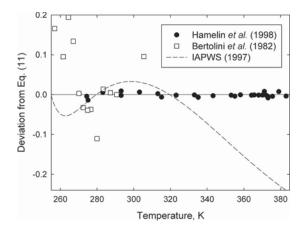

FIG. 7. Deviation of accepted dielectric-constant data from Eq. (11).

and superheated liquid regions (above 273.15 K) but is much larger (at least 1.0) for the supercooled liquid.

6. Calculations at Other Pressures

It may be of interest to calculate the properties considered here at pressures other than 0.1 MPa, such as the often-used standard atmospheric pressure of 0.101 325 MPa. The formulations for viscosity, thermal conductivity, and static dielectric constant [Eqs. (7), (9), and (11)] given here may be used for liquid water at any pressure between the vapor-liquid saturation pressure and 0.3 MPa with no significant loss in accuracy (since the change in property due to the change in pressure is smaller by more than an order of magnitude than the uncertainty of the property itself).

For some thermodynamic properties, additional calculations beyond the level of the basic Eqs. (2)–(4) may be necessary to maintain the required accuracy at pressures differing from 0.1 MPa. These calculations are described in Secs. 2.4 and 2.5.

7. Discussion

Correlations have been developed for the thermodynamic properties, viscosity, thermal conductivity, and static dielectric constant of liquid water at a pressure of 0.1 MPa. These correlations are much simpler than the more comprehensive and wide-ranging IAPWS formulations for these properties while retaining the same accuracy.

The same strategy could be applied to other IAPWS formulations, such as those for the refractive index[23,24] and the ionization constant of water.[25,26] However, the work presented here can already simplify the calculation of other properties. The IAPWS formulations are functions of independent variables temperature and density (and wavelength, in the case of the refractive index). Previously, calculation of a property at a pressure such as 0.1 MPa required iteratively solving the IAPWS-95 formulation for density. Now, Eq. (3) can be used to calculate the density in a straightforward manner, and this density can be input along with the temperature to calculate these additional properties.

TABLE 8. Sample points for computer-program verification of calculated properties at 0.1 MPa

Property	Units	Value at 260 K	Value at 298.15 K	Value at 375 K
Gibbs energy g_0	J kg^{-1}	−1 265.989 2	−4 561.753 7	−71 058.802 1
Entropy s_0	J kg^{-1} K^{-1}	−209.985 55	367.201 45	1 328.066 16
Isobaric heat capacity c_{p0}	J kg^{-1} K^{-1}	4 300.147 72	4 181.446 18	4 217.746 97
Density $\rho_0 = 1/v_0$	kg m^{-3}	997.068 360	997.047 013	957.009 710
$10^7 v_{T0}$	m^3 kg^{-1} K^{-1}	−3.865 509 41	2.580 541 78	7.947 066 23
$10^8 v_{TT0}$	m^3 kg^{-1} K^{-2}	3.274 425 03	0.972 020 76	0.620 241 04
$10^{13} v_{p0}$	m^3 kg^{-1} Pa^{-1}	−5.820 968 20	−4.538 033 40	−5.156 665 28
$10^{15} v_{pT0}$	m^3 kg^{-1} Pa^{-1} K^{-1}	7.809 382 94	1.000 385 67	−2.270 735 94
Speed of sound w_0	m s^{-1}	1 324.872 58	1 496.699 22	1 541.466 11
Viscosity μ	μPa s	3 058.360 75	889.996 774	276.207 245
Thermal conductivity λ	W m^{-1} K^{-1}	n/a	0.607 198 237	0.679 647 057
Static dielectric constant ε	(unitless)	93.455 835	78.375 218	55.266 199

For purposes of computer-program verification, Table 8 contains values of properties calculated at three different temperatures from the correlations presented here.

8. Acknowledgments

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