

# New International Formulation for the Thermal Conductivity of Heavy Water

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## ABSTRACT

The International Association for the Properties of Water and Steam (IAPWS) has adopted new formulations for the thermodynamic and transport properties of heavy water. This manuscript describes the development of a formulation for the thermal conductivity of heavy water that was adopted as an international standard in 2021. It is consistent with the equation of state adopted in 2017, revised slightly in 2018, and is valid for fluid states up to 825 K and 250 MPa with uncertainties ranging from 1.5% to 6% depending on the state point. Comparisons with experimental data and with an earlier thermal-conductivity formulation are presented. The 2021 formulation accounts for the critical enhancement of the thermal conductivity, which was not incorporated in the previous formulation. Furthermore, in the zero-density limit, the 2021 formulation is based on thermal conductivity values at temperatures from 250 to 2500 K obtained from the kinetic theory of polyatomic gases. In addition, the 2021 formulation is applicable in a larger range of pressures than the previous formulation.

Key words: heavy water; IAPWS; thermal conductivity.

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## 1. Introduction

Recently a paper was published that describes a new international formulation for the viscosity of heavy water;<sup>1</sup> this is a companion work on the development of a new formulation for the thermal conductivity of heavy water. The formulation provided in this work is recommended for calculating the thermal conductivity of heavy water, which the International Association for the Properties of Water and Steam (IAPWS) defines as water whose hydrogen atoms are entirely the deuterium isotope ( $^2\text{H}$  or  $\text{D}$ ) and whose oxygen isotopes have the same abundance as in ordinary water.<sup>2</sup> The new formulation for the thermal conductivity of heavy water described in this work has recently been adopted by IAPWS as an international standard, and one of the purposes of this manuscript is to document the new standard.<sup>3</sup>

In 1980, Nagashima and Matsunaga<sup>4</sup> proposed the first correlation for the thermal conductivity of heavy water, deuterium oxide ( $\text{D}_2\text{O}$ , CAS No. 7789-20-0), covering liquid and gaseous states in the range of temperature between 276.96 K and 873.15 K, and up to 250 MPa. Due to insufficient number of available data on the critical enhancement of the thermal conductivity, it was impossible to formulate a reliable equation in the vicinity of the critical point (within  $T_c \pm 1.5$  K,  $0.8 < \rho/\rho_c < 1.2$ ), where  $T_c$  is the critical temperature,  $\rho$  is the density, and  $\rho_c$  is the critical density. For the development of the correlation, the density of  $\text{D}_2\text{O}$  was calculated with the aid of the 1977 equation of state by Ikeda *et al.*<sup>5</sup> in the liquid region up to 100 MPa, and with the aid of the modified law of corresponding states and the 1975 equation of state for  $\text{H}_2\text{O}$  by Pollak<sup>6</sup> in all other regions.

In 1982, an equation of state for heavy water was developed by Hill *et al.*<sup>7</sup> Following this, and on the request of the Executive Committee of IAPS (International Association for the Properties of Steam), Matsunaga and Nagashima<sup>8</sup> in 1983 published a new correlation for the thermal conductivity of heavy water. The correlation was formulated as the multiplication of the zero-density thermal conductivity term and a residual term, while the critical enhancement was not considered. The correlation was valid up to 100 MPa and from the triple-point temperature up to 825 K, within an uncertainty of 2% to 10%. However, no uncertainties were assigned in the region contained within  $T_c \pm 1.5$  K,  $0.8 < \rho/\rho_c < 1.2$ , because, although the actual thermal conductivity should diverge at the critical point, the thermal conductivity calculated from the equation remained finite at the critical point. It was also published together with other properties of  $\text{D}_2\text{O}$  in a paper by Kestin *et al.*,<sup>9</sup> and incorporated in the IAPS Release of 1984<sup>10</sup> and the Revised IAPWS Release of 2007.<sup>11</sup>

In 2017, a new equation of state for heavy water was developed by Herrig *et al.*<sup>12</sup> and incorporated in the IAPWS Revised Release.<sup>13</sup> The new equation of state includes densities near the critical point, which allows for the first time a calculation of the viscosity and thermal-conductivity critical enhancements. This new equation of state, the availability of some new measurements of the viscosity of heavy water

performed after 1983, advances in the calculation of the zero-density viscosity by Hellmann and Bich,<sup>14</sup> and a much better understanding of the viscosity critical enhancement were the motivation for the development of a better correlation for the viscosity of heavy water in a companion paper recently published<sup>1</sup> and adopted as a standard.<sup>15</sup> While the critical enhancement for the viscosity is only a minor effect and can be neglected for industrial applications, the critical enhancement of the thermal conductivity is very large and can never be neglected, not even for industrial applications.

The analysis that will be described here follows the procedure adopted by Matsunaga and Nagashima,<sup>8</sup> and also adopted in our correlation of the thermal conductivity of ordinary water,<sup>16</sup> applied to the best available experimental data for the thermal conductivity. Thus, a prerequisite to the analysis is a critical assessment of the experimental data. For this purpose, two categories of experimental data are defined: primary data, employed in the development of the correlation, and secondary data, used simply for comparison purposes. According to the recommendation adopted by the Subcommittee on Transport Properties (now known as The International Association for Transport Properties, IATP) of the International Union of Pure and Applied Chemistry (IUPAC), the primary data are identified by a well-established set of criteria.<sup>17</sup> These criteria have been successfully employed to establish standard reference values for the viscosity and thermal conductivity of fluids over wide ranges of conditions, with uncertainties in the range of 1%. However, in many cases, such a narrow definition unacceptably limits the range of the data representation. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a higher uncertainty, provided they are consistent with other data with lower uncertainty, or with theory. In all cases, the uncertainty claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

## 2. Experimental Data

As part of a joint project between IAPWS and IATP, experimental data on the thermal conductivity of heavy water were collected, converted to the ITS-90 temperature scale and a common set of units.<sup>18</sup> 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.

We have retained all the data examined by Matsunaga and Nagashima<sup>8</sup> in 1983, and added two more sets of measurements (those of Nagasaka *et al.*<sup>19</sup> and Tufeu *et al.*<sup>20</sup>) reported after that date. Table 1 summarizes all the available data sets; 23 papers were considered totaling 2380 thermal-conductivity measurements. The temperature range covered is from 262 to 1043 K, at pressures up to 250 MPa. In the same table, the technique employed, the quoted uncertainty, and the purity of the sample are also shown.

TABLE 1. Summary of experimental data for the thermal conductivity of D<sub>2</sub>O

1 <sup>st</sup> author	Year Publ.	Technique employed <sup>a,b</sup>	Purity <sup>b</sup> (%)	Uncertainty <sup>b</sup> (%)	No. of data	Temperature range (K)	Pressure range (MPa)
<b>Primary Data</b>							
Nagasaka <sup>19</sup>	1989	THW	na	0.5	45	277–353	0.03–40
Tufeu <sup>20,c</sup>	1986	CC	99.8	2.0	202	484–785	1.0–99.1
Curtiss <sup>21,c</sup>	1979	SHW	na	1.0	74	357–383	0.015–0.12
Yata <sup>22</sup>	1979	CC	99.8	2–3	144	327–772	10–150
Amirkhanov <sup>23,c</sup>	1978	PP	99.75	na	136	648–874	0.100–250
Rastorguev <sup>24, 25,d</sup>	1975	SHW	99.8	1.5	462	262–487	0.098–217
Vargaftik <sup>26</sup>	1975	PP	na	1.0	13	525–909	0.175
Amirkhanov <sup>27</sup>	1974	PP	99.8	2.0	351	298–623	0.100–245
Tarzimanov <sup>28,c</sup>	1974	CC	99.7	2.5	178	423–822	0.22–80
Vargaftik <sup>29,c</sup>	1973	SHW	99.8	1.5	17	400–1043	0.049–0.066
Dijkema <sup>30,c</sup>	1972	CC	na	0.5	1	333	0.018
Le Neindre <sup>31, 32,d</sup>	1968a	CC	99.75	1.8	383	316–633	0.100–96.1
Le Neindre <sup>33,c</sup>	1968b	CC	99.75	2.0	65	383–603	0.100–12.5
Le Neindre <sup>34</sup>	1965	CC	99.75	1.0	46	333–633	0.018–100
Baker <sup>35,c</sup>	1964	SHW	na	na	4	381–526	0.101
Vargaftik <sup>36,c</sup>	1963	SHW	na	1.0	12	381–775	0.098
<b>Secondary Data</b>							
Vargaftik <sup>37,c</sup>	1962	SHW	99.9	na	115	417–777	0.980–24.51
Vargaftik <sup>38</sup>	1960	SHW	99.9	1.0	65	298–633	0.0982–20
Klassen <sup>39</sup>	1959	SHW	99.5	na	14	300–346	0.101
Ziebland <sup>40</sup>	1960	CC	99.85	1.0	37	348–532	2.43–29.78
Challoner <sup>41</sup>	1956	PP	99.95	1.0	5	273–353	0.101
Meyer <sup>42</sup>	1953	na	95	1.0	5	290–329	0.101
Bonilla <sup>43</sup>	1951	PP	na	na	6	283–333	0.101

<sup>a</sup> CC, Concentric Cylinders; PP, Parallel Plate; THW, Transient Hot Wire; SHW; Steady-State Hot Wire.

<sup>b</sup> na, not available

<sup>c</sup> Includes vapor-phase measurements.

<sup>d</sup> Ref. 32 duplicates information in Ref. 31., although reported uncertainty is 1.5% ; Ref. 25 duplicates information in Ref. 24.

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In the primary data set, we included all thermal-conductivity measurements considered as such by Matsunaga and Nagashima<sup>8</sup> in 1983. We also included in the primary data set the 1986 measurements of Tufeu *et al.*,<sup>20</sup> performed in a concentric-cylinders instrument with 2% uncertainty and covering a very wide range of temperatures and pressures; as well as the 1989 measurements of Nagasaka *et al.*,<sup>19</sup> performed in a transient hot-wire instrument up to 40 MPa pressure with 0.5% uncertainty. Measurements from these two groups have been successfully included in other previous reference correlations as primary data.<sup>16, 44, 45</sup> Matsunaga and Nagashima<sup>8</sup> in 1983 did not include the measurements of Amirkhanov *et al.*,<sup>23, 27</sup> in the primary data set as they were found to deviate from other measurements. A careful examination of these two sets showed that only the 649 K and 674 K isotherms had a distinctive different slope than the rest of the measurements. Since the measurements of Amirkhanov *et al.*,<sup>23, 27</sup> extend to 250 MPa, we decided to include these measurements in the primary data set, disregarding only the 649 K and 674 K isotherms. Finally, we kept in mind that Matsunaga and Nagashima<sup>8</sup> observed a high deviation of the high-temperature measurements of Yata *et al.*<sup>22</sup> from the rest, attributed to incorrect correction of the radiation effect due to lack of proper data. They pointed out that the high-temperature measurements of Rastorguev *et al.*<sup>24</sup> may also have the same problem. We also note that, although not listed in Table 1, data from the thermal diffusivity measurements of Desmarest and coworkers<sup>46-49</sup> were used in the analysis of the critical region in Sec. 3.3 and were treated as primary data.

Looking at the secondary data set, Matsunaga and Nagashima<sup>8</sup> disregarded the measurements of Klassen<sup>39</sup> and Vargaftik *et al.*,<sup>37, 38</sup> as they were higher than all other measurements, most probably due to convective effects. The remaining secondary data were measured before 1963 and were not considered as primary data by Matsunaga and Nagashima.<sup>8</sup>

Figures 1 and 2 show the temperature-pressure ranges and the temperature-density ranges of the primary experimental data shown in Table 1. The development of the correlation requires densities; Herrig *et al.*<sup>12</sup> recently developed an accurate, wide-ranging equation of state that is valid from the triple point up to 825 K and 1200 MPa. In the homogenous liquid and vapor phase, the expanded relative uncertainties of densities calculated from the equation of state are mostly within 0.1% or smaller; liquid-phase densities at atmospheric pressure can be calculated with an uncertainty of 0.01%. We have also adopted the values for the critical point from their equation of state; the critical temperature,  $T_c$ , the critical pressure,  $p_c$ , and the critical density,  $\rho_c$ , are 643.847 K, 21.6618 MPa, and 356.0 kg m<sup>-3</sup>, respectively.<sup>12</sup> The triple-point temperature employed is 276.969 K, and the molar mass is 20.027 508 g mol<sup>-1</sup>.<sup>12</sup>

### 3. Development of the Formulation

In order to provide consistency with the conventions adopted by IAPWS in their releases on the transport properties of water and heavy water, we use the following dimensionless variables for temperature  $T$ , mass density  $\rho$ , pressure  $p$ , and thermal conductivity  $\lambda$ :

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

where the reference constants are given in Table 2. The reference values for temperature, pressure, and density are the critical parameters of the IAPWS reference equation of state for heavy water,<sup>12</sup> while  $\lambda^* = 1 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$  is the scale factor previously adopted by IAPWS for the thermal conductivity of H<sub>2</sub>O.<sup>16</sup> All temperatures are expressed in terms of the ITS-90 temperature scale.

TABLE 2. Reference constants

Constant	Value
$T^*$	643.847 K
$\rho^*$	356.0 kg m <sup>-3</sup>
$p^*$	21.6618 MPa
$\lambda^*$	$1 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$

The formulation for the thermal conductivity of D<sub>2</sub>O has the same general form as the previous formulation for H<sub>2</sub>O,<sup>16, 50</sup> namely,

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

The first factor  $\bar{\lambda}_0$  of the product represents the thermal conductivity in the zero-density limit and is a function of temperature only. The second factor  $\bar{\lambda}_1$  represents the contribution to thermal conductivity due to increasing density, while the third factor  $\bar{\lambda}_2$  represents an enhancement of the thermal conductivity in the critical region. The determination of each of these contributions will be considered in the Secs. 3.1-3.3.

### 3.1 Thermal conductivity in the limit of zero density

In 2017, Hellmann and Bich<sup>14</sup> applied the classical kinetic theory of polyatomic gases to calculate the traditional transport properties of D<sub>2</sub>O in the zero-density limit using two highly accurate *ab initio* pair potentials. Results were reported for shear viscosity, thermal conductivity, and the product of molar density and self-diffusion coefficient at temperatures between 250 and 2500 K. The expanded uncertainty (coverage factor  $k = 2$ ) of the computed values for the thermal conductivity is estimated to be 2%, rising to 4% above 1500 K. Updated values for the thermal conductivity, which are based on the recent formulation for the ideal-gas heat capacity by Herrig *et al.*,<sup>10</sup> are provided in Appendix A. The changes in the values, compared to those published by Hellmann and Bich,<sup>14</sup> are significant only at temperatures at which vibrational degrees of freedom, whose treatment in the classical kinetic theory requires the ideal-gas heat capacity, are appreciably excited. The differences are smaller than 0.2% at temperatures below 1000 K and rise to 0.8% at 2500 K. Due to the lack of a large amount of high-quality experimental data for heavy water, we chose to base the zero-density correlation on the calculations of Hellmann and Bich<sup>14</sup> alone and only compare with the experimental data; this is different than the approach taken for ordinary water.<sup>16</sup>

The values in Appendix A were fitted to the following form, as a function of the dimensionless temperature  $\bar{T}$ , as

$$\bar{\lambda}_0(\bar{T}) = \sqrt{\bar{T}} \frac{1 + 3.3620798 \bar{T} - 1.0191198 \bar{T}^2 + 2.8518117 \bar{T}^3}{0.10779213 - 0.034637234 \bar{T} + 0.036603464 \bar{T}^2 + 0.0091018912 \bar{T}^3}. \quad (3)$$

Equation (3) represents 95% of all values given in Appendix A over the temperature range 250 to 2500 K to within 0.03%. As mentioned above, the values from Hellmann and Bich<sup>14</sup> have an estimated uncertainty of 2% to 4% depending on the temperature.

Equation (3) was tested vs. the available experimental data. All available measurements in the vapor phase shown in Table 1 with a superscript “c” were employed. Figure 3 shows the experimental data and the values calculated by Eq. (3) as a function of the temperature. In Fig. 4, the deviations of the experimental thermal-conductivity data at low densities from those calculated with Eq. (3) are shown. The agreement is within the mutual uncertainties, with only some values of Amirkhanov *et al.*<sup>27</sup> exceeding 5%. In the same figure, the deviations of the correlation of IAPWS 2007<sup>11</sup> from the values calculated by Eq. (3) are also shown. The agreement is excellent down to 250 K, the lowest temperature of the kinetic-theory calculations by Hellmann and Bich.<sup>14</sup>

Therefore, Eq. (3) is considered sufficient to represent the zero-density thermal conductivity of heavy water from 250 K to 825 K with an uncertainty of 2% (at the 95% confidence level).

### 3.2 Residual contribution

The second factor  $\bar{\lambda}_1$  of the product in Eq. (2) is the residual thermal conductivity and represents the contribution to thermal conductivity due to increasing density. This term is sometimes referred to in the literature as the excess thermal conductivity, but here we follow the alternative nomenclature of residual thermal conductivity. The critical region is not considered here; it will be treated separately in Sec. 3.3. We adopt the same general form for  $\bar{\lambda}_1$  as in earlier work,<sup>11</sup> and also for ordinary water:<sup>16</sup>

$$\bar{\lambda}_1(\bar{T}, \bar{\rho}) = \exp \left[ \bar{\rho} \sum_{i=0}^4 \left( \frac{1}{\bar{T}} - 1 \right)^i \sum_{j=0}^5 L_{ij} (\bar{\rho} - 1)^j \right] \quad (4)$$

with coefficients  $L_{ij}$  to be determined by regression of experimental data and the dimensionless density as defined in Eq. (1)

All data were initially assigned weights  $1/u^2$ , where  $u$  is the estimated experimental uncertainty. The uncertainties are given in Table 1; they are those given by the original author's recommendation. In cases where no uncertainty is given by the original author, we made an estimate based on the experimental technique used and agreement of the original authors data with other reference correlations if available. All densities were computed by the aforementioned recently developed equation of state of Herrig *et al.*<sup>12</sup>

Equation (4) contains a maximum of 30 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. We used the orthogonal distance regression package ODRPACK<sup>51</sup> to perform the regression. In previous work,<sup>16</sup> some terms were eliminated because they were statistically insignificant, but in the present work all terms were statistically significant and were retained. During the regression it was necessary to manually adjust some of the weighting factors to compensate for regions where there were few data points. Some datasets received additional weight in order to represent them to near, or within, their experimental uncertainty. The critical region was represented by a theoretical formulation<sup>52</sup> that contains a single parameter  $\bar{q}_D^{-1}$ , determined by an iterative process, as will be discussed in Sec. 3.3. 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  $L_{ij}$  in Eq. (4) for  $\bar{\lambda}_1$ 

$j$ $i$	0	1	2	3	4	5
0	1.509 335 76	-0.658 310 78	0.111 174 263	0.140 185 152	-0.065 622 772 2	0.007 851 552 13
1	2.841 471 5	-2.982 657 7	1.343 579 32	-0.599 233 641	0.281 163 37	-0.053 329 283 3
2	4.860 957 23	-6.197 844 68	2.209 418 67	0.224 691 518	-0.322 191 265	0.059 620 465 4
3	2.061 560 07	-3.486 124 56	1.479 623 09	0.625 101 458	-0.561 232 25	0.097 444 613 9
4	-2.061 056 87	0.416 240 028	2.925 245 13	-2.817 035 83	1.005 514 76	-0.127 884 416

### 3.3 Critical region

To represent the critical-region term  $\bar{\lambda}_2$  in Eq. (2), we use a simplified crossover model developed by Olchowy and Sengers,<sup>52</sup> which has yielded a good practical representation of the thermal conductivity of many fluids, including ordinary water, in the critical region<sup>16, 53-60</sup>

$$\bar{\lambda}_2(T, \rho) = \frac{\rho c_p R_D k_B T}{6\pi\mu\xi\lambda^*} \left\{ \bar{\Omega}(q_D \xi) - \bar{\Omega}_0(q_D \xi) \right\}, \quad (5)$$

where the specific heat capacity at constant pressure,  $c_p(T, \rho)$ , is obtained from the equation of state,<sup>12</sup>  $k_B$  is Boltzmann's constant, and the viscosity,  $\mu(T, \rho)$ , is from the 2020 IAPWS viscosity standard<sup>1, 15</sup> which includes a critical-enhancement term.  $R_D$  is a universal dynamic amplitude ratio,  $\xi$  is the correlation length, and  $q_D$  is a cutoff wave number that will be described below. The crossover functions  $\bar{\Omega}$  and  $\bar{\Omega}_0$  are determined by

$$\bar{\Omega}(y) = \frac{2}{\pi} \left[ (1 - \kappa^{-1}) \arctan(y) + \kappa^{-1} y \right], \quad (6a)$$

and

$$\bar{\Omega}_0(y) = \frac{2}{\pi} \left[ 1 - \exp\left( \frac{-1}{y^{-1} + y^2 / 3\bar{\rho}^2} \right) \right], \quad (6b)$$

where  $y = q_D \xi$  and where  $\kappa = c_p / c_v$  is the ratio of the isobaric and isochoric heat capacities. We find it convenient to introduce a dimensionless function  $Z$  defined by

$$Z(y) = \frac{2}{\pi y} \left\{ \left[ (1 - \kappa^{-1}) \arctan(y) + \kappa^{-1} y \right] - \left[ 1 - \exp\left( \frac{-1}{y^{-1} + y^2 / 3\bar{\rho}^2} \right) \right] \right\}. \quad (7)$$

Equation (5) for the dimensionless quantity  $\bar{\lambda}_2$  can then be rewritten as

$$\bar{\lambda}_2(T, \rho) = \frac{\rho c_p R_D k_B T q_D}{6\pi\mu\lambda^*} Z(q_D \xi). \quad (8)$$

It is important to note that Eq. (7) for  $Z(q_D \xi)$  is sensitive to the order of addition/subtraction of terms, so that parentheses have been put around the terms representing the separate contributions from  $\bar{\Omega}$  and  $\bar{\Omega}_0$  to the function  $Z$ . Problems with the summation order in Eq. (7) may occur for very small values of the correlation length  $\xi$ . To avoid numerical truncation issues in Eq. (7) for small values of  $y$ , the function  $Z(y)$  is subject to the condition

$$Z(y) = 0 \quad \text{for} \quad y < 1.2 \times 10^{-7}. \quad (9)$$

We note that the cutoff wave number  $q_D$  appearing in the crossover function for the critical thermal-conductivity enhancement is physically similar to, but numerically different from, the cutoff wave number  $q_D$  appearing in the crossover function for the critical viscosity enhancement.<sup>52, 61, 62</sup> In addition,  $\xi$  has been shown to be the same for H<sub>2</sub>O and D<sub>2</sub>O.<sup>63</sup>

To express Eq. (8) in terms of dimensionless quantities we introduce a dimensionless isobaric specific heat capacity  $\bar{c}_p$  and a dimensionless viscosity  $\bar{\mu}$ :

$$\bar{c}_p = \frac{c_p}{R}, \quad \bar{\mu} = \frac{\mu}{\mu^*}, \quad (10)$$

where  $R = 0.415\,151\,99 \text{ kJ kg}^{-1} \text{ K}^{-1}$  is the specific gas constant of D<sub>2</sub>O as defined by the Revised Release on the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water<sup>13</sup> and where  $\mu^* = 1 \times 10^{-6} \text{ Pa s}$  as defined by the IAPWS Formulation 2020 for the Viscosity of Heavy Water.<sup>15</sup> From Eq. (8) it then follows that the dimensionless critical thermal-conductivity enhancement is given by

$$\bar{\lambda}_2(\bar{T}, \bar{\rho}) = \Lambda \frac{\bar{\rho} \bar{c}_p \bar{T}}{\bar{\mu}} Z(y), \quad (11)$$

where

$$\Lambda = \frac{\rho^* T^* R R_D k_B q_D}{6\pi\mu^* \lambda^*} \quad (12)$$

is a numerical constant.

A procedure has already been developed for calculating the correlation length  $\xi$  for use in the formulation for the viscosity and thermal conductivity of  $\text{H}_2\text{O}$ <sup>16, 50, 62, 64</sup> and for the viscosity of heavy water.<sup>1,15</sup> The same procedure is used in the present formulation for the thermal conductivity of  $\text{D}_2\text{O}$ :

$$\xi = \xi_0 \left( \frac{\Delta\bar{\chi}}{\Gamma_0} \right)^{\nu/\gamma} \quad (13)$$

in terms of  $\Delta\bar{\chi} (\geq 0)$  defined by

$$\Delta\bar{\chi}(\bar{T}, \bar{\rho}) = \bar{\rho} \left[ \left( \frac{\partial\bar{\rho}(\bar{T}, \bar{\rho})}{\partial\bar{p}} \right)_{\bar{T}} - \left( \frac{\partial\bar{\rho}(\bar{T}_R, \bar{\rho})}{\partial\bar{p}} \right)_{\bar{T}} \frac{\bar{T}_R}{\bar{T}} \right] \quad (14)$$

or

$$\Delta\bar{\chi}(\bar{T}, \bar{\rho}) = \bar{\rho} \left[ \zeta(\bar{T}, \bar{\rho}) - \zeta(\bar{T}_R, \bar{\rho}) \frac{\bar{T}_R}{\bar{T}} \right], \quad (15)$$

with

$$\zeta = \left( \frac{\partial\bar{\rho}}{\partial\bar{p}} \right)_{\bar{T}}. \quad (16)$$

In these equations,  $\nu = 0.630$  and  $\gamma = 1.239$  are critical exponents,  $\xi_0 = 0.13$  nm and  $\Gamma_0 = 0.06$  are critical amplitudes,<sup>1, 63</sup> and  $\bar{T}_R = 1.5$  corresponds to a temperature  $T_R = 1.5T_c$  at which the critical fluctuations have become negligibly small. When  $\Delta\bar{\chi}$  calculated from Eq. (15) is less than zero, it must be set to zero for calculations to proceed. Due to the numerical implementation of the equation of state, the calculated singularity in the first derivative in Eq. (15) may not occur exactly at  $T_c = T^*$  and  $\rho_c = \rho^*$  as it should. Therefore, calculated values of  $\bar{\lambda}_2$  may behave unphysically at points extremely close to the critical point (approximately within  $0.01 \text{ kg m}^{-3}$  of  $\rho_c$  on the critical isotherm). The formulation should be used with caution in this very small region.

For general and scientific use, the specific heat capacity  $\bar{c}_p$  in Eq. (11), the ratio  $\kappa$  of the specific heat capacities in Eq. (7) for the function  $Z$ , and the derivatives  $(\partial\bar{\rho}/\partial\bar{p})_{\bar{T}}$  in Eq. (14) are to be calculated from the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water<sup>13</sup> and the viscosity  $\bar{\mu}$  in Eq. (11) from the IAPWS Formulation 2020 for the Viscosity of Heavy Water.<sup>1, 15</sup>

Equation (11) completely specifies the critical enhancement term  $\bar{\lambda}_2(\bar{T}, \bar{\rho})$  except for the selection of a suitable value for the universal dynamic amplitude ratio  $R_D$  and the system-dependent cutoff wave number  $q_D$ . In the present formulation for the thermal conductivity of D<sub>2</sub>O, we have adopted  $R_D = 1.01$  as found for H<sub>2</sub>O.<sup>16, 64</sup> The cutoff wave number was determined by an iterative process. Starting with an estimate for  $q_D^{-1}$ , the critical enhancement  $\bar{\lambda}_2(\bar{T}, \bar{\rho})$  was calculated and subtracted from experimental thermal-conductivity data in the critical region to get an improved estimate of the background contribution. This process was repeated until a consistent representation of the thermal-conductivity data in the critical region was obtained with  $q_D^{-1} = 0.36$  nm. The value of  $q_D^{-1}$  used here, 0.36 nm, for thermal conductivity of D<sub>2</sub>O is nearly the same as the value of 0.40 nm that was used for the thermal conductivity of water<sup>16, 50</sup> and for the viscosity of D<sub>2</sub>O,<sup>1</sup> but is different from the value used for the viscosity of water.<sup>62</sup> The values of the constants needed to compute the critical enhancement  $\bar{\lambda}_2(\bar{T}, \bar{\rho})$  from Eq. (11) for D<sub>2</sub>O are summarized in Table 4. Other than  $q_D^{-1}$  and  $\Lambda$ , which depends on the critical-point parameters that are different for H<sub>2</sub>O and D<sub>2</sub>O, all the other parameters for the critical enhancement of the thermal conductivity of D<sub>2</sub>O are the same as for H<sub>2</sub>O. In addition, for calculations one should use the value for  $\Lambda$  as given in Table 4 rather than recomputing it from Eq. (12).

TABLE 4. Critical-region constants

Constant	Value
$\Lambda$	175.9870
$q_D^{-1}$	0.36 nm
$\nu$	0.630
$\gamma$	1.239
$\xi_0$	0.13 nm
$\Gamma_0$	0.06
$\bar{T}_R$	1.5

There are two sources of detailed experimental information for D<sub>2</sub>O in the critical region: thermal-conductivity data obtained with the steady-state concentric cylinder technique by Tufeu *et al.*,<sup>20</sup> and

dynamic light-scattering measurements for the decay rate of the critical fluctuations obtained by Desmarest *et al.*<sup>46-49</sup> The light-scattering measurements yield thermal diffusivity data very close to the critical point that yield information on the thermal conductivity with accurate density and heat capacity information from the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water.<sup>13</sup> We have adopted these data sets for the thermal conductivity and thermal diffusivity of D<sub>2</sub>O as the primary data in the critical region.

Dynamic light scattering yields values for the thermal diffusivity  $D(q)$  at a finite wave number  $q$ . A procedure for converting the experimental measurements for  $D(q)$  into values for the thermal diffusivity  $D$  in the hydrodynamic limit  $q = 0$  has been presented in a previous publication.<sup>65</sup> In that publication, an estimate for the background thermal conductivity  $\lambda_b$  deduced from the 1985/2008 IAPWS Formulation<sup>66</sup> was adopted, as mentioned earlier. For the present project, the procedure was repeated but with the background thermal conductivity  $\lambda_b$  calculated from the correlation developed here [Eqs. (2) – (4) with  $\bar{\lambda}_2 = 0$ ]. The values thus deduced from the light-scattering data reported by Desmarest *et al.*<sup>48</sup> for the thermal diffusivity  $D$  as a function of  $\Delta T = T - T_c$  along the critical isochor are presented in Table 5, together with the corresponding thermal-conductivity values  $\lambda = \rho c_p D$  with  $c_p$  calculated at  $T$  and the critical density from the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water.<sup>13</sup> Also given in Table 5 is  $\Delta_c D$ , where  $\Delta_c D = D - \lambda_b / \rho c_p$ . As shown for H<sub>2</sub>O,<sup>65</sup> the values deduced for  $D$  and, hence, for  $\lambda$ , from the light-scattering measurements are insensitive to the estimates adopted for the background thermal conductivity. Thus, we adopt the thermal-conductivity values in Table 5 as primary experimental data for the thermal conductivity of D<sub>2</sub>O close to the critical temperature.

TABLE 5. Thermal diffusivity  $D(q)$  at  $\rho = \rho_c$  measured at  $q = 1.549 \times 10^7 \text{ m}^{-1}$  by Desmarest *et al.*<sup>48</sup> and the corresponding values for  $D = D(0)$  and  $\lambda$  as a function of  $\Delta T = T - T_c$ .

$\Delta T$ (K)	$D(q)$ ( $\text{m}^2 \text{ s}^{-1}$ )	$D$ ( $\text{m}^2 \text{ s}^{-1}$ )	$\lambda = \rho c_p D$ ( $\text{W m}^{-1} \text{ K}^{-1}$ )	$\Delta_c D$ ( $\text{m}^2 \text{ s}^{-1}$ )	$\mu/\mu_b$
0.030	$2.75 \times 10^{-10}$	$2.05 \times 10^{-10}$	3.112	$1.89 \times 10^{-10}$	1.19
0.054	$3.76 \times 10^{-10}$	$3.14 \times 10^{-10}$	2.643	$2.86 \times 10^{-10}$	1.16
0.080	$4.16 \times 10^{-10}$	$3.66 \times 10^{-10}$	2.072	$3.24 \times 10^{-10}$	1.15
0.109	$4.81 \times 10^{-10}$	$4.37 \times 10^{-10}$	1.807	$3.80 \times 10^{-10}$	1.14
0.144	$5.67 \times 10^{-10}$	$5.27 \times 10^{-10}$	1.640	$4.51 \times 10^{-10}$	1.13
0.165	$6.21 \times 10^{-10}$	$5.82 \times 10^{-10}$	1.577	$4.95 \times 10^{-10}$	1.13
0.198	$7.20 \times 10^{-10}$	$6.82 \times 10^{-10}$	1.532	$5.77 \times 10^{-10}$	1.12
0.246	$8.07 \times 10^{-10}$	$7.72 \times 10^{-10}$	1.387	$6.41 \times 10^{-10}$	1.11
0.298	$9.11 \times 10^{-10}$	$8.79 \times 10^{-10}$	1.292	$7.18 \times 10^{-10}$	1.11
0.352	$10.06 \times 10^{-10}$	$9.76 \times 10^{-10}$	1.206	$7.85 \times 10^{-10}$	1.10
0.432	$11.29 \times 10^{-10}$	$11.01 \times 10^{-10}$	1.096	$8.65 \times 10^{-10}$	1.09
0.540	$12.94 \times 10^{-10}$	$12.69 \times 10^{-10}$	0.996	$9.69 \times 10^{-10}$	1.09
0.648	$15.16 \times 10^{-10}$	$14.91 \times 10^{-10}$	0.962	$11.26 \times 10^{-10}$	1.08
0.760	$16.98 \times 10^{-10}$	$16.75 \times 10^{-10}$	0.908	$12.40 \times 10^{-10}$	1.08

A plot of these thermal-conductivity data as a function of  $\Delta T = T - T_c$  is presented in Fig. 5. The solid curve in this figure represents the values calculated from the present formulation, Eq. (2). The present formulation represents the experimental values with an average deviation of 5% for  $\Delta T < 0.8$  K, which is consistent with the estimated experimental uncertainty of 3% to 5% in  $D$  and 5 mK in  $\Delta T$ .<sup>46, 48</sup>

Since the critical enhancement of the viscosity  $\mu$  is only significant in a very small range of temperatures and densities around the critical point,<sup>61, 62</sup> one often approximates the viscosity  $\mu$  in Eq. (8) for the critical thermal-conductivity enhancement by the background viscosity  $\mu_b$ .<sup>52</sup> However, the light-scattering data provide information sufficiently close to the critical temperature where this approximation is no longer justified, as demonstrated by the values listed for  $\mu/\mu_b$  in Table 5. Thus, for an accurate representation of the thermal conductivity very close to the critical point the full viscosity  $\bar{\mu}$  is to be kept in Eq. (11).

It is possible to check our assumption that the value of  $R_D = 1.01 \pm 0.05$  found for H<sub>2</sub>O represents the data available for D<sub>2</sub>O. Near the critical point, the thermal-diffusivity enhancement is related to the viscosity, calculated with the reference correlation for D<sub>2</sub>O,<sup>1</sup> through the expression

$$\Delta_c D = D - \frac{\lambda_b}{\rho c_p} = \frac{R_D k_B T}{6\pi\mu\xi}, \quad (17)$$

so that

$$R_D = \frac{6\pi\mu\xi\Delta_c D}{k_B T}. \quad (18)$$

The data for the critical enhancement to the thermal diffusivity  $\Delta_c D$  of D<sub>2</sub>O are shown in Fig. 6. These thermal-diffusivity data for D<sub>2</sub>O ( $\Delta T > 0.2$  K) yield  $R_D = 1.01 \pm 0.04$  from Eq. (18). This value for D<sub>2</sub>O agrees very well with the value found for H<sub>2</sub>O.

Tufeu *et al.*<sup>20</sup> published experimental thermal-conductivity data in the critical region of D<sub>2</sub>O that were obtained with a coaxial-cylinder apparatus.<sup>67</sup> These data were obtained along isotherms as a function of pressure. The temperatures reported by Tufeu *et al.*<sup>20</sup> are on the IPTS-68 scale. All temperatures were converted to ITS-90,<sup>68, 69</sup> and the densities were recalculated according to the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water.<sup>13</sup> The authors estimate the uncertainty in thermal conductivity to be 2%. These thermal-conductivity data appear to be consistent with the dynamic light-scattering data for thermal diffusivity of Desmarest *et al.*<sup>46-49</sup> from the same laboratory.

The thermal conductivity  $\lambda$  of D<sub>2</sub>O at supercritical temperatures is shown as function of the density  $\rho$  in Fig. 7. The symbols indicate the experimental data reported by Tufeu *et al.*<sup>20</sup> The curves represent the values calculated from the present formulation. There are some deviations at  $T = 650$  K, which is only 5 K above  $T_c$ , where it becomes difficult to measure the thermal conductivity very accurately with the coaxial-cylinder technique. Moreover, close to the critical temperature the effects of increased uncertainty

in the density on the thermal conductivity become appreciable. Figure 8 shows the thermal-conductivity measurements of Tufeu *et al.*<sup>20</sup> along with the thermal conductivity deduced from the light-scattering data of Desmarest *et al.*<sup>48</sup> much closer to the critical point. We know from Figs. 5 and 8 that the thermal-conductivity formulation does reproduce the correct limiting behavior near the critical temperature. Hence, we conclude that the formulation yields a satisfactory description of the critical enhancement consistent with the available experimental accuracy.

### 3.4 Computer-program verification

Tables 6 and 7 are provided to assist the user in computer-program verification. The thermal-conductivity values are calculated as a function of the tabulated temperatures and densities. There are two situations where the contribution  $\bar{\lambda}_2$  must be set to zero. The first is at the zero-density limit, since some derivatives from the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water<sup>12, 13</sup> diverge at  $\rho=0$ ; for those points in Table 6,  $\bar{\lambda}_2$  must be set to zero. A second case occurs when  $\Delta\bar{\chi}$  calculated from Eq. (15) is less than zero, for example, for the liquid points at 298.15 K. As stated in Sec. 3.3,  $\Delta\bar{\chi}$  must be set to zero for calculations to proceed and  $\bar{\lambda}_2=0$ .

TABLE 6. Sample points for computer-program verification of the correlating equation, Eq. (2). At these points,  $\bar{\lambda}_2=0$ .

$T$ (K)	$\rho$ (kg m <sup>-3</sup> )	$\lambda$ (mW m <sup>-1</sup> K <sup>-1</sup> )
298.15	0	17.749 8
298.15	1104.5	599.557
298.15	1200	690.421
825.00	0	76.449 2

TABLE 7. Sample points for computer-program verification of the correlating equation, Eq. (2), including the critical-enhancement contribution  $\bar{\lambda}_2$ . For all points,  $T = 644.10$  K and  $\bar{\lambda}_0 = 52.149\ 66$ .

$\rho$ (kg m <sup>-3</sup> )	$\bar{\lambda}_1$	$\bar{\lambda}_2$	$\lambda$ (mW m <sup>-1</sup> K <sup>-1</sup> )
1	1.005 807 6	0.000 133 2	52.452 7
106	1.791 564 9	9.912 756 7	103.342
256	3.390 704 3	217.787 846	394.612
306	3.963 958 7	594.662 792	801.382
356	4.518 682 1	1042.775 41	1278.423
406	5.041 459 0	407.922 272	670.833
456	5.529 512 3	135.240 705	423.603
750	8.598 246 1	6.450 078 1	454.846

### 3.5 Liquid D<sub>2</sub>O at 0.1 MPa

It is useful to have a simpler correlating equation than Eq. (2), which is a function of temperature and density, for the properties of liquid heavy water at atmospheric pressure that has uncertainties no greater than those of the more complex formulation. For liquid ordinary water at 0.1 MPa, there is a formulation for the thermal conductivity as a function of temperature only.<sup>16</sup> We present here a similar correlation for liquid heavy water.

The dimensionless thermal conductivity  $\bar{\lambda}$  of liquid heavy water at a pressure of 0.1 MPa is described by the following equation:

$$\bar{\lambda} = \frac{1000 (c_1 + c_2 \tilde{T} + c_3 \tilde{T}^2 + c_4 \tilde{T}^3 + c_5 \tilde{T}^4)}{c_6 + \tilde{T}}, \quad (19)$$

where  $\tilde{T} = T / (300 \text{ K})$  and  $c_i$  are coefficients given in Table 8. Equation (19) is recommended for use in the following temperature range:

$$276.97 \text{ K} \leq T \leq 374.19 \text{ K}, \quad (20)$$

and extrapolates in a physically reasonable manner down to 250 K, describing points in the metastable supercooled region below the triple point. It agrees with the full correlation, Eq. (2), to within 0.021% over the range specified in Eq. (20). In addition, it extrapolates in a physically reasonable manner into the metastable liquid region at 0.1 MPa above 374.19 K to at least 384.19 K. Equation (19) is fitted to values from Eq. (2) in this work, and the uncertainty is the same as that of Eq. (2) that will be discussed in Sec. 4.2.

TABLE 8. Coefficients  $c_i$  in Eq. (19) for the thermal conductivity of liquid heavy water at 0.1 MPa.

$i$	$c_i$
1	-0.223 744
2	0.005 389 6
3	0.247 252
4	0.296 336
5	-0.176 540
6	-0.752 881

#### 4. Evaluation

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

$$\bar{\lambda} = \bar{\lambda}_0(\bar{T}) \times \bar{\lambda}_1(\bar{T}, \bar{\rho}) + \bar{\lambda}_2(\bar{T}, \bar{\rho}). \quad (21)$$

The function  $\bar{\lambda}_0(\bar{T})$  is given by Eq. (3), and the function  $\bar{\lambda}_1(\bar{T}, \bar{\rho})$  is given by Eq. (4) with coefficients in Table 3. The function  $\bar{\lambda}_2(\bar{T}, \bar{\rho})$  is given by Eq. (11) with the parameters presented in Table 4, thermodynamic properties from the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water,<sup>12, 13</sup> and the viscosity  $\bar{\mu}$  from the new IAPWS Formulation 2020 for the Viscosity of Heavy Water.<sup>1, 15</sup>

#### 4.1 Comparisons with experimental data and the IAPWS 2007 formulation for thermal conductivity

Table 9 presents comparisons of the experimental data with both the new formulation, Eq. (2), and with the previous IAPWS formulation for the thermal conductivity.<sup>11</sup> The table gives the number of data points, estimated uncertainty of the data, average percent deviation, average absolute percent deviation, and the standard deviation of each data source. Some points are extrapolations of the previous IAPWS correlation,<sup>11</sup> because they are outside of the recommended range of temperatures and densities. We define the percent deviation as  $P = 100(\lambda_{\text{exp}} - \lambda_{\text{fit}})/\lambda_{\text{fit}}$ , where  $\lambda_{\text{exp}}$  is the experimental value of the thermal conductivity, and  $\lambda_{\text{fit}}$  is the value calculated from the present correlation, Eq. (2). The average absolute percent deviation (AAD) is found with the expression  $\text{AAD} = (\sum |P|)/n$ , where the summation is over all  $n$  points; the average percent deviation (bias) is  $\text{AVG} = (\sum P)/n$ , the standard deviation is  $\text{STDV} = ([n\sum P^2 - (\sum P)^2]/n^2)^{1/2}$  and MAX denotes the value with the largest deviation.

Figures 9–20 show the percent deviations of the present model and the 2007 IAPWS correlation<sup>11</sup> with the primary experimental data for three different pressure ranges, both as a function of temperature and as a function of pressure. Figures displaying deviations for data at pressures up to 1 MPa (Figs. 9–12) show that the 2007 IAPWS correlation<sup>11</sup> and the present one are essentially identical in this region for liquid-phase data (Rastorguev *et al.*,<sup>24</sup> Le Neindre *et al.*,<sup>31</sup> Nagasaka *et al.*<sup>19</sup>) but show slightly better performance in the vapor region by the present correlation, that is in better agreement with the gas-phase data of Curtiss *et al.*<sup>21</sup> Similarly, Figs. 13–16 that display deviations for the fluid in the pressure range between 1 MPa and 50 MPa show that except for the region near the critical point, the correlations are very similar. The present correlation has improved performance in the critical region, as shown by the comparisons with the data of Tufeu *et al.*<sup>20</sup> that are denoted by open circles in the figures. For data in the highest-pressure range, above 50 MPa up to 250 MPa (Figs. 17–20), the present correlation displays improved performance for the data above 100 MPa. This is not surprising, since the 2007 IAPWS correlation<sup>11</sup> was developed using an equation of state that was limited to 100 MPa. The stated range of applicability for the 2007 IAPWS formulation<sup>11</sup> is  $0 \text{ MPa} \leq p \leq 100 \text{ MPa}$ , and  $277 \text{ K} \leq T \leq 825 \text{ K}$ . The equation of state used in this work has a wider range of applicability, up to 1200 MPa,<sup>13</sup> and high-pressure data sets were incorporated into the development of the present correlation.

TABLE 9. Summary of comparisons of Eq. (2) with experimental data and the 2007 IAPWS formulation<sup>11</sup> for the thermal conductivity of D<sub>2</sub>O

	Uncertainty (%) <sup>a</sup>	No. data	Present work				IAPWS 2007 formulation <sup>11</sup>			
			AAD	AVG	STDV	MAX	AAD	AVG	STDV	MAX
<b>primary data</b>										
Nagasaka <sup>19</sup>	0.5	45	0.78	-0.71	0.59	-1.72	0.61	-0.27	0.64	-1.23
Tufeu <sup>20,b</sup>	2.0	202	2.28	-2.04	1.90	-6.14	2.75	-0.82	3.77	-15.65
Curtiss <sup>21,b</sup>	1.0	74	0.37	-0.30	0.36	-1.05	2.15	-2.15	0.47	-3.14
Yata <sup>22</sup>	2-3	144	1.94	1.09	2.61	8.12	2.66	2.63	2.10	8.06
Amirkhanov <sup>23,b</sup>	na	136	3.45	-2.24	3.19	7.26	1.71	-0.17	2.22	-7.33
Rastorguev <sup>24</sup>	1.5	444	1.24	0.95	1.11	-3.79	2.02	1.89	1.28	3.98
Vargaftik <sup>26</sup>	1.0	13	3.52	2.66	3.04	9.06	2.81	1.43	2.94	7.49
Amirkhanov <sup>27</sup>	2.0	351	1.15	0.49	1.29	2.84	3.92	3.53	3.43	10.69
Tanzimanov <sup>28,b</sup>	2.5	178	1.68	-0.38	2.14	-9.68	1.90	0.58	2.84	11.50
Vargaftik <sup>29,b</sup>	1.5	17	1.71	1.34	1.68	3.95	1.13	-0.09	1.30	-2.12
Dijkema <sup>30,b</sup>	0.5	1	2.96	2.96	na	2.96	1.02	1.02	na	1.02
Le Neindre <sup>31</sup>	1.8	383	0.84	-0.58	1.04	-9.52	0.66	0.41	0.93	-8.08
Le Neindre <sup>33,b</sup>	2.0	65	1.67	-0.43	1.93	-5.22	0.63	-0.35	1.07	-6.74
Le Neindre <sup>34</sup>	1.0	46	0.70	0.48	0.80	2.70	1.57	1.57	0.74	3.33
Baker <sup>35,b</sup>	na	4	0.87	-0.71	0.93	-2.21	2.36	-2.36	0.90	-3.81
Vargaftik <sup>36,b</sup>	1.0	12	1.75	-1.60	1.45	-3.97	3.11	-3.11	1.57	-5.54
<b>secondary data</b>										
Vargaftik <sup>37,b</sup>	na	113	3.09	2.68	2.45	8.10	2.98	2.97	1.99	9.22
Vargaftik <sup>38</sup>	1.0	65	3.03	-3.01	3.88	-18.71	2.05	-1.91	3.59	-19.42
Klassen <sup>39</sup>	na	14	1.44	0.97	1.65	3.83	1.74	1.56	1.57	4.30
Ziebland <sup>40</sup>	1.0	37	1.23	1.21	0.72	2.66	1.77	1.77	0.59	3.10
Challoner <sup>41</sup>	1.0	5	1.66	-1.31	1.19	-2.46	1.21	-0.70	1.08	1.68
Meyer <sup>42</sup>	1.0	5	1.33	-1.20	1.06	-2.90	0.87	-0.52	0.96	-2.07
Bonilla <sup>43</sup>	na	6	0.68	-0.43	0.66	-1.36	0.45	0.26	0.54	1.19

<sup>a</sup> na, not available

<sup>b</sup> Indicates vapor-phase measurements

## 4.2 Range of validity and uncertainty estimates for the formulation

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

$$\begin{aligned} 0 < p \leq p_t & & \text{and} & & T_t \leq T \leq 825 \text{ K} \\ p_t \leq p \leq 250 \text{ MPa} & & \text{and} & & T_m(p) \leq T \leq 825 \text{ K}. \end{aligned} \quad (22)$$

In Eq. (22),  $T_m(p)$  is the pressure-dependent melting temperature and  $T_t = 276.969 \text{ K}$  is the triple-point temperature as given in Ref. 12. The density from the equation of state of Herrig *et al.*<sup>12</sup> 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, as mentioned in Sec. 3.1, the dilute-gas component of Eq. (2) behaves in a physically reasonable and most likely even quantitatively correct manner at temperatures up to 2500 K because it is based on advanced, theoretically predicted thermal-conductivity values up to this temperature, see Ref. 14 and the updated values listed in Appendix A. Note, however, that the effects of any partial dissociation of the gas at such high temperatures are not considered here. We note that at very high temperatures (above about 2100 K for steam<sup>70</sup>) dissociation may occur. The present equation does not account for dissociation; one may wish to consider these effects, as discussed in Refs. <sup>70,71</sup>.

Furthermore, for vapor states at temperatures below the triple-point temperature of 276.969 K and pressures less than or equal to the sublimation pressure, the thermal conductivity is dominated by the dilute-gas term, which behaves in a physically reasonable manner down to 250 K, the lowest temperature considered in the theoretical calculations it is based on. For stable fluid states outside the range of validity of Eq. (22) but within the range of validity of the Revised Release on the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water,<sup>13</sup> the extrapolation behavior of Eq. (2) is physically reasonable. There are no experimental data for comparisons, but the behavior of Eq. (2) in the supercooled liquid region is also physically reasonable without any poles or unusual behavior.

For the development of the estimates of uncertainty, we relied upon comparisons with the previous IAPWS formulation for the thermal conductivity <sup>8,11</sup> 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. Figure 21 shows the relative uncertainties in this formulation. The uncertainty estimates can be considered as estimates of an expanded uncertainty with a coverage factor of two. The critical enhancement of thermal conductivity is significant in a large range of temperatures and densities. This is illustrated in Fig. 22, which shows contours in the temperature-density plane encompassing regions around the critical point where the relative contribution from the critical enhancement term  $\bar{\lambda}_2(\bar{T}, \bar{\rho})$  to the total

thermal conductivity  $\bar{\lambda}(\bar{T}, \bar{\rho})$  exceeds 5%, 1%, 0.5%, and 0.1%. In this figure,  $T_R = T^* \bar{T}_R$  as discussed in Sec. 3.3. The information in this figure can be used as a guide at which temperatures and densities the critical-enhancement term needs to be included to calculate the thermal conductivity with a given accuracy. We note that the range of the critical thermal-conductivity enhancement for H<sub>2</sub>O and D<sub>2</sub>O is comparable to that observed for other fluids such as carbon dioxide.<sup>72</sup> The critical enhancement calculation requires values for the viscosity from the IAPWS Formulation for D<sub>2</sub>O,<sup>12</sup> which is not validated for temperatures above 775 K. Figure 22 shows that the critical enhancement is less than 5% for temperatures above 775 K. Extrapolation of the viscosity correlation during calculations at temperatures above 775 K does not introduce significant error in the thermal conductivity.

## 5. Recommendations for Industrial Applications

Many industrial applications do not operate close to the critical point and computational speed in process design can become very important. Since the critical enhancement of viscosity is only significant very close to the critical point, the background viscosity is recommended for computing the critical enhancement of thermal conductivity for industrial applications. This is consistent with the recommendations in the formulation for the viscosity of heavy water for industrial applications.<sup>1, 15</sup> The critical enhancement of the thermal conductivity requires two evaluations of the equation of state. First, the equation of state is needed at the temperature and pressure or density of interest and then it is evaluated again at the reference temperature and the density of interest. The two equation-of-state evaluations represent the largest computational time, so that eliminating the second equation-of-state evaluation at the reference temperature will dramatically decrease the computational time for thermal conductivity. For this purpose, a polynomial function in terms of density is provided for evaluation of the compressibility of D<sub>2</sub>O at the reference temperature. This polynomial function eliminates the second equation of state calculation and is recommended for industrial applications to reduce computation time.

### 5.1 Industrial application of the correlating equation

The recommended formulation for calculating the thermal conductivity for industrial applications has a form similar to Eq. (2):

$$\bar{\lambda}_1(\bar{T}, \bar{\rho}) = \bar{\lambda}_0(\bar{T}) \times \bar{\lambda}_1(\bar{T}, \bar{\rho}) + \bar{\lambda}_{21}(\bar{T}, \bar{\rho}), \quad (23)$$

where the functions  $\bar{\lambda}_0(\bar{T})$  and  $\bar{\lambda}_1(\bar{T}, \bar{\rho})$  are identical to those specified in Eqs. (4) and (5), but where for the industrial application we use

$$\bar{\lambda}_{21}(\bar{T}, \bar{\rho}) = \Lambda \frac{\bar{\rho} \bar{c}_p \bar{T}}{\bar{\mu}_0 \bar{\mu}_1} Z(\bar{q}_D \xi_1). \quad (24)$$

The dimensionless background viscosity,  $\bar{\mu}_0 \bar{\mu}_1$ , in Eq. (24) should be calculated from the recommended viscosity correlation for industrial application as described in the IAPWS Formulation 2020 for the Viscosity of Heavy Water,<sup>1, 15</sup> which does not include the critical enhancement of viscosity. In Eq. (24), the isobaric specific heat capacity,  $\bar{c}_p$ , as well as the density derivative in Eq. (16) for specifying the correlation length in Eqs. (11) and (13) for the function  $Z$ , are to be calculated with the Revised Release on the IAPWS Formulation 2017 for the Thermodynamic Properties of Heavy Water.<sup>13</sup> The function  $\zeta(\bar{T}_R, \bar{\rho})$  in Eq. (16) is calculated from

$$\zeta(\bar{T}_R, \bar{\rho}) = \frac{1}{\sum_{i=0}^{10} A_i \bar{\rho}^i}, \quad (25)$$

with coefficients  $A_i$  given in Table 10. Note that Eq. (25) is only a function of density and does not require an additional evaluation of the equation of state at the reference temperature. All evaluations of the IAPWS Formulation should be done once for each state point of interest to reduce computation time.

TABLE 10. Coefficients  $A_i$  in Eq. (25) for  $\zeta(\bar{T}_R, \bar{\rho})$

$i$	$A_i$
0	6.584 360
1	-5.362 300
2	-0.611 633
3	21.445 300
4	-45.055 900
5	54.050 400
6	-39.433 200
7	17.948 500
8	-4.916 820
9	0.739 039
10	-0.046 751

## 5.2 Range of validity of the industrial equation

The range of validity for the industrial application of the thermal-conductivity correlation, Eq. (23), is:

$$\begin{aligned} 0 < p \leq p_t & \quad \text{and} \quad T_t \leq T \leq 825 \text{ K} \\ p_t \leq p \leq 250 \text{ MPa} & \quad \text{and} \quad T_m(p) \leq T \leq 825 \text{ K}. \end{aligned} \quad (26)$$

The industrial formulation has the same range of validity as the full formulation but with increased uncertainty in the critical region.

### 5.3 Estimated uncertainty of the industrial equation

The uncertainty of the industrial equation results from two contributions: (1) the uncertainty of the recommended correlating equation for general and scientific use, illustrated in Fig. 21, and (2) the deviation caused by using the industrial equation for the viscosity, and the approximation for the compressibility at the reference temperature  $T_R$ . Since the latter is much smaller than the former, the uncertainties shown in Fig. 21 are applicable to the industrial equation except for a small region near the critical point, where deviations of the industrial equation become larger. These errors are primarily due to the use of the industrial formulation for the viscosity. These relative errors are illustrated in Fig. 23, exceeding 1.5% only for  $T - T_c < 5$  K and with reduced densities near the critical point,  $0.5 \leq \bar{\rho} \leq 1.5$ .

### 5.4 Computer-program verification of the industrial equation

Table 11 is provided to assist the user in computer-program verification of the thermal conductivity formulation for industrial use.

TABLE 11. Sample points for computer-program verification of the correlating equation, Eq. (23) for thermal conductivity (industrial use), including the critical-enhancement contribution  $\bar{\lambda}_{21}$ . For all points,  $T = 644.10$  K and  $\bar{\lambda}_0 = 52.149\ 665$

$\rho$ (kg m <sup>-3</sup> )	$\bar{\lambda}_1$	$\bar{\lambda}_{21}$	$\lambda_1$ (mW m <sup>-1</sup> K <sup>-1</sup> )
1	1.005 807 6	0.000 120 7	52.452 7
106	1.791 564 9	9.912 548 0	103.342
256	3.390 704 3	222.078 865	398.903
306	3.963 958 7	631.959 374	838.678
356	4.518 682 1	1158.467 33	1394.115
406	5.041 459 0	435.258 942	698.169
456	5.529 512 3	138.464 122	426.826
750	8.598 246 1	6.449 056 0	454.845

## 6. Summary

The international task group, comprising members affiliated with IAPWS and IATP, has completed its examination of the data, theory, and models most appropriate for describing the thermal conductivity of heavy 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 thermal conductivity of heavy water for most purposes according to international consensus and within uncertainty bounds achievable with current information. As evidenced by Fig. 21, there are still regions (for example at pressures above 250 MPa or temperatures above about 825 K) where new experimental data with low uncertainties could lead to improvements in future representations of the thermal-conductivity surface of heavy water. In addition, unlike for the viscosity of heavy water, there are currently no measurements in the metastable supercooled region at atmospheric pressure. 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. 9. 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, incorporates advances in the calculation of the zero-density thermal conductivity by Hellmann and Bich,<sup>14</sup> and is consistent with the more recent consensus document for the thermodynamic properties of heavy water. The comparisons of Sec. 4 provide support for the uncertainty estimates over the full range of applicability of the correlation.

The recently adopted IAPWS Release on the Thermal Conductivity of Heavy Water<sup>3</sup> provides a concise description of the correlating equations for potential users. This paper provides a more detailed explanation of the formulation.

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## 8. Conflict of Interest

The authors have no conflicts to disclose.

## 9. Data Availability

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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## APPENDIX A

*Ab initio* calculated thermal-conductivity values for D<sub>2</sub>O in the dilute-gas limit.

The differences between the values for the thermal conductivity in the dilute-gas limit given in Table A1 and those published by Hellmann and Bich in Ref. 14 are due to the replacement of the 2013 correlation for the ideal-gas heat capacity<sup>73</sup> by a more recent one published by Herrig *et al.*<sup>12</sup> The 2013 correlation was based on calculations made in 1954 by Friedman and Haar,<sup>74</sup> the new correlation of Herrig *et al.*<sup>12</sup> is based on state-of-the-art calculations for the ideal-gas heat capacity by Simkó *et al.*<sup>75</sup> that have uncertainties of less than 0.01% up to 1800 K. The uncertainties of the new thermal-conductivity values should be only slightly smaller than those of the previous values.<sup>14</sup> Therefore, the uncertainty statement (expanded uncertainty with a coverage factor  $k = 2$ ) for the new values remains unchanged from that in Ref. 14, 2% for temperatures from 250 K to 600 K, 3% between 600 K and 1500 K, and 4% above 1500 K.

TABLE A1. *Ab initio* calculated thermal-conductivity values for D<sub>2</sub>O.

$T$ (K)	$\lambda_0$ (mW m <sup>-1</sup> K <sup>-1</sup> )	$T$ (K)	$\lambda_0$ (mW m <sup>-1</sup> K <sup>-1</sup> )
250	14.39	740	64.64
260	15.07	760	67.36
270	15.75	780	70.12
273.15	15.97	800	72.92
280	16.45	820	75.74
290	17.16	840	78.59
298.15	17.75	860	81.46
300	17.89	880	84.36
310	18.62	900	87.28
320	19.38	920	90.21
330	20.15	940	93.16
340	20.93	960	96.13
350	21.73	980	99.10
360	22.55	1000	102.1
370	23.38	1050	109.6
380	24.22	1100	117.1
390	25.09	1150	124.6
400	25.96	1200	132.1
410	26.86	1250	139.6
420	27.77	1300	147.0
430	28.69	1350	154.4
440	29.63	1400	161.7
450	30.59	1450	169.0
460	31.56	1500	176.3
470	32.55	1550	183.4
480	33.55	1600	190.5

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490	34.57	1650	197.6
500	35.60	1700	204.5
520	37.72	1750	211.5
540	39.89	1800	218.3
560	42.13	1850	225.1
580	44.42	1900	231.8
600	46.77	1950	238.5
620	49.18	2000	245.1
640	51.64	2100	258.2
660	54.14	2200	271.1
680	56.70	2300	283.7
700	59.30	2400	296.2
720	61.95	2500	308.5

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