An equation of state is presented for the thermodynamic properties of cold and supercooled water. It is valid for temperatures from the homogeneous ice nucleation temperature up to 300 K and for pressures up to 400 MPa, and can be extrapolated up to 1000 MPa. The equation of state is compared with experimental data for density, expansion coefficient, isothermal compressibility, speed of sound, and heat capacity. Estimates for the accuracy of the equation are given. The melting curve of ice I is calculated from the phase-equilibrium condition between the proposed equation and an existing equation of state for ice I.

Key words: compressibility; density; equation of state; expansivity; heat capacity; speed of sound; supercooled water; thermodynamic properties
in the metastable region as well as possible. This work only considers supercooled water above the homogeneous nucleation temperature. The equation does not cover the glassy state of water (below 136 K at atmospheric pressure).  

2. It should be possible to smoothly connect this correlation to the IAPWS-95 formulation, the current reference for the thermodynamic properties of water.\textsuperscript{20,21} IAPWS-95 is, strictly speaking, valid only at temperatures above the melting curve. When extrapolated into the supercooled region, the IAPWS-95 formulation also yields a good description of the data that were available at the time this formulation was developed. With a smooth connection, one could use IAPWS-95 at high temperatures and the present correlation at low temperatures, without significant discontinuities at the point of switching.  

3. The correlation should allow extrapolation up to 1000 MPa. There are only a few data in the supercooled region above 400 MPa, but smooth extrapolation up to 1000 MPa would be desirable.

2. Experimental Data

Most of the experimental data that were considered in this work have been reviewed before.\textsuperscript{17,20,22–25} In this section, we mainly discuss new data and data that were treated differently than in our previous work.\textsuperscript{17,18,26}

2.1. Density

The experimental density data that were considered in this work are listed in Table I and shown in Fig. 1(a). Additional references to older data can be found in the articles of Tekáč \textit{et al.}\textsuperscript{30} and Wagner and Pruss.\textsuperscript{30} In a large part of the supercooled region, the only available density data are those of Mishima.\textsuperscript{38} As a result, it is difficult to estimate the systematic error of these data at low temperatures. In a graph in his article, Mishima showed the random (type A) uncertainty for each data point, which is 0.2% on average and at most 0.5%. The systematic (type B) uncertainty can only be estimated above 253 K, in the region of overlap with density data of Kell and Whalley,\textsuperscript{30} Sotani \textit{et al.},\textsuperscript{35} and Asada \textit{et al.}.\textsuperscript{37} In this region, the densities of Mishima deviate systematically by up to 0.4% from these other data. Below 253 K, the systematic uncertainty is unknown. As in earlier work,\textsuperscript{17} we adjusted the density values of Mishima, under the assumption that the systematic deviation at low temperatures, where it is not known, is the same as at higher temperatures, where it can be calculated. It was found that the adjusted data of Mishima do not completely agree with the expansivity measurements of Ter Minassian \textit{et al.},\textsuperscript{14} which we consider to be more accurate. Therefore, the adjusted data of Mishima were included in the fit of the equation of state with a relatively low weight.  

The only experimental density data at atmospheric pressure that were included in the fit are those of Hare and Sorensen,\textsuperscript{34} which are considered to be the best available. For pressures higher than atmospheric, we included data from Sotani \textit{et al.},\textsuperscript{35} Asada \textit{et al.},\textsuperscript{37} and Kell and Whalley.\textsuperscript{30} To enable extrapolation of the equation above 400 MPa, density data from Grindley and Lind\textsuperscript{38} up to 800 MPa were included in the fit.

2.2. Density derivatives

Several data sets exist for temperature and pressure derivatives of the density $\rho$. The cubic expansion coefficient $\alpha_P$, also known as expansivity, is defined as

$$\alpha_P = -\frac{1}{\rho} \frac{\partial \rho}{\partial T}_P,$$  \hspace{1cm} (1)

where $T$ is the temperature and $P$ is the pressure. The isothermal compressibility $\kappa_T$ is defined as

$$\kappa_T = -\frac{1}{\rho} \frac{\partial \rho}{\partial P}_T.$$  \hspace{1cm} (2)

The data sets listed in Table II were all included in the fit, with the exception of the compressibility data of Mishima.\textsuperscript{38} Mishima’s data were not included because they may be affected by systematic errors of unknown size at low temperatures. In previous work,\textsuperscript{17,18} expansivities reported by Hare and Sorensen\textsuperscript{34} were included in the fit. However, Hare and Sorensen did not measure the expansivity directly, but derived it from a fit to their density data. Because we already included Hare and Sorensen’s density data in our fit, their expansivity data were not used in the fit. Expansivity values from Ter Minassian \textit{et al.}\textsuperscript{34} were calculated from their empirical correlation. The accuracy of their correlation is not given; the relative difference with expansivities calculated from IAPWS-95 is at most 3.2% in the range of 300 K to 380 K and 0 MPa to 400 MPa.  

At points in the phase diagram where the expansivity is zero, the density has a maximum with respect to temperature. The temperature at which this occurs is usually referred to as the temperature of maximum density (TMD). Caldwell\textsuperscript{51} measured the TMD for pressures up to 38 MPa, and these measurements were included in the expansivity data set of the fit as $\alpha_P = 0$ points. The recent TMD measurements of Hiro \textit{et al.}\textsuperscript{31} were not used, because they deviate systematically by about 1.5 K from more accurate data.

2.3. Speed of sound

The experimental data on the speed of sound considered in this article are given in Table III and shown in Fig. 2. Recent data that were not considered in previous work are the accurate measurements of the speed of sound by Lin and Trusler\textsuperscript{52} down to of 253 K and from 1 MPa to 400 MPa. Although there are few data points in the supercooled region, the accuracy of 0.03%–0.04% makes this an important data set. Lin and Trusler also derived densities and isobaric heat capacities by integrating their speed-of-sound data. We have not considered these derived properties in the development of the equation of state in this work for the following reason. To enable integration of the speed of sound, Lin and Trusler represented their experimental data on the speed of sound by an empirical correlation. The experimental data of Lin and Trusler are closer
FIG. 1. (a) Location of experimental H$_2$O density data considered in this work. The thick solid curve is the melting curve, the dashed curve is the homogeneous ice nucleation limit (see Appendix A), and the thin solid curves are the ice phase boundaries. (b) Location of the experimental H$_2$O density-derivative data. Ter Minassian et al. and Caldwell have measured the expansivity; other authors have measured the isothermal compressibility.

### TABLE I. Experimental density data

| Reference          | Year   | Temperature range (K) | Pressure range (MPa) | Density uncertainty (%) | Source$^d$ | Included in fit |
|--------------------|--------|-----------------------|----------------------|-------------------------|------------|-----------------|
| Adams$^{27}$       | 1931   | 298                   | 0.1–900              | 0.1                     | T          | –               |
| Grindley & Lind$^{28}$ | 1971   | 298–423               | 20–800               | 0.02                    | T          | Yes             |
| Borzunov et al.$^{29}$ | 1974   | 293–338               | 0–923                | 0.1                     | T          | –               |
| Kell and Whalley$^{30}$ | 1975   | 273–423               | 0.5–103              | 0.001–0.003             | T          | Yes             |
| Bradshaw & Schleicher$^{31}$ | 1976   | 283                   | 0.1–100              | 0.007                   | T          | –               |
| Aleksandrov et al.$^{32}$ | 1976   | 264–278               | 5–101                | 0.1$^c$                 | T          | –               |
| Hare & Sorensen$^{34}$ | 1987   | 240–268               | 0.101325             | 0.02                    | T          | Yes             |
| Sotani et al.$^{35}$ | 1998   | 253–293               | 0–200                | 0.05                    | $^b$       | –               |
| Sotani et al.$^{35}$ | 2000   | 253–298               | 0–196                | 0.03$^c$                | G          | Yes             |
| Tanaka et al.$^{36}$ | 2001   | 273–313               | 0.101325             | 0.0001                  | T          | –               |
| Asada et al.$^{37}$ | 2002   | 253–298               | 210–378              | 0.1                     | G          | Yes             |
| Guignon et al.$^{39}$ | 2010   | 254–323               | 0.1–350              | 0.2                     | T          | –               |
| Mishima$^{38}$     | 2010   | 200–275               | 39–399               | 0.5$^l$                 | S          | Yes             |

$^a$ T = table from article, S = table from supplement, G = extracted from graph

$^b$ Superseded by Sotani et al.$^{35}$

$^c$ Estimated by Wagner and Thol$^{49}$

$^d$ Uncertainty is unknown below 253 K, see the text
to the prediction of our equation of state than to their correlation, in the temperature range considered here (Sec. 4.4). Therefore, densities and heat capacities calculated from our equation of state are more accurate than the values derived by Lin and Trusler.

The work of Smith and Lawson\textsuperscript{53} deserves mention because they were likely the first to measure the speed of sound below 273 K at elevated pressures. However, their pressure calibration has an uncertainty of about 1%, as discussed by Holton et al.,\textsuperscript{54} and their data were not further considered for this work.

The most accurate measurements of the speed of sound in the range from 273 K to 300 K and up to 60 MPa are those of Belogol’skii et al.\textsuperscript{55} They presented a correlation that represents their data with a standard deviation of 0.003% in the speed of sound. We estimated the accuracy of this correlation by comparing it to the experimental data of Lin and Trusler. For this comparison, Lin and Trusler’s speeds of sound on each of their isotherms were corrected to compensate for their small deviation at atmospheric pressure. After this correction, the difference between the data of Lin and Trusler and the correlation of Belogol’skii et al. is at most 0.01%, which suggests that the correlation of Belogol’skii et al. has an accuracy of 0.01% or better in the speed of sound. Measurements of Aleksandrov and Larkin\textsuperscript{26} in this temperature and pressure range have a slightly higher uncertainty of 0.02%. The data presented by Mamedov\textsuperscript{57} are not considered here, because Mamedov published rounded data of Aleksandrov and Larkin.\textsuperscript{56} Aleksandrov and Kochetov\textsuperscript{58} used the setup described by Aleksandrov and Larkin\textsuperscript{56} to measure the speed of sound down to 266 K and up to 100 MPa. A comparison with the data of Lin and Trusler\textsuperscript{52} suggests that the accuracy of the data of Aleksandrov and Kochetov\textsuperscript{58} is about 0.1%.

To improve the extrapolation behavior of the equation above 400 MPa, data from Vance and Brown\textsuperscript{59} up to 700 MPa were included in the fit. The data from Hidalgo Baltasar et al.\textsuperscript{60} which also extend up to 700 MPa, were not included because they systematically deviate from other data (Sec. 4.4).

At atmospheric pressure in the supercooled region, the data of Taschin et al.\textsuperscript{61} seem to be the best available; they are consistent with other thermodynamic properties.\textsuperscript{61} Above 273.15 K, the data deviate at most 0.15% from the IAPWS-95 formulation, and the uncertainty below 260 K is 0.7%.

\begin{table}[h]
\centering
\caption{Experimental data on compressibility and expansivity}
\begin{tabular}{|l|l|l|l|l|}
\hline
Reference & Temperature & Pressure & Source\textsuperscript{a} & Source\textsuperscript{b} \\
\hline
\textbf{Compressibility data} & \textbf{Compressibility data} & \textbf{Compressibility data} & \textbf{Compressibility data} & \textbf{Compressibility data} \\
\hline
Speedy & Angell\textsuperscript{46} & 1976 & 247–297 & 0.101325 & G \\
Kanno & Angell\textsuperscript{47} & 1979 & 241–298 & 10–190 & G \\
Mishima\textsuperscript{38} & 2010 & 199–269 & 27–397 & S \\
\hline
\textbf{Expansivity data} & \textbf{Expansivity data} & \textbf{Expansivity data} & \textbf{Expansivity data} & \textbf{Expansivity data} \\
\hline
Caldwell\textsuperscript{45} & 1978 & 268–277 & 0.1–38 & T\textsuperscript{b} \\
Ter Minassian et al.\textsuperscript{44} & 1981 & 246–410 & 2–636 & G\textsuperscript{b} \\
\hline
\end{tabular}
\begin{flushright}
\textsuperscript{a} T = table from article, S = table from supplement, G = extracted from graph
\textsuperscript{b} An empirical correlation is also provided
\end{flushright}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Location of experimental data on the speed of sound considered in this work.\textsuperscript{52,53,55,56,58–61,68,69} The thick curve is the melting curve,\textsuperscript{40,41} and the thin curves are the ice phase boundaries.\textsuperscript{52,53} Belogol’skii et al.\textsuperscript{55} did not publish their individual data points; their reported isotherms are shown as dotted lines.}
\end{figure}

\subsection{2.4. Heat capacity}

The isobaric heat capacity $C_P$ of cold and supercooled water at atmospheric pressure has been measured by several investigators; a list is given in Table IV. There are two data sets that extend down to 236 K, those of Angell et al.\textsuperscript{71} and Archer and Carter.\textsuperscript{72} The difference between the data sets increases with decreasing temperature, and at 236 K, the heat capacity reported by Angell et al.\textsuperscript{71} is 5% higher than that found by Archer and Carter.\textsuperscript{72} Because it is not known which data set is best, the equation of the current work was initially not fitted to any heat-capacity data in the supercooled region. It was found that most of the preliminary equations predicted heat capacities in agreement with the data of Angell et al.\textsuperscript{71} and were close to values calculated from the extrapolated IAPWS-95 formulation. However, in some cases, the predicted heat capacities were slightly higher than those Angell et al.\textsuperscript{71} Therefore, to reduce the difference with the experimental data, values calculated from IAPWS-95 were added as input for the fit.

There are only few measurements of $C_P$ at elevated pressures. The data of Sirota et al.\textsuperscript{73} at pressures up to 98 MPa were included in the fit. The data of Czarnota\textsuperscript{24} were not considered accurate enough to be included in the fit.

\begin{table}[h]
\centering
\caption{Experimental data on compressibility and expansivity}
\begin{tabular}{|l|l|l|l|l|l|}
\hline
Reference & Year & Temperature & Pressure & Source\textsuperscript{a} & Source\textsuperscript{b} \\
\hline
\textbf{Compressibility data} & \textbf{Compressibility data} & \textbf{Compressibility data} & \textbf{Compressibility data} & \textbf{Compressibility data} \\
\hline
Speedy & Angell\textsuperscript{46} & 1976 & 247–297 & 0.101325 & G \\
Kanno & Angell\textsuperscript{47} & 1979 & 241–298 & 10–190 & G \\
Mishima\textsuperscript{38} & 2010 & 199–269 & 27–397 & S \\
\hline
\textbf{Expansivity data} & \textbf{Expansivity data} & \textbf{Expansivity data} & \textbf{Expansivity data} & \textbf{Expansivity data} \\
\hline
Caldwell\textsuperscript{45} & 1978 & 268–277 & 0.1–38 & T\textsuperscript{b} \\
Ter Minassian et al.\textsuperscript{44} & 1981 & 246–410 & 2–636 & G\textsuperscript{b} \\
\hline
\end{tabular}
\begin{flushright}
\textsuperscript{a} T = table from article, S = table from supplement, G = extracted from graph \\
\textsuperscript{b} An empirical correlation is also provided
\end{flushright}
\end{table}
Recently, Manyà et al. have measured $C_P$ at 4 MPa from 298 K to 465 K. The results of Manyà et al. imply that the derivative $(\partial C_P/\partial P)_T$ is positive for pressures lower than 4 MPa, which contradicts the thermodynamic relation $(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P$, where $V$ is the specific volume. Hence, the data of Manyà et al. were not considered in this work.

### 2.5. Values from IAPWS-95

To ensure a smooth connection to the IAPWS-95 formulation, the equation of state from this work was fitted to property values calculated from IAPWS-95 in the temperature and pressure range defined by

$$T/K \geq 273.15 + (P/\text{MPa} - 0.1)/12,$$

$$300 \leq T/K \leq 325.$$  \hspace{1cm} (3)

This range, shown in Fig. 3, was determined from the differences between values calculated from IAPWS-95 and from preliminary fits, as well as the deviations from experimental data. Within the range defined by Eq. (3), only IAPWS-95 values were included in the final fit. In addition, the equation of state was also fitted to values from IAPWS-95 at atmospheric pressure from 273.15 K to 300 K. The locations of all data that were included in the fit are shown in Fig. 3.

### 2.6. Adjustment of data

Temperatures in this work are expressed on the international temperature scale of 1990 (ITS-90).\textsuperscript{82} Temperatures on the IPTS-68 scale were converted to ITS-90 according to the equation of Rusby.\textsuperscript{83} Temperatures on the IPTS-48 scale were first converted to IPTS-68 and then to ITS-90. The conversion from IPTS-48 to IPTS-68 was performed according to the equations given by Bedford and Kirby;\textsuperscript{84} these conversion equations were found to agree with those of Douglas.\textsuperscript{85} In the temperature range considered in this work, the ITS-27 and IPTS-48 scales can be considered as identical.\textsuperscript{86} So temperatures on the ITS-27 scale were treated as IPTS-48 temperatures. In principle, the values of quantities that depend on temperature intervals, such as the expansion coefficient and the heat capacity, should also be converted.\textsuperscript{72,83,87} In this work, such an adjustment was only found to be necessary for the accurate heat-capacity measurements at atmospheric pressure close to the melting temperature;\textsuperscript{76,77} the changes in heat capacity due to this conversion were less than 0.1%.

| Reference | Year | Temperature range (K) | Pressure range (MPa) | Frequency (MHz) | Speed-of-sound uncertainty (%) | Source * | Included in fit |
|-----------|------|-----------------------|----------------------|-----------------|-------------------------------|----------|----------------|
| Smith & Lawson\textsuperscript{63} | 1954 | 261–402 | 0.1–923 | 12 | 0.1 \textsuperscript{a} | T | – |
| Wilson\textsuperscript{62} | 1959 | 274–364 | 0.1–97 | 5 | 0.01 | T | – |
| Del Grosso & Mader\textsuperscript{63} | 1972 | 273–368 | 0.101325 | 5 | 0.001 | T | – |
| Aleksandrov & Larkin\textsuperscript{56} | 1976 | 270–647 | 0.1–71 | 3 | 0.02\textsuperscript{c} | T | Yes |
| Trinh & Apfel\textsuperscript{54,65} | 1978 | 256–283 | 0.101325 | 2–3 | 0.2 | G | – |
| Aleksandrov & Kochetov\textsuperscript{58} | 1979 | 266–423 | 6–99 | 2.5, 5.6 | 0.1 | T | – |
| Bacri & Rajaonarison\textsuperscript{66} | 1979 | 247–280 | 0.101325 | 925 | – | G | – |
| Trinh & Apfel\textsuperscript{67} | 1980 | 240–256 | 0.101325 | 0.054 | 1.3 | G | – |
| Petit et al.\textsuperscript{68} | 1983 | 253–296 | 0.1–462 | 10 | 0.1 | T | – |
| Belogol’skii et al.\textsuperscript{55} | 1999 | 273–313 | 0.1–60 | 5–10 | 0.01\textsuperscript{d} | C | Yes |
| Benedetto et al.\textsuperscript{69} | 2005 | 274–394 | 0.1–90 | 5 | 0.05 | T | – |
| Vance & Brown\textsuperscript{59} | 2010 | 263–371 | 0.1–700 | 400–700 | 0.2–0.3 | T | Yes |
| Taschin et al.\textsuperscript{65,70} | 2011 | 244–363 | 0.101325 | 140 | 0.7 | A | Yes |
| Hidalgo Baltasar et al.\textsuperscript{60} | 2011 | 252–350 | 0.1–705 | 2 | 0.2–0.3 | T | – |
| Lin & Trusler\textsuperscript{81} | 2012 | 253–473 | 1–401 | 5 | 0.03–0.04 | T | Yes |

\* Reference Year range (K) range (MPa) Source

\* Data are at 0.101325 MPa unless otherwise specified

\* T = table from article, A = data provided by authors, G = extracted from graph, C = calculated from correlation

\* Estimated from comparison with data from Lin & Trusler\textsuperscript{52} after correcting for systematic deviations at atmospheric pressure

### Table III. Experimental data on the speed of sound

| Reference | Year | Temperature range (K) | Frequency (MHz) | Speed-of-sound uncertainty (%) | Source |
|-----------|------|-----------------------|-----------------|-------------------------------|--------|
| Osborne et al.\textsuperscript{76} | 1939 | 274–368 | T | – | \ |
| Sirota et al.\textsuperscript{73} | 1970 | 272–306 | 20–98 | T | – |
| Anisimov et al.\textsuperscript{77} | 1972 | 266–304 | G | – | \ |
| Angell et al.\textsuperscript{78} | 1973 | 235–273 | T | – | \ |
| Angell et al.\textsuperscript{71} | 1978 | 236–290 | T | – | \ |
| Czarnota\textsuperscript{74} | 1984 | 299–300 | 224–1032 | T | – |
| Bertolini et al.\textsuperscript{79} | 1985 | 247–254 | G | – | \ |
| Tombari et al.\textsuperscript{80} | 1999 | 245–283 | A | – | \ |
| Archer & Carter\textsuperscript{81} | 2000 | 236–285 | T | – | \ |

\* Temperature Pressure Frequency Included

\* Data are at 0.101325 MPa unless otherwise specified

\* T = table from article, A = data provided by authors, G = extracted from graph, C = calculated from correlation

\* Superseded by Angell et al.\textsuperscript{71}
3. Equation of State

3.1. Structure of the equation

The thermodynamic formulation presented here is a mean-field version of an equation of state developed in Ref. 18. It is based on the so-called two-state model, in which it is assumed that liquid water is a mixture of a high-density structure A and a low-density structure B. There is experimental evidence for the existence of two distinct local structures in water. 89,90

Competition between these structures naturally explains the density anomaly and other thermodynamic anomalies in cold water. In particular, if the excess Gibbs energy of mixing of these two structures is positive, the nonideality of the “mixture” can be sufficient to cause liquid–liquid separation, or, at least, to significantly reduce the stability of the homogeneous liquid phase and consequently generate the anomalies in the thermodynamic response functions. However, since experimental data are not yet available beyond the homogeneous ice nucleation limit, the possibility of a liquid–liquid transition in water must be postulated and is to be examined by indirect means. The location of the hypothesized liquid–liquid critical point, characterized by the critical temperature $T_c$ and critical pressure $P_c$, is obtained from the extrapolation of the properties far away from the transition, thus making it very uncertain. 17,18

We introduce the dimensionless quantities

$$
\hat{T} = \frac{T}{T_c}, \quad \hat{P} = \frac{PV_0}{RT_c}, \quad \hat{G} = \frac{G}{RT_c}, \quad \hat{V} = \frac{V}{V_0},
$$

$$
\hat{S} = \frac{S}{R}, \quad \hat{\omega} = \frac{T - T_c}{T_c}, \quad \hat{p} = \frac{(P - P_c)V_0}{RT_c},
$$

where $T$ is the temperature, $P$ is the pressure, $G$ is the specific Gibbs energy, $R$ is the specific gas constant, $V$ is the specific volume, $V_0$ is a reference volume, and $S$ is the specific entropy. We adopt the equation of state for the Gibbs energy in the form of “athermal mixing”, suggested in Ref. 16 and 18,

$$
\hat{G} = \hat{G}^A + \hat{T} \left[ xL + x^2 \ln x + (1 - x) \ln(1 - x) + \omega \alpha (1 - x) \right],
$$

where $\hat{G}^A$ is the Gibbs energy of the high-density structure, $x$ is the fraction of the low-density structure, $\omega$ is an interaction parameter, and

$$
L = \frac{\hat{G}^B - \hat{G}^A}{\hat{T}},
$$

with $\hat{G}^B$ the Gibbs energy of the low-density structure. The difference in Gibbs energy between the pure components $\hat{G}^B - \hat{G}^A$ is related to the equilibrium constant $K$ of the “reaction” $A \rightleftharpoons B$,

$$
\ln K \equiv L.
$$

For the interaction parameter $\omega$ in Eq. (6), a linear pressure dependence is taken,

$$
\omega = 2 + \omega_0 \hat{p}.
$$

2.7. Values for extrapolation

To enable extrapolation of the equation of state to 1000 MPa, it was found necessary to guide the fit at high pressures by including estimated values for the expansivity and speed of sound at 1000 MPa (Fig. 3).
A low-density/high-density phase-transition curve is located at \( L = 0 \), for \( \omega > 2 \), and the phase separation occurs upon increase of pressure. This phase transition lies below the homogeneous ice nucleation temperature and cannot be observed in experiments. Experiments by Mishima\(^{38,91} \) suggest that the phase transition curve, if it exists, lies close to the homogeneous nucleation curve, and has the same shape. In this work, we use a hyperbola for the \( L = 0 \) phase-transition curve, as in previous work.\(^{17,18} \)

\[
t + k_0 p + k_1 tp = 0, \tag{10}
\]

where \( k_0 \) is the slope \( \frac{dt}{dp} \) of the \( L = 0 \) curve at the critical point, and \( k_1 \) determines the curvature. In this work, the expression for \( L(t, p) \) is constructed as proportional to the distance to the \( L = 0 \) curve in the \( p-t \) diagram [Fig. 4(a)]. Consider a point in the phase diagram with dimensionless coordinates \( (t, p) \). The projection \( (t_0, p_0) \) of this point on the \( L = 0 \) curve, along a line with slope \( \frac{dp}{dt} = k_2 \), is found by the solution of the equations

\[
t_0 + k_0 p_0 + k_1 t_0 p_0 = 0, \tag{11}
\]

\[
p_0 = p + k_2 (t_0 - t), \tag{12}
\]

which are illustrated in Fig. 4(a). The field \( L \) is taken proportional to the distance between the points \((t, p)\) and \((t_0, p_0)\) with proportionality factor \( L_0 \), which results in

\[
L = L_0 \frac{K_2}{2k_1 k_2} \left[ 1 + k_0 k_2 + k_1 (p + k_2 t) - K_1 \right]. \tag{13}
\]

with

\[
K_1 = \left\{ \left[ 1 + k_0 k_2 + k_1 (p - k_2 t) \right]^2 - 4k_0 k_1 k_2 (p - k_2 t) \right\}^{1/2},
\]

\[
K_2 = (1 + k_2^2)^{1/2}. \tag{14}
\]

The expression for \( L \) in Eq. (13) yields \( L = 0 \) if Eq. (10) is satisfied, as can be verified by solving for \( p \) in Eq. (10) and substituting the result in Eqs. (13) and (14). In previous work,\(^{17,18} \) the simpler expression

\[
L = L_0 (t + k_0 p + k_1 tp) \tag{15}
\]

was used, which yields the same location [Eq. (10)] for the \( L = 0 \) curve. Equation (15) is not valid for large \( L \), corresponding to large pressures (about 1000 MPa at 310 K), where this equation generates an additional, unphysical root.

At any pressure and temperature, the equilibrium value \( x_e \) of the fraction \( x \) is found from the condition

\[
\left( \frac{\partial G}{\partial x} \right)_{T,P} = 0 \text{ at } x = x_e, \tag{16}
\]

which yields

\[
L + \ln \frac{x_e}{1 - x_e} + \omega (1 - 2x_e) = 0. \tag{17}
\]

This equation must be solved numerically for the fraction \( x_e \). The location of the critical point is defined by

\[
\left( \frac{\partial^2 G}{\partial x^2} \right)_{T,P} = 0, \quad \left( \frac{\partial^3 G}{\partial x^3} \right)_{T,P} = 0. \tag{18}
\]

In the theory of critical thermodynamic behavior, the thermodynamic properties are expressed in terms of the order parameter and the ordering field. In our equation of state, \( L \) is the ordering field, and the order parameter \( \phi \) is given by\(^{92} \)

\[
\phi = 2x_e - 1. \tag{19}
\]

The susceptibility \( \chi \) defines the liquid–liquid stability limit (spinodal) as

\[
\chi^{-1} = \frac{1}{2T} \left( \frac{\partial^2 G}{\partial x^2} \right)_{T,P} = 0, \tag{20}
\]

and is given by

\[
\chi = \left( \frac{2}{1 - \phi^2 - \omega} \right)^{-1}. \tag{21}
\]
The dimensionless volume and entropy can then be written as

\[ \hat{V} = \frac{\dot{T}}{2} \left[ \frac{\omega_0}{2} (1 - \phi^2) + L_p (\phi + 1) \right] + \hat{G}^\Lambda, \]  

\[ \hat{S} = -\frac{\dot{T} L_p}{2} (\phi + 1) - \frac{\hat{G}^\Lambda}{T} + \hat{G}^\Lambda_T, \]

with subscripts \( \dot{T} \) and \( \dot{P} \) indicating partial derivatives with respect to the subscripted quantity. Expressions for the derivatives of the field \( L \) and the Gibbs energy \( \hat{G}^\Lambda \) are given in Appendix B.

The dimensionless response functions, namely isothermal compressibility \( \hat{k}_T \), expansion coefficient \( \hat{a}_p \), and isobaric heat capacity \( \hat{C}_P \), are given by

\[ \hat{k}_T = \frac{1}{\hat{V}} \left\{ \frac{\dot{\hat{P}}}{2} \left[ \chi (L_p - \omega_0 \phi)^2 - (\phi + 1)L_{\phi\phi} \right] - \hat{G}^\Lambda_{\phi\phi} \right\}, \]

\[ \hat{a}_p = \frac{1}{\hat{V}} \left\{ \frac{L_{\phi\phi}}{2} (\phi + 1) + \frac{1}{2} \left[ \frac{\omega_0}{2} (1 - \phi^2) + L_p (\phi + 1) \right] \right. 

\left. - \frac{\dot{\hat{T}} L_p}{2} \chi (L_p - \omega_0 \phi) + \hat{G}^\Lambda_{\phi\phi} \right\}, \]

\[ \hat{C}_P = -L_{\phi\hat{P}} (\phi + 1) + \frac{\dot{\hat{T}} T^2}{2} \left[ \frac{L_{\phi\phi}}{2} \chi - L_{\phi T} (\phi + 1) \right] - \dot{\hat{T}} \hat{G}_{\phi T}. \]

These dimensionless quantities are defined as

\[ \rho = \frac{\rho_0}{\hat{V}}, \quad \hat{k}_T = \frac{\hat{k}_T}{\rho_0 RT_c}, \quad \hat{a}_p = \frac{\hat{a}_p}{RT_c}, \quad \hat{C}_P = \frac{\hat{C}_P}{RT_c}, \]

with the density \( \rho = 1/\hat{V} \), \( \rho_0 = 1/V_0 \), and \( C_P \) the specific isobaric heat capacity. The specific isochoric heat capacity \( C_V \) is found from the thermodynamic relation

\[ C_V = C_P - \frac{T \hat{a}_p^2}{\rho \hat{k}_T}, \]

and the speed of sound \( w \) is found from

\[ w = \left( \rho \hat{k}_T \frac{C_V}{C_P} \right)^{-1/2} = \left( \rho \hat{k}_T - \frac{T \hat{a}_p^2}{C_P} \right)^{-1/2}. \]

Equation (6) is a mean-field equation of state which neglects effects of fluctuations. In particular, not taking these effects into account results in a lower critical pressure, see Table VI in Appendix C. As shown earlier, a mean-field equation describes the experimental data for supercooled water equally well as a nonanalytic equation based on critical scaling theory. The reason for the good description by a mean-field approximation is that the region asymptotically close to the hidden critical point, where scaling theory would be necessary, is not experimentally accessible [Fig. 4(b)]. Moreover, in practice, a mean-field equation of state is more convenient for computational use than one incorporating scaling theory.

The Gibbs energy of the high-density structure \( \hat{G}^\Lambda \) is a function of dimensionless temperature and pressure \( \tau \) and \( \pi \), and serves as a background function in the two-state model. We selected the empirical form

\[ \hat{G}^\Lambda(\tau, \pi) = \sum_{i=1}^{n} \alpha_i \tau^a_i \pi^b_i e^{-d_i/\pi^e}, \]

where \( n \) is the number of terms and \( a_i, b_i, c_i, \) and \( d_i \) are adjustable parameters. In previous work, the exponents \( a_i \) and \( b_i \) were integers, and the dimensionless temperature and pressure were defined as \( \tau = t \) and \( \pi = p \). In this work, this definition could not be used, because \( t \) and \( p \) become negative below the critical point and powers of negative numbers with real exponents are generally complex numbers. To avoid negative \( \tau \) and \( \pi \), they were redefined as

\[ \tau = \frac{\dot{T}}{T_c}, \quad \pi = \frac{(P - P_0)V_0}{RT_c}, \]

where the offset \( P_0 = -300 \) MPa was chosen to enable extrapolation to negative pressures.

### 3.2. Optimization method

The aim of the least-squares optimization used in this work was to obtain a fit that minimizes \( \chi^2 \), the sum of squared deviations of the fit from experimental data. To make these deviations dimensionless, the differences of experimental and calculated values were divided by the experimental uncertainty. The fit of Eq. (6) requires optimization of the parameters \( L_0, \rho_0, \omega_0, \) and \( k_2 \) as well as the parameters \( a_i, b_i, c_i, \) and \( d_i \) for the Gibbs energy \( \hat{G}^\Lambda \) in Eq. (30). The optimization was carried out in two steps, and is roughly based on the procedure of Lemmon. In the first step, a bank of 135 terms of the form

\[ \tau^a_i \pi^b_i e^{-d_i/\pi^e} \]

was created, where the exponents \( a_i \) and \( b_i \) were restricted to integers in the range of 0 to 8, with \( a_i + b_i \leq 8 \). The coefficient \( d_i \) was restricted to the values 0, 0.6, and 1. The aim of the first optimization step was to find a good selection of 20 to 25 terms out of the 135 terms for the Gibbs energy \( \hat{G}^\Lambda \). Initially, \( \hat{G}^\Lambda \) contained a few manually selected terms with low values of the exponents \( a_i \) and \( b_i \). The algorithm then determined the best term to add to \( \hat{G}^\Lambda \), in the following way. The first term in the bank of terms that was not in the selection was added, and all parameters except \( a_i, b_i, \) and \( d_i \) were optimized. The newly added term was then removed, another term was added, and the parameters were optimized again. This procedure was repeated for all terms and a value of \( \chi^2 \) was computed for the addition of each term. The term that resulted in the lowest \( \chi^2 \) was then permanently added to \( \hat{G}^\Lambda \). By repeating the addition procedure, the number of terms in \( \hat{G}^\Lambda \) was increased to about 20. The quality was then further improved by deleting terms that could be deleted without significantly increasing \( \chi^2 \), and adding new terms to replace the deleted terms.

In the second optimization step, the parameters \( a_i, b_i, \) and \( d_i \) were also taken adjustable and optimized simultaneously with the other parameters. The additional degrees of freedom made it possible to delete terms while still improving the fit. Terms with similar values of the exponents were combined if that was possible without deteriorating the fit.

The shape of the liquid–liquid phase transition curve, the \( L = 0 \) curve of Eq. (10), was not taken adjustable. The parameters that determine this curve, \( k_0 \) and \( k_1 \) in Eq. (10), were derived from the shape of the experimental homogeneous nucleation curve, described in Appendix A. The initial location
of the liquid–liquid critical point was taken from the mean-field equation of state by Holten et al.\textsuperscript{18} and was later adjusted to a slightly lower temperature to improve the description of experimental data. The numerical values of all parameters are listed in Appendix C, and computer code for the equation of state is included in the supplemental material.\textsuperscript{38}

## 4. Comparison with Experimental Data

### 4.1. Density

In Fig. 5, the density calculated from Eq. (6) is plotted as a function of temperature for several isobars, and compared with experimental data. Below 250 K, Mishima’s data are the only data that are available. As described in Sec. 2.1, Eq. (6) was fitted to these data with a low weight. The equation reproduces the trend of Mishima’s data, and most of these densities are reproduced by Eq. (6) to within 0.5%. A comparison of Mishima’s data with the more accurate data of Sotani et al.\textsuperscript{35} and Asada et al.\textsuperscript{37} shows that Mishima’s data are systematically too low at low pressures and too high at high pressures, with deviations of up to 0.4%. The calculated density isobars in Fig. 5 below 150 MPa curve down at low temperature, while the isobars at higher pressures slightly curve upwards, and an inflection point is present for isobars above a certain pressure. This inflection is related to a minimum in the expansivity, as will be discussed in Sec. 4.2. For comparison purposes, figures in this section also include values calculated from the extrapolated IAPWS-95 formulation, down to 235 K at atmospheric pressure and down to 250 K at higher pressures.

In Fig. 6, experimental density values at atmospheric pressure are compared with values calculated from Eq. (6). Both Eq. (6) and the extrapolated IAPWS-95 formulation represent the data of Hare and Sorensen within the experimental scatter of about 0.02%. In the stable region, Eq. (6) differs less than 0.0001% (1 part per million) from the densities recommended by Tanaka et al.\textsuperscript{36}

Figure 7 shows differences between experimental densities up to 400 MPa and values calculated from Eq. (6). The proposed equation represents the data of Sotani et al.\textsuperscript{35} to within 0.02%, which is within the uncertainty of those data of 0.03% as estimated by Wagner and Thol.\textsuperscript{49} The data of Asada et al.\textsuperscript{37} with an uncertainty of 0.1%, are reproduced to within 0.04%. The data of Guignon et al.\textsuperscript{39} are represented to within the uncertainty of 0.2%. The density data of Gridley and Lind\textsuperscript{28} deviate systematically from other data, as was noted by Wagner and Prüß.\textsuperscript{20} At 298 K, IAPWS-95 agrees well with Eq. (6) and with the densities of Sotani et al.\textsuperscript{35} and Asada et al.\textsuperscript{37} which were not available when IAPWS-95 was developed. The density data of Aleksandrov et al.\textsuperscript{32} at temperatures above 271 K are in satisfactory agreement with the proposed equation of state. For example, at 273.15 K, the densities of Aleksandrov et al.\textsuperscript{32} differ less than 0.01% from the values calculated from Eq. (6). However, at lower temperatures, such as at 267 K and 270 K, their data show systematic deviations of up to 0.07% from the data of Sotani et al.\textsuperscript{35} and, hence, from the proposed equation.

In the stable region up to 100 MPa, there are accurate density measurements of Kell and Whalley,\textsuperscript{30} with an uncertainty
The expansivity calculated from Eq. (6) is compared with values calculated from the correlation of Ter Minassian et al.\cite{24} and IAPWS-95 in Fig. 9. At atmospheric pressure, there is little difference in the expansivity values of Eq. (6) and the extrapolated IAPWS-95 formulation down to 250 K. At higher pressures, Eq. (6) follows the correlation of Ter Minassian et al., to which it was fitted. More detailed deviations of the data of Ter Minassian et al. from Eq. (6) are shown in Fig. 10. These deviation plots use absolute instead of relative differences, because the expansivity passes through zero in the temperature and pressure range considered. Equation (6) represents the correlation of Ter Minassian et al. and most of their data points to within $2 \times 10^{-5}$ K$^{-1}$. 
Experimental and calculated values for the temperature of maximum density (TMD) are shown in Fig. 11. The TMD moves to lower temperatures with increasing pressure, and the rate at which it does so also increases with pressure. The TMD corresponding to Mishima’s data is relatively uncertain because of the scatter in his density data. Deviations of the experimental TMD values from Eq. (6) are plotted in Fig. 12. The data of Caldwell\textsuperscript{45} are represented to within 0.08 K. The uncertainty $\delta T$ in the TMD values calculated from the expansivity correlation of Ter Minassian \textit{et al.}\textsuperscript{44} can be estimated as

$$\delta T \approx \left( \frac{\partial \alpha_P}{\partial T} \right)_P \delta \alpha_P, \quad (33)$$

where the temperature derivative of the expansivity is calculated from the correlation of Ter Minassian \textit{et al.}\textsuperscript{44} With an expansivity uncertainty $\delta \alpha_P$ of at least $10^{-5}$ K$^{-1}$ (estimated from Fig. 10), Eq. (33) gives an uncertainty $\delta T$ of 0.6 K at 0 MPa, increasing to 0.8 K at 60 MPa. When one takes these uncertainties into account, the correlation of Ter Minassian \textit{et al.}\textsuperscript{44} is consistent with the data of Caldwell\textsuperscript{45} and with Eq. (6). The data of Henderson and Speedy\textsuperscript{44} are represented fairly well by both Eq. (6) and IAPWS-95, when these equations are extrapolated to negative pressure.

The existence of a minimum in the expansivity,

$$\left( \frac{\partial \alpha_P}{\partial T} \right)_P = 0, \quad (34)$$
was noticed by Ter Minassian et al.\(^4\) and by Mishima\(^3\) for temperatures lower than 300 K. The minimum in the expansivity is related to the inflection points in curves of the density versus temperature, as is visible in Fig. 5 above 200 MPa. The minimum is seen in the expansivity correlation of Ter Minassian et al.\(^4\) in Fig. 9. An expansivity minimum is also present in the expansivity derived from the volume data of Grindley and Lind,\(^28\) as shown in Fig. 13. We obtained the location of the expansivity minimum in the data of Grindley and Lind by fitting several polynomials of different order to all their volume data, and also to data on each isobar separately. For every isobar, this results in several estimated temperatures of the expansivity minimum. The differences in these temperatures were used to estimate the uncertainty of the minimum. The locus of expansivity minima of Grindley and Lind thus obtained can be smoothly connected to that of Ter Minassian et al.\(^4\) Our equation of state closely follows the expansivity minimum obtained by Ter Minassian et al.,\(^4\) as seen in Fig. 13.

### 4.3. Isothermal compressibility

Experimental data on the isothermal compressibility are shown in Fig. 14 together with values calculated from Eq. (6) and IAPWS-95. The data of Mishima\(^3\) exhibit more scatter than those of Angell and coworkers,\(^46,47\) but they show a consistent trend of a decrease in the anomalous behavior of the compressibility with increasing pressure. Deviations of the experimental data from Eq. (6) are plotted in Fig. 15. It can be seen in Fig. 15 that Eq. (6) represents the compressibility data of Speedy and Angell\(^46\) and Kanno and Angell\(^47\) to
within their scatter. The difference between the extrapolated IAPWS-95 formulation and Eq. (6) increases with decreasing temperature; this difference is related to the density difference between the two equations shown in Fig. 5. The deviation of the compressibilities measured by Mishima from Eq. (6) is shown in Fig. 16. Although Eq. (6) was not fitted to Mishima’s compressibility data, it represents them fairly well when one takes into account the experimental scatter of about ±10%.

4.4. Speed of sound

Experimental data on the speed of sound at atmospheric pressure are shown in Fig. 17 together with values calculated from Eq. (6) and IAPWS-95. In the supercooled region, Eq. (6) represents the data of Taschin et al. to within their uncertainty of 0.7%. In the stable region, Eq. (6) represents the speed-of-sound data of Del Grosso and Mader to within their uncertainty of 0.001%.

Speed-of-sound data up to 400 MPa are compared with values calculated from Eq. (6) in Fig. 18. The proposed equation represents the data of Lin and Trusler to within 0.04%. For comparison, the correlation of Lin and Trusler has deviations of up to 0.2% from their data in the temperature range considered here. The IAPWS-95 formulation was fitted to the speed-of-sound data of Petitet et al. which systematically deviate from the data of Lin and Trusler by up to 0.2%. This deviation is the reason for the difference between IAPWS-95 and Eq. (6) in the stable region in the range of 253 K to 263 K. Speed of sound values from the correlation of Belogol’skii et al. differ less than 0.01% from values from Eq. (6), and the data of Aleksandrov and Larkin are represented to within 0.02%.

In the metastable region from 253 K to 265 K and for pressures around 50 MPa, there is a rather large difference between the extrapolated IAPWS-95 formulation and Eq. (6) (Fig. 18). At 253 K, the difference is more than 1%. To investi-
FIG. 18. Percentage deviations of experimental data on the speed of sound from values calculated from Eq. (6). Values calculated from IAPWS-95 are plotted for comparison; dashed in the stable-liquid region and dotted in the metastable region. The correlations that Belogol’skii and Lin and Trusler fitted to their data are also shown. The vertical dashed lines indicate the melting pressure.

4.5. Heat capacity

In Fig. 19, values for the isobaric heat capacity calculated from Eq. (6) are compared with experimental data at atmospheric pressure. There are two sets of experimental data that extend down to 236 K, that of Angell et al. and that of Archer and Carter. Both Eq. (6) and IAPWS-95 agree better with the data of Angell et al. than with the data of Archer and Carter. In the case of IAPWS-95, this is expected, as it was fitted to the data of Angell et al. As described in Sec. 2.4, Eq. (6) was fitted to values computed from IAPWS-95.

The data of Bertolini et al. agree with those of Angell et al. after a correction that is described in Ref. 17. The data of Tombari et al. suggest even larger $C_p$ values in the supercooled region than the data of Angell et al. in the stable region, Eq. (6) represents the accurate data of Osborne et al. to within 0.1%. For the isochoric heat capacity $C_v$, both Eq. (6) and the extrapolated IAPWS-95 formulation predict a weak temperature dependence in the supercooled region at atmospheric pressure.

Sirota et al. measured the isobaric heat capacity at pressures up to 100 MPa in the stable region. These data are compared with Eq. (6) and with IAPWS-95 in Fig. 20. The data of Sirota et al. show systematic deviations from both IAPWS-95 and Eq. (6).
There are no experimental data in the supercooled region above 400 MPa, except for one expansivity data point of Ter Minassian et al. at 263 K and 569 MPa (Fig. 10), and two speed-of-sound measurements of Vance and Brown at 293 K and 700 MPa. The speed-of-sound measurements of Hidalgo Baltasar et al. in the supercooled region at 278 K and 700 MPa seem to have been affected by ice formation, because they deviate from their data in the stable-liquid region.

In the stable-liquid region below 300 K, there do exist data above 400 MPa. The expansivity data of Ter Minassian et al. extend up to 635 MPa (Fig. 10). Grindley and Lind measured densities up to 800 MPa. Figure 21 shows the deviations of experimental density data from values calculated from Eq. (6). Values calculated from IAPWS-95 are plotted for comparison; dashed in the stable-liquid region and dotted in the metastable region. The vertical dashed lines indicate the melting pressure.

Both Vance and Brown and Hidalgo Baltasar et al. have measured the speed of sound up to 700 MPa. Wang et al. determined the speed of sound at 293 K up to the melting pressure of about 900 MPa. Their data systematically deviate by about 3% from the data of Vance and Brown and will not be considered here. The differences between speed-of-sound data and Eq. (6) up to 1000 MPa are shown in Fig. 22.

The isochoric heat capacity $C_P$ was measured by Czarnota at 300 K up to 1000 MPa. Abramson and Brown derived $C_P$ values at 298 K up to 700 MPa from thermal diffusivity and thermal conductivity data. These data are compared with values calculated from Eq. (6) and IAPWS-95 in Fig. 23. Two data points of Czarnota are above the melting pressure, but Czarnota reported that the water was still liquid for those measurements.
FIG. 22. Percentage deviations of experimental data on the speed of sound\textsuperscript{52,59–62,68,69} from values calculated from Eq. (6). Values calculated from IAPWS-95 are plotted for comparison; dashed in the stable-liquid region and dotted in the metastable region. The vertical dashed lines indicate the melting pressure.

\[
\frac{100 \left( W_{\text{exp}} - W_{\text{calc}} \right)}{W_{\text{calc}}} \text{ vs. Pressure (M Pa)}
\]

FIG. 23. Isobaric heat capacities \( C_P \) at 299.5 K calculated from Eq. (6) and IAPWS-95 (dashed in the stable-liquid region and dotted in the metastable region). Also shown are experimental data of Czarnota\textsuperscript{74} in the range of 298.8 K to 300.1 K and data of Abramson and Brown\textsuperscript{97} at 298.15 K, derived from thermal diffusivity and thermal conductivity measurements. The vertical dashed line indicates the melting pressure.

4.7. Connection to IAPWS-95

Because Eq. (6) was fitted to values calculated from IAPWS-95 in a part of the temperature and pressure range (see Eq. (3) and Fig. 3), the differences between the two equations of state are small in that region. Therefore, there are no large discontinuities when one switches from Eq. (6) to IAPWS-95 there. For example, one can switch from one equation to the other at the isotherm

\[ T = 320 \text{ K}, \tag{35} \]

\begin{table}[h]
\begin{tabular}{|c|c|c|}
\hline
Quantity & Mean\textsuperscript{a} & Maximum\textsuperscript{b} \\
\hline
Density & 0.0006% & 0.0017% \\
Expansivity & 0.010 K\textsuperscript{-1} & 0.021 K\textsuperscript{-1} \\
Compressibility & 0.02% & 0.05% \\
Heat capacity \( C_P \) & 0.02% & 0.05% \\
Speed of sound & 0.005% & 0.012% \\
\hline
\end{tabular}
\caption{Differences between Eq. (6) and IAPWS-95 along Eq. (35) in the \( P-T \) plane, for pressures from 0 MPa to 400 MPa}
\end{table}

4.8. Uncertainty estimates

Uncertainty estimates for the density calculated from Eq. (6) are shown in Fig. 24. These estimates are based on the differences between Eq. (6) and experimental data, as well as on the uncertainty of the data. In a large region of the phase diagram below 253 K, only Mishima’s data are available. The estimates in that region are conservative to account for the unknown systematic error of Mishima’s data. Uncertainty estimates for the speed of sound calculated from Eq. (6) are shown in Fig. 25. In the region above atmospheric pressure and below 253 K, no estimates are given because of the absence of experimental data.

4.9. Ice I melting curve

As an additional test of the accuracy of the equation of state, the melting curve of ice I was calculated from the phase-
The calculated value agrees with the experimental value of \( (611.657 \pm 0.010) \text{ Pa} \). Equation (37) represents the convention that the specific entropy of liquid water is zero at the triple point. Equation (38) ensures that the melting curve calculated from Eq. (36) crosses the triple point.

The melting curve of ice I crosses the triple point of ice I, ice III and liquid water at about 209 MPa. Experimental locations of the I-III-L triple point are shown in Fig. 26. Bignell and Bean\(^{42}\) located the triple point in 1912. As described by Babb\(^{102}\) and La Morri\(^{103}\), Bridgman’s pressure values are about 1% low. For this work, Bridgman’s pressures were multiplied by the correction factor 1.0102, which follows from the current value of the mercury melting pressure.\(^{104}\) Kell and Whalley\(^{43}\) reported the location of the triple point as part of their investigation of the ice I-ice III phase transition line. Bignell and Bean\(^{101}\) determined the triple-point pressure with metrological accuracy (0.01%). Their measurements of the triple-point pressure and temperature are currently the best available. As seen in Fig. 26, the melting curve calculated from Eq. (36) agrees with the measurement of Bignell and Bean.\(^{101}\)

Bridgman located 14 points on the ice I melting curve.\(^{42}\)
Of these, four points are unreliable according to Bridgman, so they will not be considered here. About 60 points on the melting curve were determined by Kishimoto and Maruyama, who found a discontinuity in the melting curve at 160 MPa. In a follow-up study, Maruyama did not observe the discontinuity, and suggested that it could have been an artifact of the previous experimental setup. Mishima determined the course of the melting curve in the range where ice I is metastable. Equation (36) was used to calculate the melting curve in this range by extrapolating both the equation of state of ice and of that of supercooled water. Figure 27 shows that the calculated melting curve agrees fairly well with Mishima’s data. Figure 28 shows deviations of the experimental data from values computed from Eq. (36). The data from Henderson and Speedy are the most accurate and differ less than 1 MPa from Eq. (36). The data of Maruyama systematically lie 2 MPa below Eq. (36). The maximum pressure difference in the stable region between Eq. (36) and values from the IAPWS correlation is 0.6%, which is well within the uncertainty of 2% of the IAPWS correlation.

5. Conclusion

We have developed an equation of state for cold and supercooled water, explicit in the Gibbs energy, valid from the homogeneous nucleation temperature to 300 K and for pressures up to 400 MPa. The equation is based on a two-state model of water, combined with empirical background terms. It is the first equation of state that represents the density data of Sotani et al. and Asada et al. as well as the speed-of-sound data of Lin and Trusler in the considered temperature range. In part of the stable region of liquid water, the equation can be connected to the IAPWS-95 formulation with minimal discontinuities in the property values.

To improve the accuracy of future equations of state, density measurements with an accuracy of 0.02% or better below 250 K up to 400 MPa are desirable. Currently, this area is only covered by Mishima’s data. For the speed of sound, there are only a few measurements in the metastable region for pressures higher than atmospheric. Experimental data are needed especially down to 250 K and up to 200 MPa. Also, there are no data for the heat capacity of supercooled water above atmospheric pressure, while such data are highly desirable.

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Appendix A: Homogeneous Nucleation Curve

Liquid water can be supercooled down to the homogeneous ice nucleation temperature $T_H$, which is about 235 K at atmospheric pressure. At higher pressures, $T_H$ is lower, with a minimum of 181 K at 200 MPa. The pressure dependence of $T_H$ has been measured by Xans and Barnaud, Kanno et al. and Kanno and Miyata at pressures below 300 MPa; see Fig. 29. Mishima has measured $T_H$ at pressures from 500 MPa to 1500 MPa. At about 200 MPa, there is a break in the $T_H$ curve as a result of nucleation of a different kind of ice above this pressure (ice III according to Kanno et al. and ice II according to Kanno and Miyata). For pressures below
the break point, the shape of the $T_H$ curve can be described by an equation of the Simon type, which was also used by Wagner et al.\textsuperscript{117} to describe the melting curves of water. A fit of such an equation to the data of Kanno et al.\textsuperscript{113} and Kanno and Miyata\textsuperscript{114} yields the pressure $P_H$ on the homogeneous nucleation curve as a function of the temperature $T$,

$$ P_H/P_0 = 1 + 2282.7(1 - \theta^{6.243}) + 157.24(1 - \theta^{79.81}), \quad (A1) $$

where $\theta = T/T_0$, $T_0 = 235.15$ K, and $P_0 = 0.1$ MPa. Above the break point, a third-order polynomial was fitted to the data, including Mishima’s data up to 1500 MPa, which resulted in

$$ T_H/K = 172.82 + 0.03718 p_1 + 3.403 \times 10^{-5} p_1^2 - 1.573 \times 10^{-8} p_1^3, \quad (A2) $$

with $p_1 = P/\text{MPa}$. This polynomial is based on the assumption that the $T_H$ curve is smooth at pressures above the break point. However, because there are only few data in the range of 300 MPa to 600 MPa, the existence of other break points in the curve cannot be excluded. It must also be noted that unlike the melting curve, the homogenous nucleation curve is a kinetic limit and depends on the size and time scale of the experiment. The experimental homogenous nucleation temperatures described in this section were obtained with samples having a diameter of several micrometers.

**Appendix B: Derivatives**

The derivatives of the field $L$, given by Eq. (13), are

$$ L_T = \frac{L_0 K_2}{2} \left( 1 + \frac{-k_0 k_2 + k_1 (p - 2k_2 t)}{K_1} \right), \quad (B1) $$

$$ L_T = \frac{L_0 K_2}{K_1} (K + k_0 k_2 - k_1 p + k_1 k_2 t - 1), \quad (B2) $$

$$ L_{TT} = -\frac{2k_0 K_2 k_0 k_2}{K_1^2}, \quad (B3) $$

$$ L_{T \hat{p}} = \frac{2L_0 K_2 k_0 k_2}{K_1^2}, \quad (B4) $$

$$ L_{\hat{p} \hat{p}} = -\frac{2L_0 K_2 k_0 k_2}{K_1^2}. \quad (B5) $$

The derivatives of the Gibbs energy of the high-density structure $G_A$, given by Eq. (30), are

$$ \dot{G}_A^T(\tau, \pi) = \sum_{i=1}^{n} c_i a_i \tau^{a_i - 1} \pi^{b_i} e^{-d_i \pi}, \quad (B6) $$

$$ \dot{G}_A^\hat{p}(\tau, \pi) = \sum_{i=1}^{n} c_i a_i \tau^{a_i} \pi^{b_i - 1} (b_i - d_i \pi) e^{-d_i \pi}, \quad (B7) $$

$$ \dot{G}_{T \hat{p}}^A(\tau, \pi) = \sum_{i=1}^{n} c_i a_i (a_i - 1) \tau^{a_i - 2} \pi^{b_i} e^{-d_i \pi}, \quad (B8) $$

$$ \dot{G}_T^{\hat{p} \hat{p}}^A(\tau, \pi) = \sum_{i=1}^{n} c_i a_i \tau^{a_i - 1} \pi^{b_i - 1} (b_i - d_i \pi) e^{-d_i \pi}, \quad (B9) $$

$$ \dot{G}_{\hat{p} \hat{p}}^A(\tau, \pi) = \sum_{i=1}^{n} c_i \tau^{a_i} \pi^{b_i - 2} ((d_i \pi - b_i)^2 - b_i) e^{-d_i \pi}. \quad (B10) $$

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TABLE VIII. Calculated property values for computer program verification

| $T$ (K) | $P$ (MPa) | $\rho$ (kg m$^{-3}$) | $\alpha_p$ (10$^{-10}$K$^{-1}$) | $\kappa_p$ (10$^{-4}$MPa$^{-1}$) | $C_p$ (J kg$^{-1}$K$^{-1}$) | $w$ (ms$^{-1}$) | $\chi_e$ | $L$ |
|--------|----------|----------------------|-------------------|-----------------|--------------------|----------------|--------|------|
| 273.15 | 0.101325 | 999.842 29          | -0.683 042        | 5.088 499       | 4.218 302 2        | 1.402 388 6   | 0.096 654 72 | 0.621 204 74 |
| 235.15 | 0.101325 | 968.099 99         | -29.633 816        | 11.580 785      | 5.997 563 2       | 1.134 585 5   | 0.255 102 86 | 0.919 763 676 |
| 250    | 200      | 1 090.456 77       | 3.267 768          | 3.361 311       | 3.708 390 2       | 1.668 202 0   | 0.030 429 27 | 0.723 770 81 |
| 200    | 400      | 1 185.028 00       | 6.716 009          | 2.567 237       | 3.338 525         | 1.899 329 4   | 0.007 170 08 | 1.155 396 5  |
| 250    | 400      | 1 151.715 17       | 4.929 927          | 2.277 029       | 3.757 214 4       | 2.015 878 2   | 0.005 358 84 | 1.434 514 5  |

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