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# Experimental densities of subcooled deuterium oxide at pressures up to 160 MPa

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In this work, the experimental results of deuterium oxide density at high pressure and in a wide range of temperatures, by means of the pseudo-isochoric method, are presented. A specific stainless steel cell was devised to be used as a pycnometer and filled with variable mass of heavy water. The latter was measured by weighing with an analytical balance and using the substitution method. The volume of the pycnometric cell was measured by the gravimetric method and corrected for the effect of temperature and pressure. Each measurement cycle was performed at constant mass, measuring pressure as a function of temperature at equilibrium. From the mass and volume values, density was calculated according to its definition. Heavy water density was measured for temperatures down to 253 K and for pressures up to 163 MPa, thus both in stable and supercooled metastable states. All terms contributing to the uncertainty in determining the volume and the mass were considered, obtaining an expanded relative uncertainty of deuterium oxide density of 0.04%. *Published by AIP Publishing.*  
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## I. INTRODUCTION

Deuterium oxide (D<sub>2</sub>O), or heavy water, is of interest in different scientific fields for its applications, e.g., as a moderator in nuclear reactors, for diagnostics in nuclear magnetic resonance, or for its physiological and pharmacological effects on humans and other animals.<sup>1</sup>

Experimental measurements of the thermophysical properties are the basis for the development of fundamental equations of state (EOSs), which allow us to derive all thermodynamic properties of a fluid; furthermore, they can also help to evaluate the descriptive capacity of the dedicated EOS. In contrast to ordinary water, the thermophysical properties of deuterium oxide are far less studied and generally with lower accuracy. At present, only very few experimental data of D<sub>2</sub>O thermophysical properties are available in the literature, and measurements in metastable conditions are almost lacking. Most of the measurements were carried out at atmospheric pressure and at different temperatures, e.g., from the triple point to 308 K<sup>2</sup> or from the triple point up to about 350 K.<sup>3,4</sup> Other few studies covered partially the metastable region, e.g., Hare and Sorensen<sup>5</sup> measured D<sub>2</sub>O density down to about 254 K. Focusing on high pressure, Emmet and Millero<sup>6</sup> measured specific volume at pressures up to 100 MPa in the stable region between 275.15 and 313.15 K. In the work of Kanno and Angell,<sup>7</sup> measurements of specific volume up to 150 MPa at the temperatures of 268.15 K–273.15 K are shown. Nevolina and Seifer<sup>8</sup> measured specific volume at 293.15 K and at pressures up to 140 MPa.

Up to now, the international standard EOS for heavy water was the IAPS84 formulation by Hill *et al.*<sup>9</sup> Its range of validity

covers both liquid and vapor regions up to 600 °C and up to 100 MPa. A new EOS was developed by Herrig *et al.*,<sup>10</sup> where the range of validity was broadened up to 1200 MPa.

In this paper, the experimental procedure and accurate experimental density measurements, performed with a specific pycnometer, in the temperature range of 253–313 K and in the pressure range of 75–163 MPa, are presented and discussed.

## II. EXPERIMENT

The appropriate choice of the measuring method or instrument for density measurements is usually determined by the physical state of the sample, the accuracy required, and the investigated quantity. Among the techniques used to measure the density of fluids at very high pressures, the pseudo-isochoric method can be a promising technique, being less affected by the physical properties of the fluid, e.g., viscosity or surface tension. This technique allows relatively safe handling of dangerous fluids working in very critical operative conditions since the samples are contained in a static pressure vessel during the entire experiment.<sup>11</sup> For the same reason, they can be used for carrying out measurements in metastable states.

### A. Experimental apparatus

To measure liquid heavy water density, a pseudo-isochoric method was used. For these measurements, the principle is slightly different from the one deployed for ordinary water and explained in a previous publication<sup>12</sup> since the measuring cell is actually used as a pycnometer. The method consists in determining the volume of the pycnometric cell by the gravimetric technique and measuring the mass of the sample

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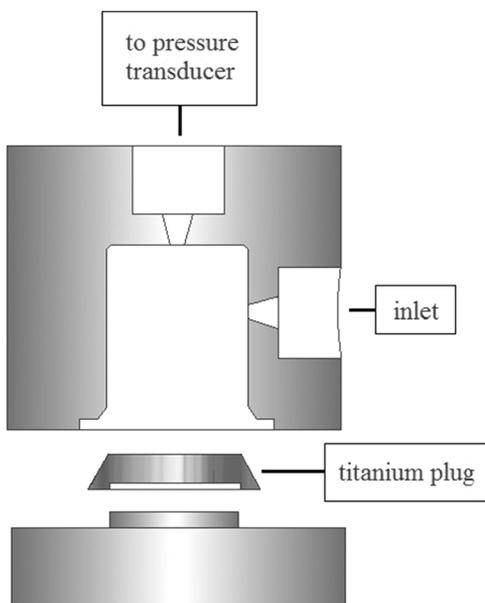


FIG. 1. Schematic representation of the pycnometric cell.

directly by weighing (by the difference between the filled and the empty pycnometer). The core of the experimental apparatus is a novel pycnometer, specifically manufactured for this purpose. The main body of the pycnometer is made of stainless steel AISI-316 while a titanium semi-conical plug with an angle of  $29^\circ$  is placed inside, where the internal cell has an angle of  $30^\circ$ , to ensure the sealing. A schematic representation of the pycnometer is shown in Fig. 1. The pycnometer was tested by filling it with ordinary water at the maximum pressure achievable (165 MPa) several times, and the pressure was monitored to assure that stabilization could be reached. The experimental apparatus was set up to control both temperature and pressure (cf. Fig. 2). In order to check and change the temperature, the pycnometric cell was placed into a liquid bath thermostat with an internal chilling unit able to stabilize the temperature of the liquid bath within  $\pm 0.01$  K. The pycnometer was linked to a high-pressure circuit consisting of a pressure amplifier, used to fill and increase the pressure inside it, and a system of valves that connected it to the sample reservoir at ambient conditions. Pressure measurements were performed

by means of a capacitance pressure transducer Sensotec TJE (calibrated and certified at INRIM) with a full-scale range of 200 MPa connected to the pycnometer. The temperature was measured by a platinum resistance thermometer (PT100), calibrated and certified at INRIM, placed in the middle of the inner volume of the pycnometer main body and a second one fastened to the pressure transducer to evaluate the temperature gradient. The thermometers were connected in the four wire configuration to two channels of an industrial thermometer bridge (Franco Corradi RP 7000). Besides, as shown in Fig. 2, the experimental apparatus was also equipped with an analytical balance with a resolution of 0.1 mg (Mettler Toledo PR 2004 Comparator) and stainless steel standard weights (Mettler Toledo 470, calibrated and certified at INRIM<sup>13</sup>) to measure the mass of heavy water (ambient temperature, pressure, and relative humidity were also measured to calculate air density).

The density measurements were carried out using a sample of  $D_2O$  provided by Sigma-Aldrich with a declared purity of 99.9% D atoms.

Each measuring cycle was performed following the same procedure herein described.

First, the pycnometer was filled at the desired pressure by using the pressure amplifier and the high pressure circuit. The pycnometer was isolated from the rest of the apparatus at ambient temperature by closing the valve and then was placed into the liquid thermostatic bath. The temperature was decreased slowly to maintain the liquid state and avoid crystallization. From 1 h to 3 h was required (at lower temperatures) to change the temperature of 1 K below the triple point. The temperature and the pressure were recorded at equilibrium, i.e., when temperature and pressure stabilization was within 0.01 K and 0.01 MPa, respectively. At the end of a measuring cycle, the pycnometer was taken off the thermostat and dried from the thermostatic liquid (ethanol) before weighing.

## B. Determination of fluid mass

For the determination of the mass of heavy water, a commercial analytical balance with stainless steel standard masses was used as a comparator. The mass of heavy water is given by the difference between the weights of the empty pycnometer and the pycnometer filled with heavy water. The technique

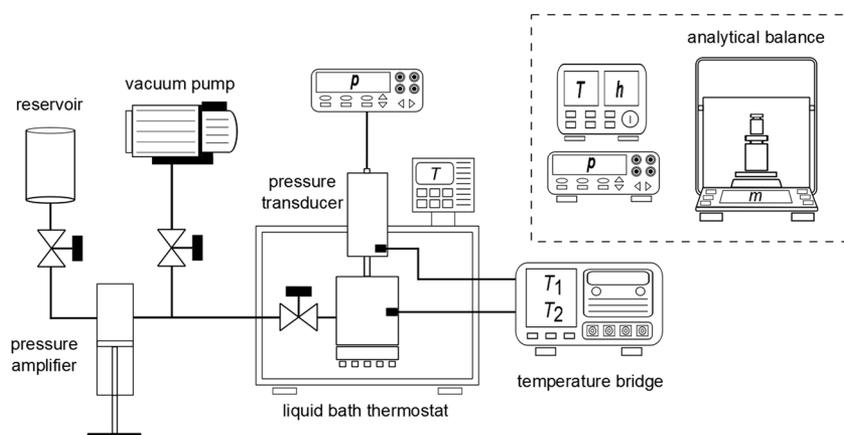


FIG. 2. Schematic representation of the experimental apparatus used to measure the density of subcooled heavy water.

used for each weighing (for the empty and the filled cell) was the double substitution weighing, generally used to perform high accuracy measurements by comparing the weight of the object (the pycnometer) with standard masses of similar nominal value.<sup>14</sup> Weight *A* (the standard masses) is compared to weight *B* (the pycnometer), defining the difference  $\Delta R$  between the two readings with each of the weights on the pan,

$$A = B + \Delta R. \quad (1)$$

For each weighing procedure, the *ABBA* calibration scheme was used. The weights were recorded in the following order: standard masses—pycnometer—pycnometer—standard masses. This procedure was repeated 10 times.

First, the empty pycnometer,  $M_0$ , was measured by

$$M_0 = M_{\text{eq}}^0 + \Delta R_0, \quad (2)$$

where  $M_{\text{eq}}^0$  is the nominal value of the standard masses (provided by the certificate). The value of Eq. (2) had to be corrected by adding the buoyancy term,

$$M_0 \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right) = (M_{\text{eq}}^0 + \Delta R_0) \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right), \quad (3)$$

where  $\rho_{\text{air}}$  is the density of air monitored during each weighing and  $\rho_{\text{std}} = 8 \text{ g cm}^{-3}$  is the density of the standard weights.

The described procedure was also applied to the mass of the pycnometer filled with the sample,  $M_{\text{D}_2\text{O}}$ . Similar to Eq. (3), the mass of the filled cell was given by

$$M_{\text{D}_2\text{O}} \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right) = (M_{\text{eq}} + \Delta R) \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right). \quad (4)$$

Thus, the  $\text{D}_2\text{O}$  mass  $m$  is obtained as

$$m = M_{\text{D}_2\text{O}} \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right) - M_0 \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right). \quad (5)$$

### C. Determination of the pycnometer volume

The gravimetric method is a standard technique used to calibrate the volume of the instruments.<sup>15</sup> It consists of weighing the empty cell first and then the cell filled with a reference fluid of known density at a specific temperature and pressure. The determination of the pycnometer volume was performed by using ordinary water as the reference fluid (bi-distilled water), considering the density data given by the EOS of the International Association for Properties of Water and Steam, i.e., the IAPWS-95 formulation,<sup>16</sup> which has an uncertainty of 0.003% at the temperature and pressure of calibration.

The empty and filled masses of the pycnometer were measured by comparison with standard weights by the double substitution method,<sup>17</sup> by using the analytical balance as comparator. The equation used to determine the volume is

$$V_0(T_0, p_0) = \frac{M_{\text{H}_2\text{O}} - M_0}{\rho_{\text{H}_2\text{O}}(T_0, p_0) - \rho_{\text{air}}} \left( 1 - \frac{\rho_{\text{air}}}{\rho_{\text{std}}} \right), \quad (6)$$

where  $M_{\text{H}_2\text{O}}$  is the mass of the pycnometer filled with ordinary water and  $M_0$  is the empty mass of the pycnometer,  $\rho_{\text{H}_2\text{O}}$  is the water density at the filling temperature  $T_0$  and pressure  $p_0$ ,

$\rho_{\text{air}}$  is the air density during the weighing, and  $\rho_{\text{std}} = 8 \text{ g cm}^{-3}$  is the standard weights density.

The reference volume of the pycnometer, determined at the temperature of  $296.93 \pm 0.01 \text{ K}$  and at the pressure of  $84.9 \pm 0.2 \text{ MPa}$ , had the value of  $V_0 = 11.520 \pm 0.002 \text{ cm}^3$ .

With the gravimetric method, the volume of the pycnometric cell  $V_0$  was established in a single thermodynamic state, i.e., the reference temperature  $T_0$  and pressure  $p_0$ . To determine the volume of the pycnometer  $V$  at any measured thermodynamic state  $(T, p)$ , the reference volume had to be corrected for the effects of temperature and pressure variations so that the volume was given by the following equation:

$$V(T, p) = V_0(T_0, p_0)[1 + \alpha(T - T_0) + \beta(p - p_0)], \quad (7)$$

where  $\alpha$  and  $\beta$  are the thermal expansion coefficient and the isothermal compressibility coefficient of the pycnometric cell, respectively. Since the pycnometer is made of different materials (stainless steel and titanium) and has a non-homogeneous shape, the values of the coefficients had to be determined experimentally.<sup>18</sup> The elastic properties of the pycnometer were estimated by temperature and pressure measurements and by the literature density of ordinary water, used as the reference fluid.<sup>16</sup> To estimate the  $\alpha$  and  $\beta$  coefficients, measurements were carried out for two samples of bi-distilled water in the temperature range of 275–313 K and at pressures between 50 and 100 MPa. Figure 3 shows the plot of the pressure measurements versus temperature, performed during the calibration.

For the calibration, a function derived from the definition of density and considering the change of volume with temperature and pressure [Eq. (7)] was used,

$$\rho(T, p) = \rho_0(T_0, p_0)[1 - \alpha(T - T_0) - \beta(p - p_0)]. \quad (8)$$

By the measurements of temperature,  $T$ , and pressure,  $p$ , and the corresponding  $\text{H}_2\text{O}$  density values,  $\rho$  (provided by the IAPWS-95 EOS<sup>16</sup>), a system of equations was built

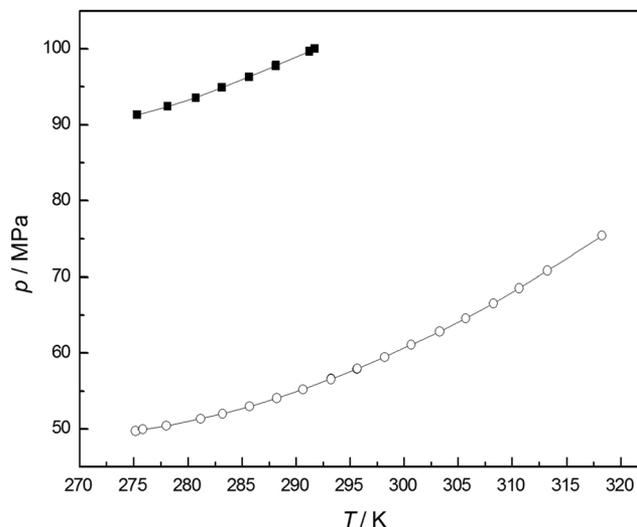


FIG. 3. Pressure measurements as a function of temperature for the volume calibration: ○, first  $\text{H}_2\text{O}$  sample; ■, second  $\text{H}_2\text{O}$  sample.

for each constant-mass curve, where  $\alpha$  and  $\beta$  are unknown parameters,

$$\begin{cases} \rho_1(T_1, p_1) = \rho_0(T_0, p_0)[1 - \alpha(T_1 - T_0) - \beta(p_1 - p_0)], \\ \rho_2(T_2, p_2) = \rho_0(T_0, p_0)[1 - \alpha(T_2 - T_0) - \beta(p_2 - p_0)], \\ \vdots \\ \rho_n(T_n, p_n) = \rho_0(T_0, p_0)[1 - \alpha(T_n - T_0) - \beta(p_n - p_0)], \end{cases} \quad (9)$$

where the different index refers to consecutive measurements.

Through the least squares analysis, it was possible to evaluate the values for  $\alpha$  and  $\beta$  from two systems of equations associated with the two fillings of different masses, resulting as

$$\begin{aligned} \alpha &= (2.2 \pm 0.2) \cdot 10^{-5} \text{ K}^{-1}, \\ \beta &= (7.5 \pm 0.2) \cdot 10^{-5} \text{ MPa}^{-1}. \end{aligned}$$

For the studied temperature and pressure range, the variations of the elastic properties with temperature and pressure were within the declared uncertainty. For this reason, they were considered constant over the whole examined  $T$ - $p$  range.

### III. UNCERTAINTY ANALYSIS

#### A. Mass uncertainty analysis

The mass of heavy water for each measuring cycle was measured by the difference between the weight of the pycnometer filled with the heavy water sample and the weight of the empty cell. According to Eqs. (2)–(5),  $m$  can be expressed as

$$m = m(\Delta R, d, M_{\text{eq}}, \rho_{\text{air}}, \rho_{\text{std}}). \quad (10)$$

The relative uncertainty in the estimation of heavy water mass,  $u(m)/m$ , was calculated with the uncertainty propagation formula by

$$\begin{aligned} \frac{u(m)}{m} &= \frac{1}{m} \left[ \sigma^2(\Delta R) + \left( \frac{d}{\sqrt{6}} \right)^2 + u^2(M_{\text{eq}}) + \left( \frac{\partial m}{\partial \rho_{\text{air}}} \right)^2 u^2(\rho_{\text{air}}) \right. \\ &\quad \left. + \left( \frac{\partial m}{\partial \rho_{\text{std}}} \right)^2 u^2(\rho_{\text{std}}) \right]^{\frac{1}{2}}, \end{aligned} \quad (11)$$

where  $\sigma(\Delta R)$  is the standard deviation of the difference of readings and  $d$  is the digital resolution of the analytical balance as a triangular distribution.<sup>19</sup> The uncertainty of the standard weights,  $u(M_{\text{eq}})$ , is provided by the calibration certificate. The contributions due to the analytical balance used as a comparator (i.e., linearity and eccentricity) are negligible. In Table I, the sources of uncertainty affecting the mass determination, along with their relative magnitude, are reported. The relative uncertainty of heavy water mass was about 0.007%.

#### B. Uncertainty of the pycnometer reference volume

The uncertainty of the pycnometer reference volume,  $V_0$ , was obtained considering the contributions of the mass of the fluid ( $\Delta M = M_{\text{H}_2\text{O}} - M_0$ ), the density of ordinary water, laboratory air, and standard weights, and the filling temperature and pressure,

TABLE I. Uncertainty budget of the heavy water density.

Uncertainty source	Relative standard uncertainty (%)
Mass	0.007
Reading standard deviation	0.010
Balance resolution	0.001
Standard weights mass	Negligible
Air density	Negligible
Standard weights density	Negligible
Volume	0.020
Reference volume	0.009
Mass of the reference fluid	0.008
Reference water density	0.003
Air density	Negligible
Standard weights density	Negligible
Temperature	0.001
Pressure	0.002
Thermal expansion coefficient	0.008
Compressibility coefficient	0.016
Temperature	0.001
Pressure	0.002
Purity	0.005
Density combined expanded uncertainty ( $k = 2$ )	0.04

$$V_0 = V_0(\Delta M, \rho_{\text{H}_2\text{O}}, \rho_{\text{air}}, \rho_{\text{std}}, T_0, p_0). \quad (12)$$

By applying the uncertainty propagation to Eq. (6), the relative uncertainty,  $u(V_0)/V_0$ , is given by

$$\begin{aligned} \frac{u(V_0)}{V_0} &= \frac{1}{V_0} \left[ \left( \frac{\partial V_0}{\partial \Delta M} \right)^2 u^2(\Delta M) + \left( \frac{\partial V_0}{\partial \rho_{\text{H}_2\text{O}}} \right)^2 u^2(\rho_{\text{H}_2\text{O}}) \right. \\ &\quad + \left( \frac{\partial V_0}{\partial \rho_{\text{air}}} \right)^2 u^2(\rho_{\text{air}}) + \left( \frac{\partial V_0}{\partial \rho_{\text{std}}} \right)^2 u^2(\rho_{\text{std}}) \\ &\quad \left. + \left( \frac{\partial V_0}{\partial T_0} \right)^2 u^2(T_0) + \left( \frac{\partial V_0}{\partial p_0} \right)^2 u^2(p_0) \right]^{\frac{1}{2}}. \end{aligned} \quad (13)$$

The uncertainty of the reference fluid mass,  $u(\Delta M) = 0.002$  g, takes into account the standard deviation of the difference of the readings, the balance resolution, and the standard weights uncertainty. The uncertainties of the standard weights density,  $u(\rho_{\text{std}})$ , and the air density,  $u(\rho_{\text{air}})$ , resulted negligible in the overall uncertainty. According to IAPWS-95,<sup>16</sup> the uncertainty of water density at 296.93 K and 84.9 MPa is  $u(\rho) = 0.003\%$ . The uncertainty  $u(T_0)$  of the temperature measurement is given by the calibration fit, the resolution of the instrument and the reading repeatability, and its value is within 0.01 K. The uncertainty of the pressure measurements  $u(p_0)$  due to the pressure transducer used and the measurement repeatability is 0.2 MPa.

The uncertainty of the pycnometer reference volume  $V_0$  was lower than 0.01%; all the contributions considered and the associated relative magnitude are summarized in Table I.

### C. Volume uncertainty analysis

According to Eq. (7), the uncertainty of the pycnometer volume was determined considering the volume  $V$  as a function of the reference volume  $V_0$ , the thermal expansion coefficient  $\alpha$ , the isothermal compressibility coefficient  $\beta$ , the temperature  $T$ , and the pressure  $p$ ,

$$V = V(V_0, \alpha, \beta, T, p).$$

The relative uncertainty,  $u(V)/V$ , was evaluated by using the standard formulation for the uncertainty propagation as follows:

$$\frac{u(V)}{V} = \frac{1}{V} \left[ \left( \frac{\partial V}{\partial V_0} \right)^2 u^2(V_0) + \left( \frac{\partial V}{\partial \alpha} \right)^2 u^2(\alpha) + \left( \frac{\partial V}{\partial \beta} \right)^2 u^2(\beta) + \left( \frac{\partial V}{\partial T} \right)^2 u^2(T) + \left( \frac{\partial V}{\partial p} \right)^2 u^2(p) \right]^{\frac{1}{2}}, \quad (14)$$

where  $u(V_0)$  is  $0.002 \text{ cm}^3$ . The uncertainties of the  $\alpha$  and  $\beta$  coefficients,  $u(\alpha)$  and  $u(\beta)$ , are due to the fitting process; other sources of uncertainty are negligible.

The uncertainty of temperature,  $u(T) = 0.02 \text{ K}$ , was estimated by the uncertainty of the calibration fit, the resolution of the instrument, the reading repeatability, and the temperature gradient measured between the two thermometers. The uncertainty of the pressure transducer  $u(p)$  is  $0.2 \text{ MPa}$ ; this value is given by the declared uncertainty of the instrument at the full-scale and the repeatability. Covariance between  $\alpha$  and  $\beta$  was calculated; however, it does not appear in Eq. (14) since it is negligible (less than  $10^{-9}$ ). In Table I, all contributions to the relative uncertainty of the corrected volume along with their relative values are reported.

### D. Density uncertainty analysis

The experimental density of heavy water can be expressed as a function of the mass  $m$ , weighted at the end of each measurement cycle, and the volume  $V$  corrected at each  $(T, p)$  thermodynamic state as follows:

$$\rho = \rho(m, V).$$

Consequently, the uncertainty propagation formula was applied to estimate the relative uncertainty of heavy water density, which can be obtained by

$$\frac{u(\rho)}{\rho} = \frac{1}{\rho} \left[ \left( \frac{\partial \rho}{\partial m} \right)^2 u^2(m) + \left( \frac{\partial \rho}{\partial V} \right)^2 u^2(V) + \left( \frac{u_{\text{purity}}}{\sqrt{12}} \right)^2 \right]^{\frac{1}{2}}, \quad (15)$$

where  $u(m)$  is the uncertainty of the mass equal to  $0.002 \text{ g}$  and  $u(V)$  is the uncertainty of the volume at the measured temperature and pressure ( $0.003 \text{ cm}^3$ ). The latter value, calculated for the worst case scenario, was considered as the uncertainty for all the volume values. Equation (15) contains also the term  $u_{\text{purity}}$ , which is the uncertainty of the composition (purity of the sample is 99.9%), considering a rectangular distribution.<sup>20</sup> As shown in Table I, the main contribution to the uncertainty is due to the volume, as expected considering the complexity of its determination. The relative uncertainty of subcooled heavy

water density, considering the worst case scenario and with a coverage factor of 2, was estimated equal to 0.04% (at 95% confidence level). The values reported in Table I were calculated by multiplying the uncertainty of the property and the corresponding sensitivity coefficient.

## IV. RESULTS

The density of subcooled deuterium oxide was measured along seven constant-mass curves at temperatures down to 253 K and in the pressure range between 75 and 163 MPa, as shown in Fig. 4. In Fig. 5, the experimental densities of the different  $\text{D}_2\text{O}$  samples as a function of temperature are presented. Both plots show curves with a smooth trend and none of them has discontinuities. This means that freezing did not occur

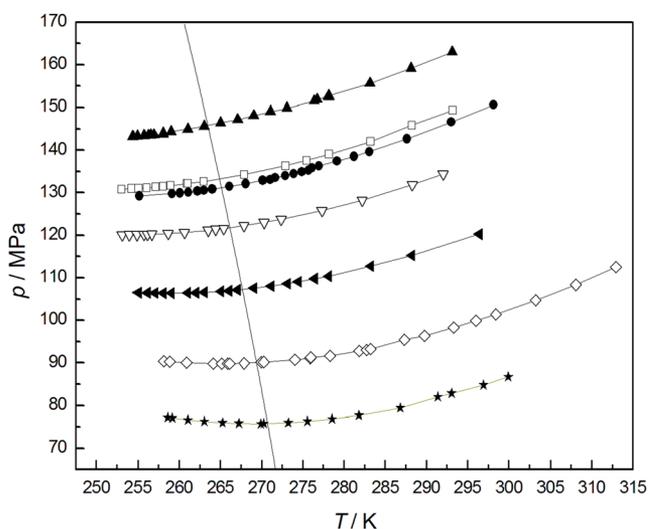


FIG. 4. Pressure as a function of temperature at constant mass:  $\blacktriangle$ ,  $m = 13.65 \text{ g}$ ;  $\square$ ,  $m = 13.57 \text{ g}$ ;  $\bullet$ ,  $m = 13.55 \text{ g}$ ;  $\nabla$ ,  $m = 13.49 \text{ g}$ ;  $\blacktriangleleft$ ,  $m = 13.40 \text{ g}$ ;  $\diamond$ ,  $m = 13.28 \text{ g}$ ;  $\star$ ,  $m = 13.18 \text{ g}$ ; —, melting curve.

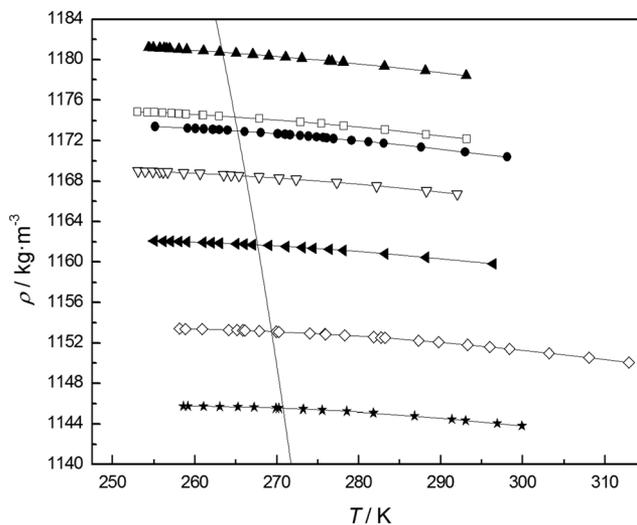


FIG. 5. Heavy water density as a function of temperature at constant mass:  $\blacktriangle$ ,  $m = 13.65 \text{ g}$ ;  $\square$ ,  $m = 13.57 \text{ g}$ ;  $\bullet$ ,  $m = 13.55 \text{ g}$ ;  $\nabla$ ,  $m = 13.49 \text{ g}$ ;  $\blacktriangleleft$ ,  $m = 13.40 \text{ g}$ ;  $\diamond$ ,  $m = 13.28 \text{ g}$ ;  $\star$ ,  $m = 13.18 \text{ g}$ ; —, melting curve.

TABLE II. Experimental deuterium oxide density  $\rho$  at temperature  $T$  and pressure  $p$ , for different masses  $m$ . The uncertainty associated with all values of density is 0.04%. Entries in italics refer to measurements carried out in metastable states of liquid heavy water.

$T$ (K)	$p$ (MPa)	$\rho$ (kg·m <sup>-3</sup> )	$T$ (K)	$p$ (MPa)	$\rho$ (kg·m <sup>-3</sup> )	$T$ (K)	$p$ (MPa)	$\rho$ (kg·m <sup>-3</sup> )
$m = 13.65$ g								
254.43	143.18	1181.19	259.06	144.37	1180.97	276.42	151.51	1179.88
254.97	143.30	1181.17	261.06	144.95	1180.86	276.75	151.88	1179.83
255.77	143.39	1181.14	263.05	145.62	1180.75	278.13	152.64	1179.73
256.26	143.47	1181.12	265.05	146.42	1180.63	278.17	152.46	1179.74
256.57	143.54	1181.11	267.10	147.17	1180.51	278.17	152.75	1179.72
256.97	143.63	1181.09	269.05	148.08	1180.37	283.16	155.64	1179.33
258.06	143.80	1181.04	271.09	149.02	1180.24	288.15	159.17	1178.89
258.09	144.03	1181.02	273.09	149.82	1180.11	293.15	162.97	1178.42
$m = 13.57$ g								
253.09	130.83	1174.88	258.97	131.68	1174.65	275.45	137.61	1173.70
254.28	130.96	1174.84	260.96	132.12	1174.56	278.20	139.01	1173.50
255.08	131.01	1174.81	261.06	132.22	1174.55	283.24	142.02	1173.10
256.08	131.16	1174.78	262.96	132.64	1174.46	288.24	145.83	1172.64
257.17	131.33	1174.73	267.91	134.26	1174.19	293.20	149.36	1172.20
258.07	131.49	1174.69	272.90	136.34	1173.88			
$m = 13.55$ g								
255.16	129.26	1173.41	268.07	132.14	1172.81	276.97	136.32	1172.21
259.13	129.79	1173.26	270.14	132.93	1172.69	279.15	137.42	1172.06
260.09	129.94	1173.22	271.04	133.10	1172.65	281.23	138.55	1171.90
261.10	130.12	1173.17	271.66	133.53	1172.60	283.07	139.67	1171.76
262.23	130.40	1173.12	272.89	134.02	1172.52	287.65	142.67	1171.37
263.00	130.59	1173.08	273.91	134.46	1172.46	293.02	146.60	1170.89
263.98	130.91	1173.03	274.90	134.89	1172.39	298.15	150.62	1170.40
264.02	130.87	1173.03	275.69	135.25	1172.34	303.04	154.89	1169.90
266.09	131.50	1172.92	276.11	135.81	1172.28			
$m = 13.49$ g								
253.14	120.07	1169.01	258.68	120.40	1168.83	270.32	123.01	1168.30
254.03	120.08	1168.98	260.65	120.65	1168.76	272.39	123.76	1168.18
254.91	120.09	1168.96	263.51	121.15	1168.64	277.34	125.79	1167.87
255.73	120.16	1168.96	264.44	121.36	1168.60	282.21	128.21	1167.53
256.15	120.17	1168.96	265.41	121.58	1168.55	288.30	131.85	1167.05
256.69	120.21	1168.96	267.88	122.25	1168.43	292.05	134.37	1166.73
$m = 13.40$ g								
255.07	106.53	1162.08	263.06	106.58	1161.87	274.46	109.08	1161.35
256.16	106.46	1162.06	265.08	106.80	1161.80	276.44	109.77	1161.24
257.07	106.43	1162.04	266.08	106.95	1161.76	278.16	110.37	1161.15
258.06	106.40	1162.02	267.08	107.18	1161.71	283.26	112.72	1160.81
259.07	106.40	1161.99	269.09	107.56	1161.63	288.25	115.25	1160.46
261.07	106.47	1161.93	271.17	108.04	1161.53	296.44	120.27	1159.81
262.06	106.48	1161.90	273.17	108.61	1161.43			
$m = 13.28$ g								
258.15	90.33	1153.41	270.25	90.20	1153.11	289.77	96.31	1152.07
258.85	90.24	1153.40	274.02	90.77	1152.96	293.30	98.25	1151.81
260.90	90.02	1153.36	275.91	91.03	1152.89	296.01	99.85	1151.60
264.16	89.78	1153.30	275.98	91.36	1152.86	298.44	101.35	1151.41
265.19	89.77	1153.27	278.32	91.63	1152.77	303.26	104.69	1151.00
265.90	89.78	1153.26	281.88	92.77	1152.58	308.08	108.34	1150.56
266.15	89.80	1153.25	282.77	93.08	1152.53	312.96	112.47	1150.07
267.90	89.89	1153.19	283.22	93.24	1152.51			
269.97	90.14	1153.12	287.35	95.40	1152.21			
$m = 13.18$ g								
258.62	77.19	1145.73	269.92	75.70	1145.56	286.84	79.43	1144.80
259.18	77.03	1145.72	270.28	75.82	1145.54	291.40	81.97	1144.47
261.07	76.62	1145.71	273.24	76.00	1145.45	293.07	82.83	1144.35
263.07	76.26	1145.69	275.57	76.29	1145.37	296.93	84.78	1144.08
265.26	76.00	1145.66	278.56	76.86	1145.24	299.94	86.72	1143.84
267.25	75.85	1145.62	281.82	77.70	1145.08			

during the whole measuring process. All experimental densities along the constant-mass curves are reported in Table II, where the values related to metastable states are expressed in italics.

## V. DISCUSSION

The experimental values of this work were compared to the new EOS provided by Herrig *et al.*<sup>10</sup> In Figs. 6 and 7, the deviations from the EOS (the zero line) and the experimental densities are shown as a function of the measured temperature and pressure, respectively. The measurements differ from the EOS within  $\pm 0.08\%$ , and for most of them the deviations are negative. As depicted in Fig. 6, the deviations are usually higher at the lower temperatures (metastable region).

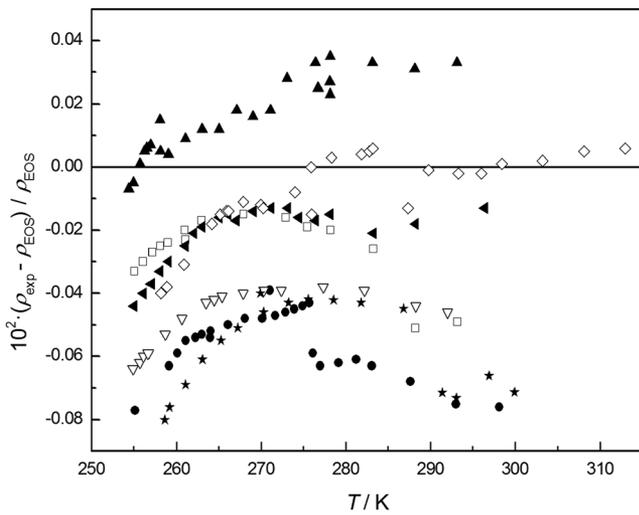


FIG. 6. Deviations of experimental density of heavy water from the values of the equation of state<sup>10</sup> (zero line) as a function of temperature:  $\blacktriangle$ ,  $m = 13.65$  g;  $\square$ ,  $m = 13.57$  g;  $\bullet$ ,  $m = 13.55$  g;  $\nabla$ ,  $m = 13.49$  g;  $\blacktriangleleft$ ,  $m = 13.40$  g;  $\diamond$ ,  $m = 13.28$  g;  $\star$ ,  $m = 13.18$  g.

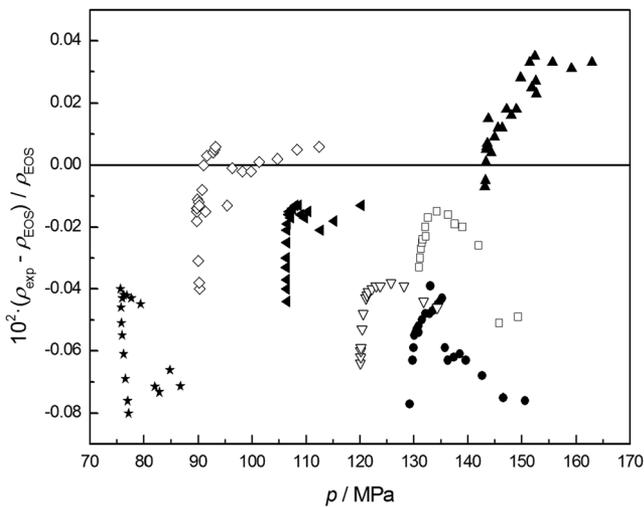


FIG. 7. Deviations of experimental density of heavy water from the values of the equation of state<sup>10</sup> (zero line) as a function of pressure:  $\blacktriangle$ ,  $m = 13.65$  g;  $\square$ ,  $m = 13.57$  g;  $\bullet$ ,  $m = 13.55$  g;  $\nabla$ ,  $m = 13.49$  g;  $\blacktriangleleft$ ,  $m = 13.40$  g;  $\diamond$ ,  $m = 13.28$  g;  $\star$ ,  $m = 13.18$  g.

TABLE III. Coefficients for the interpolation function of density [Eq. (16)] determined from the experimental densities, temperatures, and pressures (lower than 107 MPa) by means of the least squares method.

$i$	$j$	$\rho_{ij}$ (kg m <sup>-3</sup> K <sup>-i</sup> MPa <sup>-j</sup> )
0	0	1153.25
0	1	0.516
0	2	$-1.40 \times 10^{-3}$
1	0	-0.0660
1	1	-0.003 88
1	2	$4.91 \times 10^{-5}$
2	0	-0.005 59
2	1	$1.08 \times 10^{-4}$
2	2	$-2.23 \times 10^{-6}$

The measurements presented in this work were also compared with the most recent experimental data series: the relative densities measured by Duška *et al.*<sup>21</sup> In that work, the authors carried out D<sub>2</sub>O measurements up to 100 MPa, covering the supercooled region with temperatures down to 254 K. The comparison considers the measurements performed in the overlapping thermodynamic region, i.e.,  $80 \leq p \leq 100$  MPa and  $259 \leq T \leq 293$  K. Since the measurements were performed at different thermodynamic states, a polynomial function of temperature and pressure in a boundary of  $(T_0, p_0)$  was used to calculate and, thus compare, values exactly at the same  $(T, p)$  states. The data of Table II corresponding to pressures lower than 107 MPa were regressed by

$$\rho(T, p) = \sum_{i=0}^2 \sum_{j=0}^2 \rho_{ij} (T - T_0)^i (p - p_0)^j, \quad (16)$$

where  $T_0 = 268.0$  K and  $p_0 = 90.1$  MPa. Table III reports the values of the  $\rho_{ij}$  coefficients obtained by the least squares analysis. Figure 8 shows the deviations between the experimental densities and the values obtained at the same temperatures and pressures by means of Eq. (8). The calculated values differ from the measurements by less than  $\pm 0.015\%$ . Equation (16) is valid for pressures up to 107 MPa.

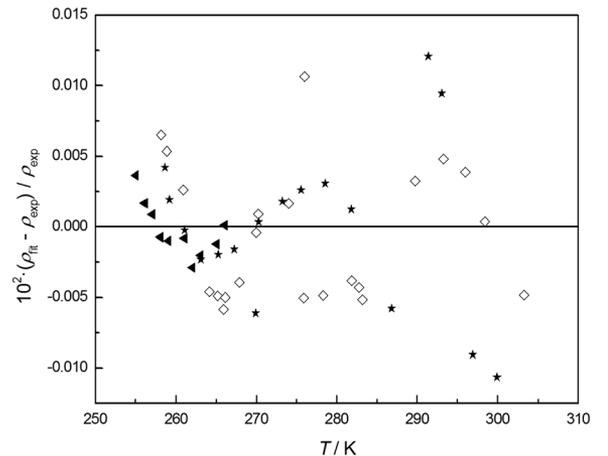


FIG. 8. Deviations of relative D<sub>2</sub>O density calculated by fitting the experimental data through Eq. (16) and the experimental values of Table II as a function of temperature:  $\blacktriangleleft$ ,  $m = 13.40$  g;  $\diamond$ ,  $m = 13.28$  g;  $\star$ ,  $m = 13.18$  g.

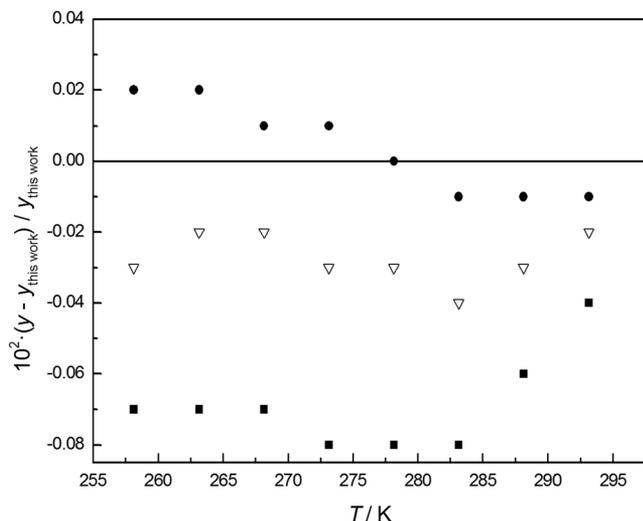


FIG. 9. Deviations of relative D<sub>2</sub>O density of Duška *et al.*<sup>21</sup> from the relative density of this work (zero line) as a function of temperature: ■,  $p = 80$  MPa; ▽,  $p = 90$  MPa; ●,  $p = 100$  MPa.

The comparison was made by considering the relative density defined by the ratio between the measured density and the reference density (at 298.15 K and at different pressures: 80 MPa, 90 MPa, or 100 MPa),

$$y(T, p) = \frac{\rho(T, p)}{\rho_{\text{ref}}(T_{\text{ref}}, p_{\text{ref}})}. \quad (17)$$

Figure 9 shows the deviations of the relative densities obtained by means of Eq. (16) from the values of Duška *et al.*,<sup>21</sup> as a function of temperature and for three isobars (80 MPa, 90 MPa, and 100 MPa). The two series differ within  $\pm 0.08\%$ , and most of the deviations are within the declared uncertainty, i.e.,  $\pm 0.04\%$  (see Table I).

## VI. CONCLUSION

In this work, the results of deuterium oxide (D<sub>2</sub>O) density performed in extreme conditions are presented. The measurements were carried out in a wide range of temperatures and pressures, partially covering a  $(T, p)$  region where experimental data were not available in the literature. A pycnometric cell purposely designed for this goal was used. The measurement principle consists in the determination of the pycnometer volume (i.e., the volume occupied by the fluid sample) and the measure of the D<sub>2</sub>O mass. The volume was determined by the gravimetric method, and its value was then corrected for the effect of temperature and pressure by means of the thermal expansion and compressibility coefficients, experimentally obtained. The heavy water mass was measured by weighing through an analytical balance for comparison with the standard weights.

D<sub>2</sub>O density was measured from 255 to 313 K and at pressures between 75 and 163 MPa. All terms contributing to the uncertainty in determining the volume and the mass were considered, leading to an expanded relative uncertainty for heavy water density around 0.04%, at 95% confidence level. The measurements were compared with the dedicated equation of state in the new formulation of Herrig *et al.*<sup>10</sup> The comparison shows that the equation and the experimental densities are in agreement within 0.08%. The measurements performed up to 100 MPa were also compared to the recent measurements performed by Duška *et al.*<sup>21</sup> All deviations between the two data sets of D<sub>2</sub>O relative densities are lower than 0.08%.

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