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Assessment of the Pressure-Volume-Temperature (PVT) Data of Water Since 1990

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Since the beginning of last century, a huge number of measurements and atomic or molecular level simulations have been carried out for the pressure-volume-temperature (*PVT*) properties of water. In the last decades, many people or organizations spent a lot of time on the collection and evaluation of water *PVT* data. In particular, the International Association for the Properties of Water and Steam (IAPWS) collected and evaluated the thermophysical data of water published before 1990, where the selected high-quality data have been incorporated into a very accurate equation of state developed by Wagner and Pruss (2002) and adopted by IAPWS in the IAPWS-95 formulation. The formulation can reproduce all thermodynamic properties of water from 273.16 to 1275 K and from 0 to 1 GPa, with experimental accuracy (or an accuracy close to it). In view of these facts, this work only assesses the *PVT* data of water since 1990 (Table 1).

Recently, Zhang and Duan (2005) made isothermal-isobaric molecular dynamics simulations of water based on the SPCE potential. They obtained 258 *PVT* data in a wide *P-T* range (523.15–4273.15 K, 100–50000 MPa). These data agree very well with the IAPWS-95 formulation or its extrapolation. It is found that even the pressure range of the isothermal extrapolation is four times that of the fitted data (0–1000 MPa), the maximum and average deviations are only 1.52% and 0.41%, respectively. With the accurate simulated data, Zhang and Duan (2005) and Duan and Zhang (2006) proposed two different equations of state for water, which are abbreviated as ZD05 and DZ06 in this work. The ZD05 equation is valid above 100 MPa, and the DZ06 equation is valid for 0–10 GPa. Compared with the simulated volume data of Zhang and Duan (2005), the average deviations of the two equations are 0.27% and 0.34%, respectively, and the maximum deviations are 1.75% and 2.77%, respectively. Compared with the IAPWS-95 formulation in the range 673.15–1273.15 K and 0–1000 MPa, the maximum deviation of the DZ06 equation is less than 0.6%, and the average deviation is about 0.1%.

Belonoshko and Saxena (1991) obtained 97 *PVT* data through molecular dynamics simulations. Under comparable conditions, the simulated data show large deviations from the IAPWS-95 formulation, where the maximum and average deviations are up to 15.54% and 2.74%, respectively. Beyond the applicable range of the IAPWS-95 formulation (T>1275 K, P>1000 MPa), their simulated data also deviate notably from the calculated results of ZD05 and DZ06 equations. The average deviations are 5.04% and 4.11%, respectively, and the maximum deviations are 38.15% and 37.90%, respectively.

Brodholt and Wood (1993) obtained a group of water *PVT* data using molecular dynamics simulations based on the TIP4P potential, where some data are below the critical temperature of water (647.096 K). Compared with the IAPWS-95 formulation below 1000 MPa, their average and maximum deviations are 27.88%, and 277.39%, respectively. Compared with the ZD05 equation above 1000 MPa, their average and maximum deviations are 9.35% and 73.96%, respectively. At 647.096–1275 K and 0–1000 MPa, their average and maximum deviations from the IAPWS-95 formulation are 7.99% and 30.27%, respectively. Compared with the ZD05 and DZ06 equations above 1275 K or 1000 MPa, the average deviations are 1.37% and 1.86%, respectively, and the maximum deviations are 7.28% and 7.13%, respectively.

Goldman et al. (2009) reported first principles simulations of water under shock loading and the chemical reactivity under hot, compressed conditions. Their results show reversible ionization reaction in water. Compared with the ZD05 equation, the average and maximum

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Table 1 *PVT* data of water from experiments and molecular simulations since 1990

Authors	Temperature (K)	Pressure (MPa)	Density (d, g/ cm^3) or molar volume (V, cm^3/mol)	Number of data
Belonoshko and Saxena (1991)	655–4356	135–90511.6	7–30 (V)	97
He and Zoller (1991)	302.15–525.65	0–200	16.83–22.53 (V)	467
Brodholt and Wood (1993)	671–2632	51–34927	0.2–1.9 (d)	97[(a)]
	298–595	–138–8940	0.2–1.7 (d)	47[(b)]
Brodholt and Wood (1994)	1203.15–1873.15	950–2500	19.15–25.86 (V)	9
Frost and Wood (1997)	1273.15–1673.15	1450	20.03–23.15 (V)	5
Larrieu and Ayers (1997)	1073.15–1593.15	850–2000	0.7294–1.048(d) 17.19–24.70 (V)	14
Wiryana et al. (1998)	353.15–473.15	250–3500	0.984–1.406(d)	42
Withers et al. (2000)	983.15–1373.15	1400–4000	0.99–1.18 (d)	10
Abramson and Brown (2004)	673.15	1000–6000	1.0564–1.4999 (d)	26[(a)]
	373.15–623.15	1000–6000	1.0802–1.5262 (d)	105[(b)]
Zhang and Duan (2005)	523.15–4273.15	100–50000	9.28–372.84 (V)	258
Goldman et al. (2009)	434	8300	1.54(d)	1[(a)]
	791–3654	18200–67800	1.80–2.36(d)	5[(b)]
Asahara et al. (2010)	730–900	11500–24100	1.72–2.03(d)	11[(a)]
	550–590	5300–6300	1.49–1.53(d)	2[(b)]
Lin and Trusler (2012)	253.20–473.14	0.1–400	15.6966–20.8628 (V)	90[(c)]
Sanchez-Valle et al. (2013)	673	1300–7100	No report	16[(a),(d)]
	293–573	0–4820	No report	75[(b),(d)]

Note：(a) T > 647.096 K ; (b) T < 647.096 K; (c) There are 14 data points measured in metastable states; (d) The number of data points of all velocities of sound, where most are used to fit their density model, except for those at 293 K and low pressures (<1 GPa).

deviations of the simulated volumes are 6.36% and 11.65%, respectively.

He and Zoller (1991) measured a group of *PVT* data of water using a high pressure dilatometer. Their average and maximum volume deviations from the IAPWS-95 formulation are 0.15% and 0.47%, respectively.

Brodholt and Wood (1994) measured the *PVT* data of water up to 2500 MPa and 1873.15 K using synthetic fluid inclusion in corundum. Compared with the DZ06 equation, their volume data have obvious positive deviations, where the average deviation is 2.66%, and the maximum deviation is 4.77%. Frost and Wood (1997) obtained 5 *PVT* data points with the same technology, so they have similar precision to those of Brodholt and Wood (1994). These data all have positive deviations from the DZ06 equation and the extrapolation of the IAPWS-95 formulation, which are 1.46-2.61% (2.07% average) and 1.97%, respectively. The deviations have an increasing tendency as temperature increases.

Larrieu and Ayers (1997) obtained some *PVT* data of water with a new method for measuring the volumes of fluids in a piston cylinder apparatus. The deviations of these data from the IAPWS-95 formulation or its extrapolation are very close to those from the DZ06 equation. Among the deviations at $T \leq$ 1273.15 K, only those at 1073.15K or 2000 MPa are small, the others are all large positive values, which are up to 4.39%–4.75%.

Withers et al. (2000) used a new NMR method to determine the densities of water at high pressures and temperatures. The volume deviations of these data from the isothermal extrapolation of the IAPWS-95 formulation and DZ06 equation are all positive, the average values are 1.35% and 1.1%, respectively, and the maximum values are 2.04% and 2.39%, respectively.

Wiryana et al. (1998) derived some *PVT* data from measured velocities of sound in liquid water in the heated high-pressure diamond-anvil cell. Below 1000 MPa, their data agree well with the IAPWS-95 formulation, where the average deviation is 0.06%, and the maximum deviation is 0.15%. Above 1000 MPa, their data agree well with the ZD05 equation and the extrapolation of the IAPWS-95 formulation, where the average volume deviations are 0.14% and 0.18%, respectively, and the maximum volume deviations are 0.39% and 0.33%, respectively.

Abramson and Brown (2004) reported a group of density data of water based on the velocities of sound measured in diamond-anvil cell. At 1000 MPa, these data are in excellent agreement with the IAPWS-95 formulation, where the average and maximum volume deviations are only 0.0037% and 0.0071%, respectively. Above 1000MPa, their data can be reproduced by the isothermal extrapolation of the IAPWS-95 formulation within 0.39%, with an average volume deviation of 0.2%.

Asahara et al. (2010) obtained some density data of water by measuring the velocities of sound up to 25 GPa and 900 K using a laser heated diamond anvil cell with a combined system of Brillouin scattering and synchrotron X-ray diffraction. The experimental volumes have obvious systematic deviations from the ZD05 equation. The deviations vary from positive to negative with the increase of temperature or pressure, where the average and maximum deviations are 1.8% and3.3%, respectively.

Lin and Trusler (2012) obtained the density data by measuring the velocities of sound in high-purity water at 253–473 K and 0.1–400 MPa. These data include 14 points measured in metastable states. The data in stable states agree very well with the IAPWS-95 formulation, where the average and maximum volume deviations are 0.005% and 0.031%, respectively.

Sanchez-Valle et al. (2013) measured the velocities of sound in water at high *P-T* conditions. The densities inverted from the velocities of sound were combined with the data from the IAPWS-95 formulation below 1 GPa and 373 K to generate a best-fit empirical density model, where the data at 293 K and low pressures (<1 GPa) were not used. The density model agrees well with the IAPWS-95 formulation. In the range 0.6–1 GPa and 293–673 K, the average deviation is 0.16%, and the maximum deviation is 0.24%. The density model also agree well with the ZD05 equation in the range 1–7 GPa and 293–673 K, where the average and maximum deviations are 0.21% and 0.52%, respectively.

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Key words: Assessment, water, *PVT* properties, density, equation of state, systematic deviation, molecular dynamics simulation, first principles

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