ICRN 30

# IAPWS Certified Research Need – ICRN

# Thermophysical Properties of Supercooled Water

The IAPWS Working Group “Thermophysical Properties of Water and Steam” and the IAPWS “Subcommittee on Seawater” have examined the published work and the experimental data available for a description of supercooled water under conditions appearing in industrial processes, in the ocean and in the atmosphere, and in biological and medical systems.

The available information on thermophysical properties of supercooled water is not sufficiently accurate and comprehensive with respect to specific applications, and does not cover the full pressure range relevant for industrial applications. In the present ICRN specific needs for further research are identified.

Although encouraging this work, IAPWS is not generally able to provide financial support. The IAPWS contact can provide any further development information and will liaise between research groups.

**Issued by the**
**International Association for the Properties of**
**Water and Steam**


**President:** **Dr. David Guzonas**
**Canadian Nuclear Laboratories**
**Chalk River, Ontario, Canada**

**Executive Secretary:** **Dr. R. B. Dooley**
**Structural Integrity Associates, Inc**
**Southport, Merseyside, UK**
**Email: bdooley@structint.com**

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## Thermophysical Properties of Supercooled Water

### Background

Supercooled water is a metastable state of liquid water occurring in the temperature range bounded by the pressure-dependent temperatures of homogeneous ice nucleation, $T_{HN}(P)$, and of ice melting, $T_M(P)$. The knowledge of rheological and thermophysical properties of supercooled water (viscosity, thermal conductivity, thermal diffusivity, mass density, heat capacity, isothermal compressibility, thermal expansion coefficient, speed of sound) is of key importance for a variety of environmental and industrial applications, such as (i) elucidation of cloud micro-physical processes in terrestrial and extraterrestrial atmospheres, (ii) description of ice formation in oceanic water, (iii) search for habitable planets and moons in the solar system and its nearest neighbors (extraterrestrial life in form of cold-loving organisms (psychophiles)), (iv) development of effective technologies for food production, freeze-waste-water treatment, cryo-desalination of seawater, and ice-heat storage.

### Range of properties required

Supercooled water properties are required in the temperature range $T_{HN}(P) < T < T_M(P)$. Due to the lack of empirical data on the maximum pressure occuring under planetary conditions including extraterrestrial environments, the upper limit of the pressure for which thermophysical properties of supercooled water are relevant is fixed to an *ad hoc* value of $P_{max}$ = 1400 MPa, representing the maximum pressure realizable for high-pressure processing in the food industry (Norton and Sun, 2008).

### Previous work and further requirements

**Rheological properties:**

The IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance (IAPWS, 2008) is based on a correlating equation for the viscosity of thermodynamically stable fluid water as function of $T$ and $P$, proposed by Huber *et al.* (2009). Its validity is restricted to temperatures $T > T_M(P)$. For application at atmospheric pressure ($P$ = 0.1 MPa), Huber *et al.* (2009, Eq. (37) therein) derived a simplified correlating equation, the validity of which is extented into the supercooled temperature region, 253.15 K < $T$ < 383.15 K. At some temperatures within this range, the equilibrium phase at 0.1 MPa is a solid or a vapour. At these conditions the correlating equation describes the viscosity of the metastable liquid phase. The uncertainty of the viscosity correlating equation is reported to be 1% for the stable liquid region; no uncertainty estimate is given for the metastable region, but the agreement with available data for the supercooled region is reported to be within 5% (Huber *et al.,* 2009, Sec. 3.7). The only experimental data below 255 K are those from Osipov *et al.* (1977) (238 K < $T$ < 273 K) with a reported uncertainty of 3%. For application to supercooled atmospheric water, extension of viscosity data in the temperature range down to $T_{HN}$ is desirable.

**Thermal conductivity:**

Computer simulations have indicated that the thermal conductivity of supercooled water may go though a minimum at a temperature of about 230 K (Biddle *et al.,* 2013, Bresme *et al.,* 2014). However, experimental data for the thermal diffusivity are only available down to 250 K and there are no experimental thermal-conductivity data to verify the existence of such a minimum. The validity of the IAPWS Formulation for the Thermal Conductivity of $H_2O$ (IAPWS, 2011) is restricted to temperatures $T > T_M(P)$. For application at atmospheric pressure ($P$ = 0.1 MPa), the formulation has an uncertainty of about 1.5% in the stable liquid region (Huber *et al.,* 2012). It can only be extrapolated to 250 K with an estimated uncertainty of 5%. Reliable experimental data for the thermal conductivity and/or thermal diffusivity of supercooled water in the temperature range down to $T_{HN}$ are desirable.

**Thermodynamic properties:**

The IAPWS Guideline on Thermodynamic Properties of Supercooled Water (IAPWS, 2015, hereafter called IAPWS-15) provides an equation of state of supercooled liquid water for the temperature range $T_{HN}(P) < T < T_M(P)$ and the pressure range 0 MPa < $P$ < 400 MPa. IAPWS-15 is based on an equation of state for supercooled water developed by Holten *et al.* (2014). To improve the accuracy of this equation, new experimental data are desirable, especially at pressures and temperatures where no data now exist, or where the existing data suffer from low accuracy. A revision of IAPWS-15 should extend the pressure range from 400 MPa to 1400 MPa.

The saturation vapor pressure of supercooled water is important, but it has been calculated by thermodynamic methods (Murphy and Koop, 2005; Holten *et al.*, 2014) with accuracy that is sufficient and that exceeds the accuracy that can be obtained in experimental measurement of this quantity.

**(a) Density**

In the temperature range from the homogeneous ice-nucleation temperature $T_{HN}$ to $T$ = 200 K at pressures from 160 MPa to 400 MPa, there are no density measurements available (see Holten *et al.* 2014, Fig. 1(a)). The IAPWS-15 equation of state has an estimated density uncertainty of 2% in this region. In the temperature range 200 K < $T$ < 253 K at 40 MPa < $P$ < 400 MPa, there are only density data of Mishima (2010) available, the systematic error of which is unknown. In this region the IAPWS-15 density uncertainty is reported to be 0.5% to 1.5%. To improve the accuracy of the equation of state, density measurements with an uncertainty of 0.05% or lower in the range $T_{HN} < T < 253$ K and $P < 400$ MPa are desirable. To extend the equation of state to pressures beyond 400 MPa, new density measurements are essential.

**(b) Speed of sound**

At atmospheric pressure below the melting curve, $P(T_M)$, the data of Taschin *et al.* (2011) are the most accurate ones; these data have an uncertainty of 0.7% in the speed of sound and extend down to 244.15 K. Data with a smaller uncertainty down to 240 K or even lower are desirable. At pressures above atmospheric pressure, there are virtually no data available for the speed of sound of supercooled water (see Holten *et al.*, 2014, Fig. 2). Experimental data are desired in the entire region $T_{HN} < T < T_M$ and 0 MPa < $P$ < 40 MPa, especially for the temperature range 250 K < $T < T_M$ and pressures $P$ < 200 MPa, where the uncertainty of IAPWS-15 for the speed of sound is reported to be 0.5%.

**(c) Heat capacity**

At atmospheric pressure, the different data sets for the isobaric heat capacity, $C_p$, do not agree at $T$ < 260 K; at $T$ = 236 K, the difference between the data of Angell *et al.* (1982) and the data of Archer and Carter (2000) amounts to 5% (see Holten *et al.* 2014, Section 2.4) To resolve this discrepancy, new data are needed in the temperature range $T_{HN} < T < 260$ K, preferably with an accuracy of 0.5% or better. There are neither measurements of the isobaric nor of the isochoric heat capacity of supercooled water at pressures above atmospheric pressure.

**Relation between microscopic structure of supercooled water and its thermophysical properties:**

The present model of thermodynamic properties of supercooled water is based on a theoretical model of the liquid as a mixture of two “components“, where the components represent different local molecular orderings in the liquid phase (Holten and Anisimov, 2012) While this approach proved to be efficient for data fitting (Holten *et al.,* 2014), additional theoretical, experimental, and simulation research is desirable to get more information on the local structure of supercooled water and on the relation between molecular structure and thermophysical properties.

## References


Angell, C.A., J. Sichina, and M. Oguni, 1982: Heat capacity of water at extremes of supercooling and superheating, J. Phys. Chem. **86**, 998-1002.

Archer, D.G., and R.W. Carter, 2000: Thermodynamic properties of the NaCl+$H_2O$ system. 4. Heat capacities of $H_2O$ and NaCl (aq) in cold-stable and supercooled states, J. Phys. Chem. B **104**, 8563-8584.

Biddle, J.W., V. Holten, J.V. Sengers, and M.A. Anisimov, 2013: Thermal conductivity of supercooled water, Phys. Rev. E **87**, 042302.

Bresme, F., J.W. Biddle, J.V. Sengers, and M.A. Anisimov, 2014: Communication: Minimum in the thermal conductivity of supercooled water: A computer simulation study, J. Chem. Phys. **140**, 161104.

Holten, V., J.V. Sengers, and M.A. Anisimov, 2014: Equation of state for supercooled water at pressures up to 400 MPa, J. Phys. Chem. Ref. Data **43**, 043101.

Holten, V., and M.A. Anisimov, 2012: Entropy-driven liquid-liquid separation in supercooled water, Scientific Reports **2**: 713.

Huber, M.L., R.A. Perkins, A. Laesecke, D.G. Friend, J.V. Sengers, M.J. Assael, I.N. Metaxa, E. Vogel, R. Mareš, and K. Miyagawa, 2009: New International Formulation for the Viscosity of $H_2O$, J. Phys. Chem. Ref. Data **38**, 101-125.

Huber, M.L, R.A. Perkins, D.G. Friend, J.V. Sengers, M.J. Assael, I.N. Metaxa, K. Miyagawa, R. Hellmann, and E. Vogel, 2012: New International Formulation for the Thermal Conductivity of $H_2O$, J. Phys. Chem. Ref. Data **41**, 033102.

IAPWS, 2008: Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance, The International Association for the Properties of Water and Steam.

IAPWS, 2011: Release on the IAPWS Formulation 2011 for the Thermal Conductivity of Ordinary Water Substance, The International Association for the Properties of Water and Steam.

IAPWS, 2015: Guideline on Thermophysical Properties of Supercooled Water, The International Association for the Properties of Water and Steam.

Mishima, O., 2010: Volume of supercooled water under pressure and the liquid-liquid critical point, J. Chem. Phys. **133**, 144503.

Murphy, D.M., and T. Koop, 2005: Review of the vapour pressures of ice and supercooled water for atmospheric applications, Quart. J. Roy. Meteorol. Soc. **131**, 1539-1565.

Norton, T., and D.-W. Sun, 2008: Recent advances in the use of high pressure as an effective processing technique in the food industry, Food Bioprocess Technol. **1**, 2-34.

Osipov, Yu.A., B.V. Zheleznyi, and N.F. Bondarenko, 1977: The shear viscosity of water supercooled to −35°C, Russ. J. Phys. Chem. **51**, 748-749.

Taschin, A., R. Cucini, P. Bartolini, and R. Torre, 2011: Does there exist an anomalous sound dispersion in supercooled water?, Phil. Mag. **91**, 1796-1800.

**IAPWS Contact:**

Dr. Olaf Hellmuth
Leibniz-Institut für Troposphärenforschung e.V.
Permoserstrasse 15
D-04318 Leipzig, Germany
E-mail: olaf@tropos.de
Tel: +49 341 2717-7047

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