LibIAPWS

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Abstract

LibIAPWS is a C++ library to implement IAPWS [1] (International Association for the Properties of Water and Steam) formulation. It contains parametrizations for thermodynamic properties, including enthalpy, entropy, heat capacities and latent heat, as functions of temperature, pressure and mass density of $\rm H_2O$. Coexisting phases among water vapor, liquid and ice are also computed and tabulated.

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1 Library functions

1.1 R1-76 (2014) - IAPWS::Lib76 class

IAPWS R1-76 [2] release provides a parametrization for the surface tension σ of the interface between water vapor and liquid. There is one function **get_tension_surf**, which takes temperature T as input and returns the surface tension.

function	input	output
get_tension_surf	temperature T (K)	surface tension σ (J/m ²)

Table 1: Library functions in IAPWS::Lib76 class

1.2 R6-95 (2018) - IAPWS::Lib95 class

IAPWS R6-95 [3] release provides parametrizations for the specific Helmholtz free energy f and thermodynamic quantities of water vapor and liquid. The mass density ρ and temperature T are considered as independent variables. The parametrized functions for single-phase are listed in Table 2.

function	input	output	
get_param_f	mass density ρ (kg/m ³) temperature T (K)	specific Helmholtz free energy f (J/kg)	
get_param_g	mass density ρ (kg/m ³) temperature T (K)	specific Gibbs free energy f (J/kg)	
get_param_pressure	mass density ρ (kg/m ³) temperature T (K)	pressure p (Pa = N/m ²)	
get_param_dpress_drho	mass density ρ (kg/m ³) temperature T (K)	derivative of pressure $\frac{\partial p}{\partial \rho}\Big _T$ (m ² /sec ²)	
get_param_erg_int	mass density ρ (kg/m ³) temperature T (K)	specific internal energy u (J/kg)	
get_param_entropy	mass density ρ (kg/m ³) temperature T (K)	specific entropy s (J/kg K)	
get_param_enthalpy	mass density ρ (kg/m ³) temperature T (K)	specific enthalpy h (J/kg)	
get_param_heat_c_v	mass density ρ (kg/m ³) temperature T (K)	specific isochoric heat capacity c_v (J/kg K)	
get_param_heat_c_p	mass density ρ (kg/m ³) temperature T (K)	specific isobaric heat capacity c_p (J/kg K)	
get_param_speed_sound	mass density ρ (kg/m ³) temperature T (K)	speed of sound w (m/sec)	

Table 2: Library functions for single-phase thermodynamic quantities in IAPWS::Lib95 class

In addition, one can utilize the parametrized Helmholtz free energy to obtain coexisting phases (saturation curve) between water vapor and liquid. In IAPWS::Lib95 class, iterative root-finding algorithms are implemented to specify the saturation curve. (More details can be found in the following sections.) Table 3 presents functions to handle the tabulated saturation curve. One can call $make_tab_coex$ to produce a table for saturation curve by specifying number of temperature bins and maximum temperature. The minimum temperature for tabulation is set to be that of the triple point $T_{trip} = 273.16$ K. It is possible to expedite calculations in $make_tab_coex$ function, by providing a function pointer to better initial guess for the saturation pressure. One option is to use $get_param4_sat_pressure$ function in IAPWS::Lib97 class and it is demonstrated in $make_tab_IAPWS95$.cpp source file. export_tab_coex and import_tab_coex functions can be used to write and read the tabulated saturation curve, respectively.

Once the tabulated saturation curve is produced or imported, one can call functions listed in Table 4 to obtain thermodynamic quantities on the saturation curve. The tabulated saturation curve is interpolated by means of natural cubic spline. All functions take temperature T (in K) as the input parameter.

function	input	
make_tab_coex	number of temperature bins (int) maximum temperature (K) function pointer to initial guess for the saturation pressure (double (*ptr)(double), default: NULL)	void
export_tab_coex	name of output file (char *)	void
import_tab_coex	name of input file (char *)	void

Table 3: Library functions for tabulated coexisting phases in IAPWS::Lib95 class

function	input	output	
get_coex_pressure	temperature T (K)	saturation pressure p_{coex} (Pa)	
get_coex_mden_vap	temperature T (K)	mass density of vapor $\rho_{\rm vap}~({\rm kg/m^3})$	
get_coex_mden_liq	temperature $T(K)$	mass density of liquid ρ_{liq} (kg/m ³)	
<pre>get_coex_enthalpy_vap</pre>	temperature $T(K)$	specific enthalpy of vapor h_{vap} (J/kg)	
<pre>get_coex_enthalpy_liq</pre>	temperature $T(K)$	specific enthalpy of liquid h_{liq} (J/kg)	
get_coex_entropy_vap	temperature $T(K)$	specific entropy of vapor s_{vap} (J/kg K)	
get_coex_entropy_liq	temperature $T(K)$	specific entropy of liquid s_{liq} (J/kg K)	
<pre>get_coex_heat_latent</pre>	temperature $T(K)$	specific latent heat $h_{\text{latent;vap-liq}}$ (J/kg)	

Table 4: Library functions for coexisting phases (saturation curve) in IAPWS::Lib95 class

1.3 R12-08 (2008) - IAPWS::Lib08V class

IAPWS R12-08 [6] release provides a parametrization for the shear viscosity μ as a function of the mass density ρ and temperature T. Functions to be used are listed in Table 5. Note that one also needs to have an instance of IAPWS::Lib95 class to implement the critical enhancement. There is a class (pointer) variable ptr_lib95_ to connect a IAPWS::Lib95 object and one can call set_ptr_lib95 function to set it up.

function	input	output
set_ptr_lib95	pointer to an instance of Lib95 class (IAPWS::Lib95 *ptr)	void
get_param_viscosity	mass density ρ (kg/m ³) temperature T (K)	shear viscosity μ (Pa·sec)

Table 5: Library functions for coexisting phases (saturation curve) in IAPWS::Libo8V class

2 Derivation for thermodynamic quantities

2.1 From the Helmholtz free energy $f(\rho, T)$

If one has mass density ρ (equivalently specific volume $v = 1/\rho$) and temperature T as independent variables, thermodynamic quantities can be derived from the specific Helmholtz free energy f

$$\frac{f(\rho, T)}{RT} = \phi \left(\delta \equiv \frac{\rho}{\rho_*}, \tau \equiv \frac{T_*}{T} \right) \tag{1}$$

where R is the specific gas constant. In addition, dimensionless quantities δ and τ are introduced in terms of reference mass density ρ_* and temperature T_* , respectively. For instance, specific entropy s and pressure p can be given by first derivatives of the Helmholtz free energy.

$$s = -\frac{\partial f}{\partial T}\Big|_{\rho} = R(\tau\phi_{\tau} - \phi) \quad \text{where} \quad \phi_{\tau} \equiv \frac{\partial \phi}{\partial \tau}$$
 (2)

$$p = -\frac{\partial f}{\partial v}\Big|_{T} = \rho^{2} \frac{\partial f}{\partial \rho}\Big|_{T} = \rho RT \,\delta\phi_{\delta} \quad \text{where} \quad \phi_{\delta} \equiv \frac{\partial \phi}{\partial \delta}$$
 (3)

The specific internal energy u and enthalpy h can be subsequently obtained as

$$u = f + Ts = RT \tau \phi_{\tau} \tag{4}$$

$$h = u + pv = RT \left(\tau \phi_{\tau} + \delta \phi_{\delta}\right). \tag{5}$$

The isochoric heat capacity c_v is given by the partial derivative of u with respect to T.

$$c_v = \frac{\partial u}{\partial T}\Big|_{\rho} = -R \tau^2 \phi_{\tau\tau} \quad \text{where} \quad \phi_{\tau\tau} = \frac{\partial^2 \phi}{\partial \tau^2}$$
 (6)

The isobaric heat capacity c_p is defined as the partial derivative of h with respect to T, while the pressure is kept constant.

$$c_{p} = \frac{\partial h}{\partial T}\Big|_{p}$$

$$= \lim_{\Delta T \to 0} \frac{h(\rho + \Delta \rho, T + \Delta T) - h(\rho, T)}{\Delta T} \quad \text{where} \quad \frac{\partial p}{\partial \rho}\Big|_{T} \Delta \rho + \frac{\partial p}{\partial T}\Big|_{\rho} \Delta T = 0.$$
(7)

$$= \frac{\partial h}{\partial T} \bigg|_{0} - \frac{\partial h}{\partial \rho} \bigg|_{T} \frac{\partial p/\partial T|_{\rho}}{\partial p/\partial \rho|_{T}}$$

$$(8)$$

$$= c_v + \frac{1}{\rho} \frac{\partial p}{\partial T} \bigg|_{\rho} - \left(\frac{\partial u}{\partial \rho} \bigg|_{T} + \frac{1}{\rho} \frac{\partial p}{\partial \rho} \bigg|_{T} - \frac{p}{\rho^2} \right) \frac{\partial p/\partial T|_{\rho}}{\partial p/\partial \rho|_{T}} = c_v + \frac{1}{\rho} \left(\frac{p}{\rho} - \rho \frac{\partial u}{\partial \rho} \bigg|_{T} \right) \frac{\partial p/\partial T|_{\rho}}{\partial p/\partial \rho|_{T}}$$
(9)

Derivatives of p and u can be written in terms of ϕ as following.

$$\rho \left. \frac{\partial u}{\partial \rho} \right|_{T} = RT \, \delta \tau \phi_{\delta \tau} \quad \text{where} \quad \phi_{\delta \tau} = \frac{\partial^{2} \phi}{\partial \delta \, \partial \tau}$$

$$(10)$$

$$\frac{1}{\rho} \left. \frac{\partial p}{\partial T} \right|_{\rho} = R \left(\delta \phi_{\delta} - \delta \tau \phi_{\delta \tau} \right) \tag{11}$$

$$\frac{\partial p}{\partial \rho}\Big|_{T} = RT \left(2 \delta \phi_{\delta} + \delta^{2} \phi_{\delta \delta}\right) \text{ where } \phi_{\delta \delta} = \frac{\partial^{2} \phi}{\partial \delta^{2}}$$
 (12)

which lead one to obtain

$$c_p = c_v + R \frac{(\delta \phi_\delta - \delta \tau \phi_{\delta \tau})^2}{2 \delta \phi_\delta + \delta^2 \phi_{\delta \delta}}.$$
 (13)

The speed of sound w can be computed by taking derivative of p with respect to ρ , while the specific entropy is kept constant.

$$w^{2} = \frac{\partial p}{\partial \rho}\Big|_{s}$$

$$= \lim_{\Delta \rho \to 0} \frac{p(\rho + \Delta \rho, T + \Delta T) - p(\rho, T)}{\Delta \rho} \quad \text{where} \quad \frac{\partial s}{\partial \rho}\Big|_{T} \Delta \rho + \frac{\partial s}{\partial T}\Big|_{\rho} \Delta T = 0$$

$$= \frac{\partial p}{\partial \rho}\Big|_{T} - \frac{1}{\rho} \frac{\partial p}{\partial T}\Big|_{s} \frac{\rho \partial s/\partial \rho|_{T}}{\partial s/\partial T|_{\rho}}$$

$$(15)$$

Derivatives of s can be written in terms of ϕ as following.

$$\rho \left. \frac{\partial s}{\partial \rho} \right|_{T} = -R \left(\delta \phi_{\delta} - \delta \tau \phi_{\delta \tau} \right) \tag{16}$$

$$\left. \frac{\partial s}{\partial T} \right|_{\rho} = -\frac{R}{T} \tau^2 \phi_{\tau\tau} \tag{17}$$

which result in the following expression for w.

$$w^{2} = RT \left[2 \delta \phi_{\delta} + \delta^{2} \phi_{\delta \delta} - \frac{(\delta \phi_{\delta} - \delta \tau \phi_{\delta \tau})^{2}}{\tau^{2} \phi_{\tau \tau}} \right]$$
(18)

2.2 From the Gibbs free energy g(T, p)

If one has pressure p and temperature T as independent variables, thermodynamic quantities can be derived from the specific Gibbs free energy q

$$\frac{g(T,p)}{RT} = \gamma \left(\tau \equiv \frac{T_*}{T}, \Pi \equiv \frac{p}{p_*} \right) \tag{19}$$

where we have a dimensionless quantity Π defined in terms of the reference pressure p_* . One can obtain the specific entropy s and specific volume v from first derivatives of the Gibbs free energy.

$$s = -\frac{\partial g}{\partial T}\Big|_{p} = R(\tau \gamma_{\tau} - \gamma) \quad \text{where} \quad \gamma_{\tau} \equiv \frac{\partial \gamma}{\partial \tau}$$
 (20)

$$v = \frac{\partial g}{\partial p}\Big|_{T} = \frac{RT}{p} \Pi \gamma_{\Pi} \quad \text{where} \quad \gamma_{\Pi} \equiv \frac{\partial \gamma}{\partial \Pi}$$
 (21)

which lead to the following expressions for the specific enthalpy and internal energy.

$$h = g + Ts = RT \tau \gamma_{\tau} \tag{22}$$

$$u = h - pv = RT \left(\tau \gamma_{\tau} - \Pi \gamma_{\Pi} \right). \tag{23}$$

The isobaric heat capacity c_p is given by

$$c_p = \frac{\partial h}{\partial T}\Big|_p = -R \tau^2 \gamma_{\tau\tau} \quad \text{where} \quad \gamma_{\tau\tau} = \frac{\partial^2 \gamma}{\partial \tau^2} \,.$$
 (24)

The isochoric heat capacity c_v is given by the partial derivative of u with respect to T, while the specific volume is kept constant.

$$c_{v} = \frac{\partial u}{\partial T}\Big|_{v}$$

$$= \lim_{\Delta T \to 0} \frac{u(T + \Delta T, p + \Delta p) - u(T, p)}{\Delta T} \quad \text{where} \quad \frac{\partial v}{\partial T}\Big|_{p} \Delta T + \frac{\partial v}{\partial p}\Big|_{T} \Delta p = 0.$$
(25)

$$= \frac{\partial u}{\partial T}\Big|_{p} - \frac{\partial u}{\partial p}\Big|_{T} \frac{\partial v/\partial T|_{p}}{\partial v/\partial p|_{T}}$$

$$(26)$$

$$= c_p - p \left. \frac{\partial v}{\partial T} \right|_{T} - \left(\left. \frac{\partial h}{\partial p} \right|_{T} - p \left. \frac{\partial v}{\partial p} \right|_{T} - v \right) \frac{\partial v/\partial T|_{p}}{\partial v/\partial p|_{T}} = c_p + \left(pv - p \left. \frac{\partial h}{\partial p} \right|_{T} \right) \frac{\partial v/\partial T|_{p}}{p \left. \partial v/\partial p|_{T}}$$
(27)

Derivatives of h and v can be written in terms of γ as following.

$$p \left. \frac{\partial h}{\partial p} \right|_{T} = RT \prod_{\tau} \gamma_{\Pi\tau} \quad \text{where} \quad \gamma_{\Pi\tau} = \frac{\partial^2 \gamma}{\partial \prod_{\tau} \partial \tau}$$
 (28)

$$\left. \frac{\partial v}{\partial T} \right|_{p} = \left. \frac{R}{p} \Pi \left(\gamma_{\Pi} - \tau \gamma_{\Pi \tau} \right) \right. \tag{29}$$

$$p \left. \frac{\partial v}{\partial p} \right|_{T} = \frac{RT}{p} \Pi^2 \gamma_{\Pi\Pi} \quad \text{where} \quad \gamma_{\Pi\Pi} = \frac{\partial^2 \gamma}{\partial \Pi^2}$$
 (30)

which result in the following expression for c_v .

$$c_v = c_p + R \frac{(\gamma_{\Pi} - \tau \gamma_{\Pi\tau})^2}{\gamma_{\Pi\Pi}}$$
(31)

The speed of sound can be computed in a similar manner as one does with the Helmholtz free energy.

$$w^{2} = \frac{\partial p}{\partial \rho}\Big|_{s}$$

$$= -v^{2} \left[\lim_{\Delta p \to 0} \frac{v(T + \Delta T, p + \Delta p) - v(T, p)}{\Delta p} \right]^{-1} \quad \text{where} \quad \frac{\partial s}{\partial T}\Big|_{p} \Delta T + \frac{\partial s}{\partial p}\Big|_{T} \Delta p = 0$$
(32)

$$= -v^2 \left(\frac{\partial v}{\partial p} \Big|_T - \frac{\partial v}{\partial T} \Big|_p \frac{\partial s/\partial p|_T}{\partial s/\partial T|_p} \right)^{-1} = (pv)^2 \left(pT \left. \frac{\partial v}{\partial T} \Big|_p \frac{p \, \partial s/\partial p|_T}{T \, \partial s/\partial T|_p} - p^2 \left. \frac{\partial v}{\partial p} \Big|_T \right)^{-1}$$
(33)

Derivatives of s can be written in terms of γ as following.

$$p \left. \frac{\partial s}{\partial p} \right|_{T} = -R \Pi \left(\gamma_{\Pi} - \tau \gamma_{\Pi \tau} \right) \tag{34}$$

$$T \left. \frac{\partial s}{\partial T} \right|_{p} = -R \tau^{2} \gamma_{\tau\tau} \tag{35}$$

which lead to the following expression for the speed of sound.

$$w^{2} = RT \left[\frac{\gamma_{\Pi}^{2}}{(\gamma_{\Pi} - \tau \gamma_{\Pi\tau})^{2} / (\tau^{2} \gamma_{\tau\tau}) - \gamma_{\Pi\Pi}} \right]$$
(36)

3 Phase diagram from R6-95 and R10-06

IAPWS R6-95 [3] release provides parametrization for the specific Helmholtz free energy f of water vapor and liquid for wide range of temperature T and mass density ρ . Thermodynamic quantities, such as pressure, internal energy, enthalpy, entropy and heat capacity, can be obtained from derivatives of the Helmholtz free energy. When a system undergoes first-order phase transition between water vapor and liquid, the saturation pressure p_{coex} remains constant while the mass density changes between ρ_{vap} and ρ_{liq} . Such coexisting phase can be determined by applying the Maxwell construction.

$$p_{\text{coex}}(T) = p(\rho_{\text{vap}}, T) = p(\rho_{\text{liq}}, T)$$
 (37)

$$p(\rho, T) = -\frac{\partial f}{\partial v}\Big|_{T} = \rho^2 \frac{\partial f}{\partial \rho}\Big|_{T}$$
(38)

$$f(\rho_{\text{liq}}, T) - f(\rho_{\text{vap}}, T) = p_{\text{coex}} (v_{\text{vap}} - v_{\text{liq}})$$

$$= p_{\text{coex}} \left(\frac{1}{\rho_{\text{vap}}} - \frac{1}{\rho_{\text{liq}}} \right) \quad \text{where specific volume } v = \frac{1}{\rho}.$$
(39)

The specific latent heat h_{latent} , which is amount of heat required to transform unit mass of liquid water into vapor in this case, is given by difference in specific enthalpy or entropy.

$$h_{\text{latent;vap-liq}}(T) = h(\rho_{\text{vap}}, T) - h(\rho_{\text{liq}}, T) = T\left[s(\rho_{\text{vap}}, T) - s(\rho_{\text{liq}}, T)\right]$$
(40)

One can demonstrate that equation (40) is equivalent to what is given by the Clapeyron equation. Let us consider infinitesimally small deviations $\Delta \rho_{\text{vap}}$, $\Delta \rho_{\text{liq}}$ and ΔT in mass densities and temperature, respectively. Then left- and right-hand sides (LHS and RHS) of equation (39) become

LHS =
$$f(\rho_{\text{liq}} + \Delta \rho_{\text{liq}}, T + \Delta T) - f(\rho_{\text{vap}} + \Delta \rho_{\text{vap}}, T + \Delta T)$$

= $f(\rho_{\text{liq}}, T) - f(\rho_{\text{vap}}, T)$
 $+\Delta T \left[\frac{\partial f}{\partial T} \Big|_{\rho} (\rho_{\text{liq}}, T) - \frac{\partial f}{\partial T} \Big|_{\rho} (\rho_{\text{vap}}, T) \right] + \Delta \rho_{\text{liq}} \frac{\partial f}{\partial \rho} \Big|_{T} (\rho_{\text{liq}}, T) - \Delta \rho_{\text{vap}} \frac{\partial f}{\partial \rho} \Big|_{T} (\rho_{\text{vap}}, T)$
= $f(\rho_{\text{liq}}, T) - f(\rho_{\text{vap}}, T) + \Delta T \left[s(\rho_{\text{vap}}, T) - s(\rho_{\text{liq}}, T) \right] - p_{\text{coex}} \left(\frac{\Delta \rho_{\text{vap}}}{\rho_{\text{vap}}^2} - \frac{\Delta \rho_{\text{liq}}}{\rho_{\text{liq}}^2} \right)$ (41)

RHS =
$$p_{\text{coex}} \left(\frac{1}{\rho_{\text{vap}}} - \frac{1}{\rho_{\text{liq}}} \right) + \Delta T \frac{dp_{\text{coex}}}{dT} \left(\frac{1}{\rho_{\text{vap}}} - \frac{1}{\rho_{\text{liq}}} \right) - p_{\text{coex}} \left(\frac{\Delta \rho_{\text{vap}}}{\rho_{\text{vap}}^2} - \frac{\Delta \rho_{\text{liq}}}{\rho_{\text{liq}}^2} \right)$$
 (42)

By equating LHS and RHS, one obtains the Clapeyron equation for the latent heat.

$$h_{\text{latent;vap-liq}}(T) = \left(\frac{1}{\rho_{\text{vap}}} - \frac{1}{\rho_{\text{liq}}}\right) T \frac{dp_{\text{coex}}}{dT}$$
 (43)

Once LibIAPWS library is built, one can run make_tab_IAPWS95.exec executable to obtain the coexistence curve (saturation curve) between water vapor and liquid. It produces a text file tab_coex_IAPWS95.txt which contains the tabulated coexistence curve as functions of temperature.

The phase diagram can be extended to incorporate the ice phase, by implementing IAPWS R10-06 [5] release. The specific Gibbs free energy g is parametrized as function of temperature T and pressure p, and coexistence curve can be obtained from continuity condition of the Gibbs free energy. The specific Gibbs free energy g_{fluid} for fluid (vapor

or liquid) can be obtained from the parametrization in R6-95 release and it must match to g_{ice} provided in R10-06 release

$$g_{\text{ice}}(T, p_{\text{coex}}) = g_{\text{fluid}}(\rho_{\text{fluid}}, T)$$

$$= f_{\text{fluid}}(\rho_{\text{fluid}}, T) + \frac{p_{\text{coex}}}{\rho_{\text{fluid}}}$$
(44)

For given temperature and pressure, mass density ρ_{fluid} of fluid is found by equation (38) and used to compute g_{fluid} . The specific latent heat between fluid and ice can be found in a similar manner as equation (40).

$$h_{\text{latent;fluid-ice}}(T) = h_{\text{fluid}}(\rho_{\text{fluid}}, T) - h_{\text{ice}}(T, p_{\text{coex}}) = T \left[s_{\text{fluid}}(\rho_{\text{fluid}}, T) - s_{\text{ice}}(T, p_{\text{coex}}) \right]$$
(45)

After running make_tab_IAPWS95.exec to tabulate the saturation curve, one can run make_tab_IAPWS06.exec executable to obtain the coexistence curve between water fluid and ice. It produces two text file tab_coex_IAPWS06.txt and tab_melt_IAPWS06.txt tab_coex_IAPWS06.txt provides the coexistence curve (sublimation curve) between water vapor and ice, while tab_melt_IAPWS06.txt contains the coexistence curve (melting curve) between water liquid and ice. The resulting phase diagram on the T-p plane is presented in Figure 1.

H₂O Phase Diagram

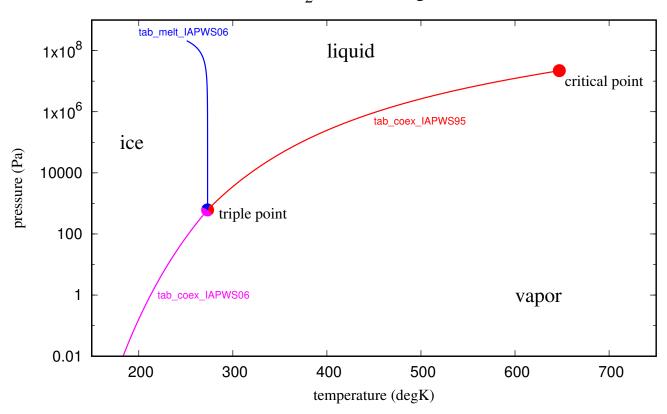


Figure 1: Phase diagram of H₂O derived from IAPWS R6-95 and R10-06 releases.

References

- [1] https://iapws.org
- [2] IAPWS, Revised Release on Surface Tension of Ordinary Water Substance (2014).
- [3] IAPWS, Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use (2018).

- [4] IAPWS, Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam (2012).
- [5] IAPWS, Revised Release on the Equation of State 2006 for H_2O Ice Ih (2009).
- [6] IAPWS, Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance (2008).