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 H_2O. Coexisting phases among water vapor, liquid and ice are also computed and tabulated.

Contents

1 Derivation for thermodynamic quantities

1.1 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.

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

$$p = \left. -\frac{\partial f}{\partial v} \right|_T = \left. \rho^2 \frac{\partial f}{\partial \rho} \right|_T = \rho RT \, \delta \phi_\delta \quad \text{where} \quad \phi_\delta \equiv \frac{\partial \phi}{\partial \delta} \tag{3}$$

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.

$$c_v = \left. \frac{\partial u}{\partial T} \right|_\rho = -R \tau^2 \phi_{\tau\tau} \quad \text{where} \quad \phi_{\tau\tau} = \frac{\partial^2 \phi}{\partial \tau^2} \tag{6}$$

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

$$c_p = \left. \frac{\partial h}{\partial T} \right|_p$$

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

$$= \left. \frac{\partial h}{\partial T} \right|_\rho - \left. \frac{\partial h}{\partial \rho} \right|_T \frac{\partial p / \partial T |_\rho}{\partial p / \partial \rho |_T} \tag{8}$$

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

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

$$\rho \left. \frac{\partial u}{\partial \rho} \right|_T = RT \, \delta \tau \phi_{\delta\tau} \quad \text{where} \quad \phi_{\delta\tau} = \frac{\partial^2 \phi}{\partial \delta \, \partial \tau} \tag{10}$$

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

$$\left. \frac{\partial p}{\partial \rho} \right|_T = RT \left(2 \, \delta \phi_\delta + \delta^2 \phi_{\delta\delta} \right) \quad \text{where} \quad \phi_{\delta\delta} = \frac{\partial^2 \phi}{\partial \delta^2} \tag{12}$$

which lead one to obtain

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

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

$$w^2 = \left. \frac{\partial p}{\partial \rho} \right|_s$$

$$= \lim_{\Delta T, \Delta \rho \to 0} \frac{p(\rho + \Delta \rho, T + \Delta T) - p(\rho, T)}{\Delta \rho} \quad \text{where} \quad \left. \frac{\partial s}{\partial \rho} \right|_T \Delta \rho + \left. \frac{\partial s}{\partial T} \right|_\rho \Delta T = 0 \tag{14}$$

$$= \left. \frac{\partial p}{\partial \rho} \right|_T - \frac{1}{\rho} \left. \frac{\partial p}{\partial T} \right|_\rho \frac{\rho \, \partial s / \partial \rho |_T}{\partial s / \partial T |_\rho} \tag{15}$$

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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.

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

1.2 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 g

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

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.

$$s = -\left.\frac{\partial g}{\partial T}\right|_p = R(\tau\gamma_\tau - \gamma) \quad \text{where} \quad \gamma_\tau \equiv \frac{\partial \gamma}{\partial \tau} \tag{20}$$

$$v = \left.\frac{\partial g}{\partial p}\right|_T = \frac{RT}{p}\Pi\gamma_\Pi \quad \text{where} \quad \gamma_\Pi \equiv \frac{\partial \gamma}{\partial \Pi} \tag{21}$$

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

$$c_p = \left.\frac{\partial h}{\partial T}\right|_p = -R\tau^2\gamma_{\tau\tau} \quad \text{where} \quad \gamma_{\tau\tau} = \frac{\partial^2\gamma}{\partial\tau^2}. \tag{24}$$

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.

$$c_v = \left.\frac{\partial u}{\partial T}\right|_v$$

$$= \lim_{\Delta T, \Delta p \to 0}\frac{u(T+\Delta T, p+\Delta p) - u(T,p)}{\Delta T} \quad \text{where} \quad \left.\frac{\partial v}{\partial T}\right|_p \Delta T + \left.\frac{\partial v}{\partial p}\right|_T \Delta p = 0. \tag{25}$$

$$= \left.\frac{\partial u}{\partial T}\right|_p - \left.\frac{\partial u}{\partial p}\right|_T \frac{\partial v/\partial T|_p}{\partial v/\partial p|_T} \tag{26}$$

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

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

$$p\left.\frac{\partial h}{\partial p}\right|_T = RT\,\Pi\tau\gamma_{\Pi\tau} \quad \text{where} \quad \gamma_{\Pi\tau} = \frac{\partial^2\gamma}{\partial\Pi\,\partial\tau} \tag{28}$$

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

$$p\left.\frac{\partial v}{\partial p}\right|_T = \frac{RT}{p}\Pi^2\gamma_{\Pi\Pi} \quad \text{where} \quad \gamma_{\Pi\Pi} = \frac{\partial^2\gamma}{\partial\Pi^2} \tag{30}$$

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which result in the following expression for c_v.

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

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

$$
\begin{aligned}
w^2 &= \left. \frac{\partial p}{\partial \rho} \right|_s \\
&= -v^2 \left[\lim_{\Delta T, \Delta p \to 0} \frac{v(T + \Delta T, p + \Delta p) - v(T, p)}{\Delta p} \right]^{-1} \quad \text{where} \quad \left. \frac{\partial s}{\partial T} \right|_p \Delta T + \left. \frac{\partial s}{\partial p} \right|_T \Delta p = 0 \quad (32) \\
&= -v^2 \left(\left. \frac{\partial v}{\partial p} \right|_T - \left. \frac{\partial v}{\partial T} \right|_p \frac{\partial s / \partial p|_T}{\partial s / \partial T|_p} \right)^{-1} = (pv)^2 \left(pT \left. \frac{\partial v}{\partial T} \right|_p \frac{p \, \partial s / \partial p|_T}{T \, \partial s / \partial T|_p} - p^2 \left. \frac{\partial v}{\partial p} \right|_T \right)^{-1} \quad (33)
\end{aligned}
$$

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.

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

2 Phase diagram from R6-95 and R10-06

IAPWS R6-95 [2] 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 mass density changes between ρ_{vap} and ρ_{liq}. Such coexisting phase can be determined by applying the Maxwell construction.

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

$$p(\rho, T) = -\left. \frac{\partial f}{\partial v} \right|_T = \rho^2 \left. \frac{\partial f}{\partial \rho} \right|_T \tag{38}$$

$$
\begin{aligned}
f(\rho_{\text{liq}}, T) - f(\rho_{\text{vap}}, T) &= p_{\text{coex}} (v_{\text{vap}} - v_{\text{liq}}) \\
&= p_{\text{coex}} \left(\frac{1}{\rho_{\text{vap}}} - \frac{1}{\rho_{\text{liq}}} \right) \quad \text{where} \quad \text{specific volume } v = \frac{1}{\rho}. \quad (39)
\end{aligned}
$$

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.

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

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

$$
\begin{aligned}
\text{LHS} &= f(\rho_{\text{liq}} + \Delta\rho_{\text{liq}}, T + \Delta T) - f(\rho_{\text{vap}} + \Delta\rho_{\text{vap}}, T + \Delta T) \\
&= f(\rho_{\text{liq}}, T) - f(\rho_{\text{vap}}, T) \\
&\quad + \Delta T \left[\left. \frac{\partial f}{\partial T} \right|_\rho (\rho_{\text{liq}}, T) - \left. \frac{\partial f}{\partial T} \right|_\rho (\rho_{\text{vap}}, T) \right] + \Delta\rho_{\text{liq}} \left. \frac{\partial f}{\partial \rho} \right|_T (\rho_{\text{liq}}, T) - \Delta\rho_{\text{vap}} \left. \frac{\partial f}{\partial \rho} \right|_T (\rho_{\text{vap}}, T) \\
&= f(\rho_{\text{liq}}, T) - f(\rho_{\text{vap}}, T) + \Delta T \left[s(\rho_{\text{vap}}, T) - s(\rho_{\text{liq}}, T) \right] - p_{\text{coex}} \left(\frac{\Delta\rho_{\text{vap}}}{\rho_{\text{vap}}^2} - \frac{\Delta\rho_{\text{liq}}}{\rho_{\text{liq}}^2} \right) \quad (41)
\end{aligned}
$$

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

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

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

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 [3] 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.

$$
\begin{aligned}
g_{\text{ice}}(T, p_{\text{coex}}) &= g_{\text{fluid}}(\rho_{\text{fluid}}, T) \\
&= f_{\text{fluid}}(\rho_{\text{fluid}}, T) + \frac{p_{\text{coex}}}{\rho_{\text{fluid}}}
\end{aligned}
\tag{44}
$$

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).

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

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.

References

[1] https://iapws.org

[2] IAPWS, *Revised Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use* (2018).

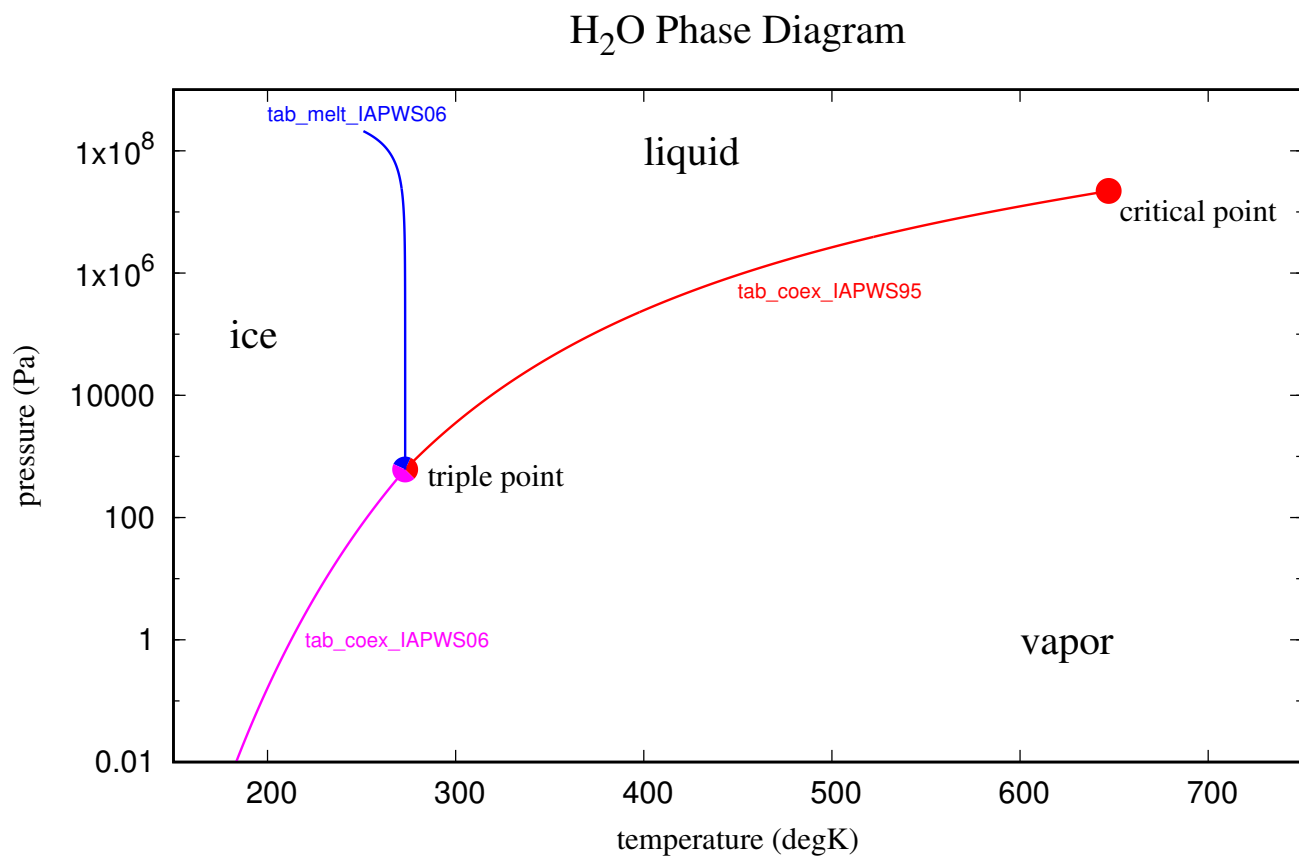[3] IAPWS, *Revised Release on the Equation of State 2006 for H_2O Ice Ih* (2009).

H₂O Phase Diagram

Figure 1: Phase diagram of H$_2$O derived from IAPWS R6-95 and R10-06 releases.