

Analytical description of thermodynamic properties of steam, water and the phase interface for use in CFD

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Abstract. We present a system of analytical equations for computation of all thermodynamic properties of dry steam and liquid water (undersaturated, saturated and metastable supersaturated) and properties of the liquid-vapor phase interface. The form of the equations is such that it enables computation of all thermodynamic properties for independent variables directly related to the balanced quantities - total mass, liquid mass, energy, momenta. This makes it suitable for the solvers of fluid dynamics equations in the conservative form. Thermodynamic properties of dry steam and liquid water are formulated in terms of special thermodynamic potentials and all properties are obtained as analytical derivatives. For the surface tension, the IAPWS formula is used. The interfacial internal energy is derived from the surface tension and it is used in the energy balance. Unlike common models, the present one provides real (contrary to perfect gas approximation) properties of steam and water and reflects the energetic effects due to the surface tension. The equations are based on re-fitting the reference formulation IAPWS-95 and selected experimental data. The mathematical structure of the equations is optimized for fast computation.

1 Introduction

The need of enhancing the efficiency of steam turbines and lowering the costs of experimental development provides a driving force to the improvement of mathematical models of condensing steam flow. All needed thermodynamic properties of condensing steam are described most accurately by the so-called scientific formulation IAPWS-95 [1,2]. This formulation is based on all experimental data available. However, no data were found for the properties of the metastable supersaturated (or subcooled) region. Therefore, the properties of the supersaturated steam are obtained as an extrapolation of the properties in the stable region. It was recognized that IAPWS-95 predicts a gas-to-liquid spinodal somewhat too close to the saturation line. Therefore, the so called “gas equation” [1], essentially a virial equation of state, is recommended for the properties of supersaturated steam. For power cycle computations, the so-called industrial formulation IAPWS-IF97 [3, 4] is recommended. IAPWS-IF97 is based on data generated from IAPWS-95 rather than on the original experimental data. For this reason, IAPWS-IF97 is slightly less accurate than IAPWS-95. The industrial formulation divides the (p, T) diagram into several regions. A separate equation is used for the metastable steam. This equation is based on data generated from the gas equation. Unlike most studies published so far, we consider here thermodynamic effects of the phase interface dividing the

gas and liquid phases. All properties needed will be derived from the IAPWS-adopted surface tension formula [5,6]. This completes the set of relations needed for the computation of thermodynamic properties in a condensing steam flow simulation. However, as we discuss below, neither IAPWS-95 nor IAPWS-IF97 are suitable for computational fluid dynamics (CFD) because their use requires millions of evaluations of lengthy formulas and, even more importantly, iterations are necessary to convert from the original set of variables to the required one. Consequently, most present computations are based on ideal-gas approximation [7,8], although various models including the real gas effects have been proposed in the past [9].

To fix ideas, we assume a finite-volume numerical method. Temporal change of a balanced quantity Y in a volume element i of volume V considered here as a thermodynamic system will depend on the fluxes F from neighboring elements and on its source S inside the element,

$$\frac{dY_i}{dt} = \sum_{j \neq i} F_{ji}(z_i, z_j) + S_i(z_i). \quad (1)$$

The balanced quantities are:

- m , the total mass of the system,
- m_L , the mass of the condensate in the system,
- E , the total energy of the system,

E_L , the part of energy contained in the condensate,
 U_S , the part of internal energy contained in the phase interface (since zero mass is assumed for the phase interface, it does not carry any kinetic energy),
 I_x, I_y, I_z , components of the vector of momentum accumulated in the volume element. The fluxes and sources depend on other thermodynamic properties z : temperature (for heat fluxes), pressure (for momentum fluxes), droplet radius (for interphase mass and energy fluxes). Thermodynamic equations are needed to obtain the quantities z needed for fluxes and sources from the balanced quantities Y . The subject of this study is development of thermodynamic equations which would be complete, accurate and at the same time allow a fast evaluation as necessary in CFD, in particular avoiding iterations. We assume here that all droplets have the same radius and the same temperature. The temperature of the liquid phase may differ from the temperature of the gas phase. The temperature of the phase interface is assumed to lay between the liquid and gas temperatures,

$$T_S = (1-g)T_L + gT_G, \quad 0 \leq g \leq 1. \quad (2)$$

Typically, the phase interface can be assumed to be at the temperature of the liquid phase ($g = 0$), because the heat transport inside the droplet is more efficient than the heat transport in the gaseous neighborhood. Droplets are assumed to move at the same velocity as the gas phase. Including a distribution of droplet sizes, temperatures, and velocities is possible at the price of increasing the number of conserved quantities.

2 Phase interface

Usually, the only property of the phase interface considered is the surface (or interfacial) tension σ . It is known to be a property entering the nucleation rate computation. However, when the liquid phase is dispersed in a form of very small droplets, the liquid-vapor interfacial area can be large enough such that the phase interface contributes significantly to the energy balance. To derive a formula allowing to compute the internal energy of the phase interface, we first realize, that the surface tension expresses the interfacial excess of the grand potential of a system containing a phase interface with respect of a grand potential of a hypothetical system containing only the homogeneous phases. Consequently, the following equation can be derived

$$\sigma = u_S - \mu n_S - T s_S. \quad (3)$$

Equation (3) relates the surface tension to the interfacial (excess) internal energy u_S per unit of interfacial area (J m^{-2}), μ is the chemical potential (J kmol^{-1}), n_S is the interfacial (excess) number of moles (kmol m^{-2}), T is thermodynamic temperature (K), and s_S is the interfacial (excess) entropy per unit of interfacial area ($\text{J K}^{-1} \text{m}^{-2}$). To derive the formula for the interfacial internal energy, we

assume in this section that temperature and chemical potential are homogeneous throughout the two-phase system. The interfacial internal energy obtained in this way can also be used in case these conditions are not satisfied as is the case of a non-equilibrium condensation process. Besides the Euler-type equation (3), the so-called Gibbs adsorption equation can be derived for the phase interface

$$d\sigma = -n_S d\mu - s_S dT. \quad (4)$$

The pressure p_L inside the droplet of radius r is related to the pressure of the gas phase p_G by the Laplace equation

$$\Delta p = p_L - p_G = \frac{2\sigma}{r}. \quad (5)$$

Gibbs adsorption equation (4) is an analogue to the Gibbs-Duhem equation valid for each homogeneous phase,

$$dp_L = n_L d\mu + \eta_L dT, \quad (6)$$

$$dp_G = n_G d\mu + \eta_G dT. \quad (7)$$

Here, $n_{L/G}$ is the molar density of the homogeneous liquid/gas phase (kmol m^{-3}), and $\eta_{L/G}$ is the entropy density of the homogeneous liquid/gas phase ($\text{J K}^{-1} \text{m}^{-3}$). From equations (4) to (7) we derive for an isothermal change

$$\frac{d\sigma}{d\Delta p} = -\frac{n_S}{n_L - n_G}. \quad (8)$$

Equation (8) relates the change of the surface tension due to the change of the droplet radius to the interfacial excess number of moles. The ratio on the right-hand side is related to the Tolman length and it is very small (of the order of 10^{-11} m). Consequently, the interfacial excess number of moles can be neglected when considering droplets outside the nucleation range, say $r > 5$ nm. This fact greatly simplifies the surface thermodynamics. The surface tension can be considered as function of temperature only. From equation (4) we obtain the interfacial entropy as a derivative of the surface tension

$$s_S = -\frac{d\sigma}{dT} \quad (9)$$

and from equation (3) we obtain the interfacial internal energy

$$u_S = \sigma + T s_S = \sigma - T \frac{d\sigma}{dT}. \quad (10)$$

Surface tension of water is accurately represented by equation [6]

$$\sigma = B\tau^\mu (1 + b\tau), \quad (11)$$

where $\tau \equiv 1 - T/T_*$, $T_* = 647.096$ K is the critical temperature, $\mu = 1.256$ is an universal critical exponent, and $B = 235.8$ mN/m and $b = -0.625$ are fitted parameters. Using equation (9) we obtain the interfacial entropy from the surface tension as given by equation (11),

$$s_s = \frac{B}{T_c} \left[\mu \tau^{\mu-1} + b(\mu+1)\tau^\mu \right], \quad (12)$$

and further using equation (10) we obtain the interfacial internal energy as

$$u_s = B \left[\mu \tau^{\mu-1} + (1+b+b\mu-\mu)\tau^\mu - b\mu\tau^{\mu+1} \right]. \quad (13)$$

The interfacial entropy as given by equation (12) is shown in figure 1 and the interfacial internal energy together with the surface tension are shown in figure 2.

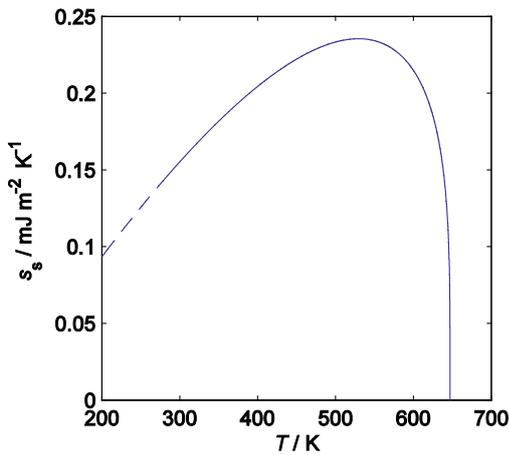


Figure 1. Interfacial entropy for water as given by equation (12)

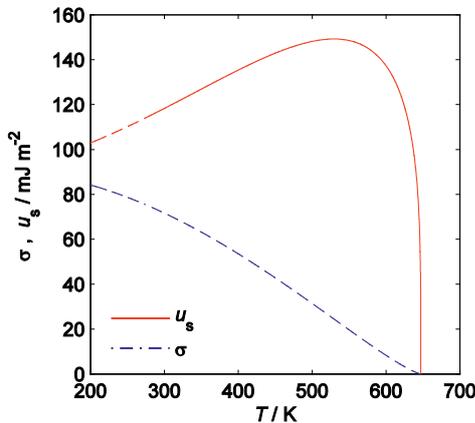


Figure 2. Surface tension σ of ordinary water as given by equation (11) and interfacial internal energy u_s as given by equation (13). Values below the triple point temperature 273.16 K are extrapolated.

3 Dry steam

Metastable supersaturated (or subcooled) steam is the continuous phase in the two-phase mixture of condensing steam. Desired independent variables for the evaluation

of thermodynamic properties of dry steam are gas-phase density ρ_G and specific internal energy of the gas phase u_G . The properties to be computed are primarily the pressure p_G and temperature T_G of the gas phase, needed for the computation of momentum and energy fluxes. Other properties which might be needed in CFD are soundspeed, thermal capacities and various other derivative properties. If these properties are programmed as separate tables or, say, polynomial fits, they will not satisfy thermodynamic relations. A clean way of representing thermodynamic properties for the desired set of independent variables is expressing them on the basis of a single function – entropy $s_G(\rho_G, u_G)$. This approach was suggested by the present authors earlier [10] and just a short overview is given here. For n reversible process, the change of entropy can be expressed as

$$ds = \frac{1}{T} du - \frac{p}{T\rho^2} d\rho. \quad (14)$$

Consequently, temperature and pressure can be expressed using derivatives of the entropy function with respect to internal energy and density,

$$T = \left(\frac{\partial s}{\partial u} \right)_\rho^{-1}, \quad p = -T\rho^2 \left(\frac{\partial s}{\partial \rho} \right)_u. \quad (15)$$

All other thermodynamic properties can also be expressed from the entropy function. The entropy function comprises the ideal-gas part and the residual part,

$$\eta(\psi, \delta) = \eta^I(\psi) - \ln \delta + \eta^R(\psi, \delta) + \ln \frac{\rho_{\text{ref}}}{\rho_*}, \quad (16)$$

where $\eta = s_G/R$ is dimensionless entropy, the R is the specific gas constant, $\delta = \rho_G/\rho_*$ is dimensionless density, ρ_* is a scaling density, $\psi = u_G/(RT_*)$ is dimensionless internal energy and T_* is a scaling temperature. The reference state is chosen such that $\rho_{\text{ref}} = \rho_*$ so that the last term in (16) vanishes. To obtain an efficient fit, we further transform the dimensionless internal energy to variables $x = (\psi - \beta_1)^{-1}$ and $\xi = \beta_2 - x$, where β_1, β_2 are empirical parameters. The ideal gas part is represented as a polynomial

$$\eta^I = \sum_{i=1}^{10} c_i \xi^{i-1}. \quad (17)$$

The residual part is obtained in a form analogous to the virial equation of state, however with coefficients depending on the internal energy rather than temperature:

$$\eta^R(\xi, \delta) = - \sum_{i \geq 1} \frac{a_i(\xi)}{i} \delta^i \quad (18)$$

The dependence of the coefficients on the internal energy parameter x is expressed as a polynomial function

$$a_i(\xi) = \sum_{j \geq 1} b_{ij} \xi^{kj} . \quad (19)$$

4 Condensate

As condensate we denote the liquid water phase at conditions close to the saturation. In the steam turbine, the condensate is dispersed in the form of fine primary droplets ranging approximately between 1 nm and 500 nm in diameter, and larger secondary droplets ranging from about 1 μm to 50 μm in diameter which formed by atomization of the liquid films formed on turbine blades and other internal surfaces. The fact that the droplets within a volume element have various history means that also their radii and temperatures differ. For an accurate representation of the condensate in a CFD code, it is necessary to consider various classes of droplets. This is a complicated problem and we do not want to enter it here. Instead, we assume that all droplets have the same temperature T_L and radius r . As it will be shown in Section 5, for an iteration-free computation, the suitable set of independent variables are the specific internal energy of the liquid phase u_L and the liquid phase pressure p_L . We attempt to model the properties of the condensate in a thermodynamically consistent manner based on a thermodynamic potential. Unfortunately, it does not seem possible to find a thermodynamic potential with pressure and internal energy as natural variables. This problem can be circumvented by defining an unusual thermodynamic potential

$$\zeta = \frac{s_L}{R} - \frac{pv_L}{RT_L} , \quad (20)$$

where s_L is the specific entropy of the liquid phase and v_L is its specific volume. From definition (20) and equation (14) it follows for a differential of potential ζ

$$d\zeta = t d\Psi - \phi d\theta , \quad (21)$$

where the natural variables are the dimensionless internal energy $\Psi = u_L / (RT_*)$ and a dimensionless ratio of pressure and temperature $\theta = p_L / (T_L \rho_* R)$. The coefficients in equation (21) have the meaning of

$$t = \frac{T_*}{T_L} = \left(\frac{\partial \zeta}{\partial \Psi} \right)_\theta \quad (22)$$

and dimensionless volume

$$\phi = \rho_* v_L = - \left(\frac{\partial \zeta}{\partial \theta} \right)_\Psi . \quad (23)$$

Because the thermodynamic state of the condensate is not very far from the saturation boundary, it appears

sufficient to consider a linear dependence on parameter θ in the form

$$\zeta(\Psi, \theta) = \zeta_0(\Psi) - \phi_{\text{sat}}(\Psi) \theta , \quad (24)$$

where $\phi_{\text{sat}}(\Psi)$ is the value of parameter ϕ for saturated liquid of given dimensionless internal energy Ψ . Further, $\zeta_0(\Psi)$ is the value of potential ζ extrapolated to zero pressure at given dimensionless internal energy Ψ which is found as

$$\zeta_0(\Psi) = \zeta_{\text{sat}}(\Psi) + \phi_{\text{sat}}(\Psi) \theta_{\text{sat}}(\Psi) , \quad (25)$$

where $\zeta_{\text{sat}}(\Psi)$ and $\theta_{\text{sat}}(\Psi)$, respectively, are the value of potential ζ and dimensionless pressure-to-temperature ratio θ for saturated liquid of given dimensionless internal energy Ψ . Data for functions $\zeta_{\text{sat}}(\Psi)$, $\phi_{\text{sat}}(\Psi)$ and $\theta_{\text{sat}}(\Psi)$ were generated from the IAPWS-95 formulation of thermodynamic properties of ordinary water. For the present purposes, the functions $\zeta_0(\Psi)$ and $\phi_{\text{sat}}(\Psi)$ were represented in a form of tables and they are shown in Figure 3 and Figure 4, respectively.

Temperature is obtained from the linear model given by equation (24) as

$$T_L = \frac{T_*}{\zeta'_0} + \frac{\phi'_{\text{sat}}}{\zeta'_0 \rho_* R} p_L \quad (26)$$

the prime denotes a derivative with respect to dimensionless internal energy Ψ . The specific volume obtained from the linear model (24) is independent of pressure,

$$v_L = \phi_{\text{sat}}(\Psi) / \rho_* . \quad (27)$$

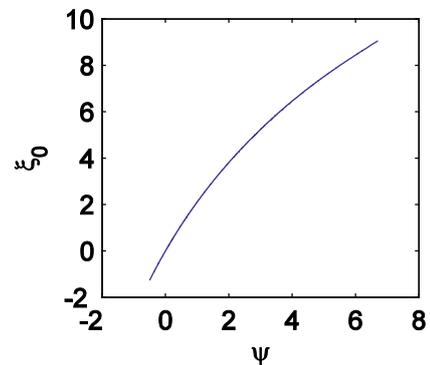


Figure 3. Function $\zeta_0(\Psi)$ given by equation (25) evaluated from the IAPWS-95 formulation [1,2].

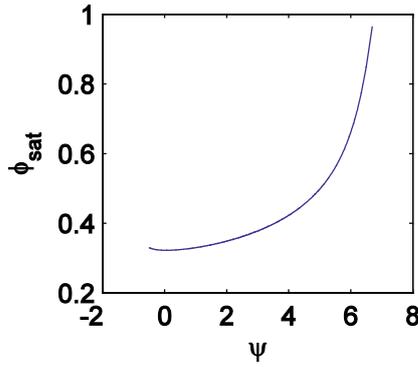


Figure 4. Function $\phi_{\text{sat}}(\Psi)$ evaluated from the IAPWS-95 formulation [1,2].

5 Solution of the complete model

In this section we combine the models of gas and liquid phases and the model of the phase interface to provide a complete mathematical model which can be solved iteration-free to obtain quantities z needed for evaluation of the fluxes and sources for given values of the balanced quantities Y .

First, we obtain components of the flow velocity c_x, c_y, c_z and its magnitude c ,

$$c_k = \frac{I_k}{m}, \quad c^2 = \sum c_k^2, \quad k = x, y, z. \quad (28)$$

Further we obtain total internal energy and the internal energy for the liquid phase, internal energies for the liquid and gas phases

$$U = E - \frac{1}{2}mc^2, \quad U_L = E_L - \frac{1}{2}m_Lc^2. \quad (29)$$

The internal energy of the gas phase is given as a complement

$$u_G = \frac{U - U_L - U_S}{m - m_L}. \quad (30)$$

We determine the dimensionless liquid internal energy

$$\Psi = \frac{U_L}{m_L RT_*}. \quad (31)$$

For the linear model (25), we obtain the specific volume of the liquid from equation (27) and the volume of the liquid phase

$$V_L = m_L v_L. \quad (32)$$

Then, because the phase interface in the Gibbsian representation does not occupy any volume, we obtain the density of the gas phase as

$$\rho_G = \frac{m - m_L}{V - V_L}. \quad (33)$$

For a known density and specific internal energy of the gas phase, it is possible to determine the temperature T_G and the pressure p_G of the gas phase using equation (15).

The remaining part of the solution is less straightforward. The volume of the liquid is related to the number of droplets n and to the radius r of the droplets as

$$V_L = n \frac{4}{3} \pi r^3. \quad (34)$$

The internal energy of the phase interface is given as

$$U_S = n 4 \pi r^2 u_S(T_S). \quad (35)$$

The left-hand sides of equations (34) and (35) are known. To be determined are the number of droplets n , droplet radius r , and the characteristic temperature of the phase interface T_S emerging as an unknown argument of the interfacial energy given by equation (13). T_S is related by equation (2) to the already known gas temperature T_G and unknown temperature of the liquid T_L which, in turn, is related via equation (26) to the already known dimensionless liquid internal energy Ψ and unknown liquid pressure p_L . The system of equations is closed by the Laplace equation (5), containing the surface tension σ depending again on the interfacial temperature by equation (11). Combining all the mentioned equations together, a cubic equation is obtained:

$$b\tau^3 - (M + Qb - Pb)\tau^2 - (1 + Q + PM)\tau - P = 0, \quad (36)$$

where

$$M = \frac{1+b}{\mu} + b - 1, \quad (37)$$

$$P = \frac{(1-g)}{\zeta'_0} \left[\frac{p_G \phi'_{\text{sat}}}{p_*} + 1 \right] - 1, \quad (38)$$

$$Q = \frac{2(1-g)U_S \phi'_{\text{sat}}}{3\mu p_* V_L \zeta'_0}, \quad (39)$$

and a scaling pressure is defined as $p_* = RT_* \rho_*$. For the physically relevant root of equation (36) we find the characteristic interfacial temperature

$$T_S = (1 - \tau)T_*, \quad (40)$$

the temperature of the liquid phase using equation (2)

$$T_L = \frac{T_S - gT_G}{1 - g}, \quad (41)$$

and pressure of the liquid phase using equation (26)

$$p_L = \left(\frac{T_L}{T_*} \zeta'_0 - 1 \right) \frac{p_*}{\phi'_{\text{sat}}}, \quad (42)$$

the surface tension (11) and interfacial internal energy (13). Droplet radius can be obtained either by combining equations (34) and (35), as

$$r = \frac{3V_L u_S}{U_S} \quad (43)$$

or, providing a possible check, from the Laplace equation (5)

$$r = \frac{2\sigma}{p_L - p_G}. \quad (44)$$

The number of droplets can be obtained either from equation (34) or from equation (35).

Conclusions

In this study, a complete set of relations is developed describing thermodynamic properties of the gas and liquid phases of condensing steam as well as the contribution of the phase interface. The model assumes that separate balance equations are written for the total energy of the liquid phase and for the internal energy of the phase interface. The set of equations can be solved without iterations, which is an important advantage over the existing accurate formulations such as IAPWS-95 or IAPWS-IF97. The model is developed for the case of monodispersed droplets. A generalization in the form of histogram or by method of moments is possible. In this study we only focused on thermodynamic properties. Kinetic properties needed for evaluation of the fluxes and sources were not considered here. However, because temperature, pressure, and density are known as the result of the present computation, the kinetic properties can be determined relatively easily using standard property formulations.

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