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Partial derivatives of thermodynamic state properties for dynamic simulation

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The thermodynamic behaviour of fluids can be accurately described by equations of state (EoS) in terms of the Helmholtz energy, with temperature and density as independent variables. The known properties in dynamic simulations of power or refrigeration cycles are usually different from temperature and density. Partial derivatives of state properties with respect to the known properties of the simulation have to be transformed into partial derivatives with respect to the independent variables of the EoS. This transformation is demonstrated step by step for the single-phase region, along the saturation line and within the two-phase region.

1 Introduction

For the simulation and design of thermodynamic systems like power or refrigeration cycles, accurate properties of the working fluid are indispensable. For a wide variety of working fluids, accurate equations of state (EoS) are available that have been set up in terms of Helmholtz energy. From such EoS all thermodynamic state properties, like pressure p or specific entropy s , as well as all partial derivatives of thermodynamic state properties, can be calculated by means of partial differentiation.

The independent variables of the Helmholtz energy EoS are temperature and density (T, ρ), but the thermodynamic state can also be defined by specifying any other combination of two independent state properties. In fluid cycle simulations, the known variables are usually pressure and specific enthalpy (p, h), pressure and temperature (p, T) or pressure and specific entropy (p, s) (see, e. g., Wagner et al., 2000, Table 1).

In dynamic simulations, the equations for energy, mass

and momentum balance of a control volume are written in terms of derivatives with respect to time t . The mass balance, for example, contains the derivative of density with respect to time. If the properties pressure and specific enthalpy (and their development over time) are known, the derivative of density can be rewritten as

$$\frac{d\rho}{dt} = \left(\frac{\partial\rho}{\partial p}\right)_h \frac{dp}{dt} + \left(\frac{\partial\rho}{\partial h}\right)_p \frac{dh}{dt}$$

using the chain rule. To do so, the partial derivatives with respect to the known variables of the simulation are needed, in this case the partial derivatives of density with respect to pressure and enthalpy. The time derivatives of other properties, like specific internal energy u , can be rewritten in the same way. For a more detailed discussion of control volume balance equations in the context of object-oriented dynamic simulation of thermodynamic systems see, e. g., Bauer, 1999, Tummescheit, 2002 or Richter, 2008.

Other partial derivatives are also frequently used in engineering applications, e. g., volume expansivity β or isothermal compressibility κ . Also, partial derivatives may be used in iterative procedures like the Newton-Raphson root finding algorithm. Typical examples of such iterative procedures include vapour-liquid equilibrium calculations or flash calculations, like pT -flash. Higher order partial derivatives may be used for stability analysis and for extrapolation or Taylor series.

The following text demonstrates, for pure fluids, how arbitrary partial derivatives can be transformed into partial derivatives with respect to the independent variables of the EoS in the single-phase region, along the saturation boundary, and within the two-phase region.

2 Helmholtz energy equation of state

According to Gibbs, 1873, all thermodynamic properties of a fluid phase can be calculated from a single fundamental

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Table 1: Thermodynamic state properties

Property	Formulation
Pressure p	$p = \varrho TR [1 + \delta \alpha_{\delta}^r]$
Specific entropy s	$s = R [\tau(\alpha_{\tau}^0 + \alpha_{\tau}^r) - (\alpha^0 + \alpha^r)]$
Specific internal energy u	$u = TR [\tau(\alpha_{\tau}^0 + \alpha_{\tau}^r)]$
Specific enthalpy h	$h = TR [(1 + \delta \alpha_{\delta}^r) + \tau(\alpha_{\tau}^0 + \alpha_{\tau}^r)]$
Specific Gibbs-energy g	$g = TR [(1 + \delta \alpha_{\delta}^r) + (\alpha^0 + \alpha^r)]$
$\alpha_{\tau}^0 = \left(\frac{\partial \alpha^0}{\partial \tau} \right)_{\delta}, \quad \alpha_{\tau}^r = \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta}, \quad \alpha_{\delta}^r = \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau}$	

equation of state. Such an equation can be constructed with different pairs of independent properties and their proper characteristic functions (see, e. g., Baehr, 1998, in German). Out of the possible functions, only two are usually used in practical applications: Gibbs energy as a function of pressure p and temperature T or Helmholtz energy as a function of temperature T and specific volume v or density ϱ . Even though predictive equations of state based on theoretical considerations have been developed, empirical multiparameter equations of state will today still yield better accuracy for fluids where comprehensive experimental data are available. The following part of this section refers to a certain type of empirical multiparameter EoS in terms of the Helmholtz energy as described, e. g., in the overview article by Span et al., 2001.

In this work, the independent properties of the EoS, temperature T and density ϱ , are made dimensionless using their critical values. The Helmholtz energy f is made dimensionless by dividing it by the specific gas constant R and the temperature T . The dimensionless Helmholtz energy α is split up into an ideal gas contribution α^0 and a residual contribution α^r .

$$\tau = \frac{T_c}{T}, \quad \delta = \frac{v_c}{v} = \frac{\varrho}{\varrho_c}, \quad \alpha = \frac{f}{RT} = \alpha^0 + \alpha^r$$

The functional form for $\alpha^0 = \alpha^0(\tau, \delta)$ and the functional form for $\alpha^r = \alpha^r(\tau, \delta)$ are then developed independently. Details on the functional form, the bank of terms and the fitting of the parameters to experimental data are given by, e. g., Span, 2000, Wagner and Pruß, 2002 section 5.4, or Lemmon and Jacobsen, 2005.

Once the functional form and values for the parameters are known, all state properties can be calculated as simple combinations of the partial derivatives of the Helmholtz energy. Formulations are given in the literature (see, e. g., Baehr and Tillner-Roth, 1995; Lemmon et al., 2000; Span, 2000); an extract is shown in Table 1.

The partial derivatives of the state properties with re-

Table 2: Partial derivatives w. r. t. density and temperature

Property	Formulation
$\left(\frac{\partial p}{\partial \varrho} \right)_T$	$TR [1 + 2\delta \alpha_{\delta}^r + \delta^2 \alpha_{\delta\delta}^r]$
$\left(\frac{\partial p}{\partial T} \right)_{\varrho}$	$\varrho R [1 + \delta \alpha_{\delta}^r - \tau \delta \alpha_{\tau\delta}^r]$
$\left(\frac{\partial s}{\partial \varrho} \right)_T$	$\frac{R}{\varrho} [-(1 + \delta \alpha_{\delta}^r - \tau \delta \alpha_{\tau\delta}^r)]$
$\left(\frac{\partial s}{\partial T} \right)_{\varrho}$	$\frac{R}{T} [-\tau^2 (\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r)]$
$\left(\frac{\partial u}{\partial \varrho} \right)_T$	$\frac{TR}{\varrho} [\tau \delta \alpha_{\tau\delta}^r]$
$\left(\frac{\partial u}{\partial T} \right)_{\varrho}$	$R [-\tau^2 (\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r)]$
$\left(\frac{\partial h}{\partial \varrho} \right)_T$	$\frac{TR}{\varrho} [\tau \delta \alpha_{\tau\delta}^r + \delta \alpha_{\delta}^r + \delta^2 \alpha_{\delta\delta}^r]$
$\left(\frac{\partial h}{\partial T} \right)_{\varrho}$	$R [-\tau^2 (\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r) + (1 + \delta \alpha_{\delta}^r - \tau \delta \alpha_{\tau\delta}^r)]$
$\left(\frac{\partial g}{\partial \varrho} \right)_T$	$\frac{TR}{\varrho} [1 + 2\delta \alpha_{\delta}^r + \delta^2 \alpha_{\delta\delta}^r]$
$\left(\frac{\partial g}{\partial T} \right)_{\varrho}$	$R [-\tau(\alpha_{\tau}^0 + \alpha_{\tau}^r) + (\alpha^0 + \alpha^r) + (1 + \delta \alpha_{\delta}^r - \tau \delta \alpha_{\tau\delta}^r)]$
$\alpha_{\tau\tau}^0 = \left(\frac{\partial^2 \alpha^0}{\partial \tau^2} \right)_{\delta}, \quad \alpha_{\tau\tau}^r = \left(\frac{\partial^2 \alpha^r}{\partial \tau^2} \right)_{\delta}, \quad \alpha_{\delta\delta}^r = \left(\frac{\partial^2 \alpha^r}{\partial \delta^2} \right)_{\tau}, \quad \alpha_{\tau\delta}^r = \left(\frac{\partial^2 \alpha^r}{\partial \tau \partial \delta} \right)$	

spect to *temperature* and *density* in the single-phase region can also be calculated directly, because temperature and density (or their dimensionless counterparts) are the independent variables of the Helmholtz energy equation of state. Formulations for the calculation of the partial derivatives with respect to temperature and density are given in Tables 2 and 3.

3 Partial derivatives in the single-phase region

Partial derivatives with respect to variables other than the independent variables of the equation of state cannot be calculated directly. This is the case for some commonly used derived properties, examples for such derived properties are given in Table 4. These derived properties have to be transformed into partial derivatives with respect to different, more favourable properties. This transformation can be carried out using various methods.

One method is the use of tables by Bridgman, 1914.

Table 3: Second order partial derivatives

Property	Formulation
$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_T$	$= \frac{TR}{\rho} [2\delta\alpha_\delta^r + 4\delta^2\alpha_{\delta\delta}^r + \delta^3\alpha_{\delta\delta\delta}^r]$
$\left(\frac{\partial^2 p}{\partial T^2}\right)_\rho$	$= \frac{\rho R}{T} [\tau^2\delta\alpha_{\tau\tau\delta}^r]$
$\left(\frac{\partial^2 p}{\partial \rho \partial T}\right)$	$= R [1 + 2\delta\alpha_\delta^r + \delta^2\alpha_{\delta\delta}^r - 2\tau\delta\alpha_{\tau\delta}^r - \tau\delta^2\alpha_{\tau\delta\delta}^r]$
$\left(\frac{\partial^2 s}{\partial \rho^2}\right)_T$	$= \frac{R}{\rho^2} [1 - \delta^2\alpha_{\delta\delta}^r + \tau\delta^2\alpha_{\tau\delta\delta}^r]$
$\left(\frac{\partial^2 s}{\partial T^2}\right)_\rho$	$= \frac{R}{T^2} [\tau^3(\alpha_{\tau\tau\tau}^0 + \alpha_{\tau\tau\tau}^r) + 3\tau^2(\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r)]$
$\left(\frac{\partial^2 s}{\partial \rho \partial T}\right)$	$= \frac{R}{T\rho} [-\tau^2\delta\alpha_{\tau\tau\delta}^r]$
$\left(\frac{\partial^2 u}{\partial \rho^2}\right)_T$	$= \frac{TR}{\rho^2} [\tau\delta^2\alpha_{\tau\delta\delta}^r]$
$\left(\frac{\partial^2 u}{\partial T^2}\right)_\rho$	$= \frac{R}{T} [\tau^3(\alpha_{\tau\tau\tau}^0 + \alpha_{\tau\tau\tau}^r) + 2\tau^2(\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r)]$
$\left(\frac{\partial^2 u}{\partial \rho \partial T}\right)$	$= \frac{R}{\rho} [-\tau^2\delta\alpha_{\tau\tau\delta}^r]$
$\left(\frac{\partial^2 h}{\partial \rho^2}\right)_T$	$= \frac{TR}{\rho^2} [\tau\delta^2\alpha_{\tau\delta\delta}^r + 2\delta^2\alpha_{\delta\delta}^r + \delta^3\alpha_{\delta\delta\delta}^r]$
$\left(\frac{\partial^2 h}{\partial T^2}\right)_\rho$	$= \frac{R}{T} [\tau^3(\alpha_{\tau\tau\tau}^0 + \alpha_{\tau\tau\tau}^r) + 2\tau^2(\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r) + \tau^2\delta\alpha_{\tau\tau\delta}^r]$
$\left(\frac{\partial^2 h}{\partial \rho \partial T}\right)$	$= \frac{R}{\rho} [\delta^2\alpha_{\delta\delta}^r - \tau^2\delta\alpha_{\tau\tau\delta}^r + \delta\alpha_\delta^r - \tau\delta^2\alpha_{\tau\delta\delta}^r - \tau\delta\alpha_{\tau\delta}^r]$
$\left(\frac{\partial^2 g}{\partial \rho^2}\right)_T$	$= \frac{TR}{\rho^2} [-1 + 3\delta^2\alpha_{\delta\delta}^r + \delta^3\alpha_{\delta\delta\delta}^r]$
$\left(\frac{\partial^2 g}{\partial T^2}\right)_\rho$	$= \frac{R}{T} [\tau^2(\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r) + \tau^2\delta\alpha_{\tau\tau\delta}^r]$
$\left(\frac{\partial^2 g}{\partial \rho \partial T}\right)$	$= \frac{R}{\rho} [1 + 2\delta\alpha_\delta^r - 2\tau\delta\alpha_{\tau\delta}^r + \delta^2\alpha_{\delta\delta}^r - \tau\delta^2\alpha_{\tau\delta\delta}^r]$

$$\alpha_{\tau\tau\tau}^0 = \left(\frac{\partial^3 \alpha^0}{\partial \tau^3}\right)_\delta, \alpha_{\tau\tau\tau}^r = \left(\frac{\partial^3 \alpha^r}{\partial \tau^3}\right)_\delta, \alpha_{\tau\tau\delta}^r = \left(\frac{\partial^3 \alpha^r}{\partial \tau^2 \partial \delta}\right), \alpha_{\tau\delta\delta}^r = \left(\frac{\partial^3 \alpha^r}{\partial \tau \partial \delta^2}\right), \alpha_{\delta\delta\delta}^r = \left(\frac{\partial^3 \alpha^r}{\partial \delta^3}\right)_\tau$$

These tables contain formulations that allow the expression of any first order partial derivative as a combination of c_p , β and κ . These properties were chosen because they are accessible for experimental measurement, but different base sets of three first order partial derivatives are also possible. When all properties are calculated from an EoS, a convenient base set would consist of derivatives with respect to the independent variables of the EoS, e. g., $(\partial p/\partial T)_\rho$, $(\partial p/\partial \rho)_T$ and $(\partial u/\partial T)_\rho$ in case of the Helmholtz en-

Table 4: Derived properties for engineering applications

Property	Definition
Isochoric heat capacity c_v	$T \left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v$
Isothermal compressibility κ	$-\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p}\right)_T$
Isothermal throttling coeff. δ_T	$\left(\frac{\partial h}{\partial p}\right)_T$
Volume expansivity β	$\frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_p$
Isobaric heat capacity c_p	$T \left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p$
Speed of sound w	$\sqrt{\left(\frac{\partial p}{\partial \rho}\right)_s}$
Joule-Thomson coefficient μ	$\left(\frac{\partial T}{\partial p}\right)_h$

ergy EoS. Second order partial derivatives can be reduced to a base set of four second order partial derivatives.

Another method for partial derivative transformation is to express the partial derivative as a Jacobian matrix (also referred to as functional determinant) and manipulate it using the rules for Jacobian matrix transformations as described in the literature (see, e. g., Shaw, 1935; Crawford, 1949a; Hakala, 1964; Carroll, 1965; Somerton and Arnas, 1985). These rules are not repeated here in detail, only the resulting mathematical relations are given that are useful for the transformation of partial derivatives:

$$\left(\frac{\partial x}{\partial b}\right)_y = \left(\frac{\partial b}{\partial x}\right)_y^{-1} \quad (\text{Reciprocity})$$

$$\left(\frac{\partial a}{\partial b}\right)_x = \left(\frac{\partial a}{\partial y}\right)_x \left(\frac{\partial b}{\partial y}\right)_x^{-1} \quad (\text{Chain rule})$$

$$\left(\frac{\partial x}{\partial y}\right)_c = -\left(\frac{\partial c}{\partial y}\right)_x \left(\frac{\partial c}{\partial x}\right)_y^{-1} \quad (\text{Triple product rule}).$$

Combinations are also possible:

$$\left(\frac{\partial a}{\partial x}\right)_c = \left(\frac{\partial a}{\partial x}\right)_y - \left(\frac{\partial a}{\partial y}\right)_x \left(\frac{\partial c}{\partial x}\right)_y \left(\frac{\partial c}{\partial y}\right)_x^{-1}$$

and finally

$$\left(\frac{\partial a}{\partial b}\right)_c = \frac{\left(\frac{\partial a}{\partial x}\right)_y \left(\frac{\partial c}{\partial y}\right)_x - \left(\frac{\partial a}{\partial y}\right)_x \left(\frac{\partial c}{\partial x}\right)_y}{\left(\frac{\partial b}{\partial x}\right)_y \left(\frac{\partial c}{\partial y}\right)_x - \left(\frac{\partial b}{\partial y}\right)_x \left(\frac{\partial c}{\partial x}\right)_y}$$

Table 5: Transformation of partial derivatives

Definition	Transformation
$\left(\frac{\partial u}{\partial T}\right)_v$	$\left(\frac{\partial u}{\partial T}\right)_\rho$
$\left(\frac{\partial \rho}{\partial p}\right)_T$	$\left(\frac{\partial p}{\partial \rho}\right)_T^{-1}$
$\left(\frac{\partial h}{\partial p}\right)_T$	$\left(\frac{\partial h}{\partial \rho}\right)_T \left(\frac{\partial p}{\partial \rho}\right)_T^{-1}$
$\left(\frac{\partial \rho}{\partial T}\right)_p$	$-\left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial p}{\partial \rho}\right)_T^{-1}$
$\left(\frac{\partial h}{\partial T}\right)_p$	$\left(\frac{\partial h}{\partial T}\right)_\rho - \left(\frac{\partial h}{\partial \rho}\right)_T \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial p}{\partial \rho}\right)_T^{-1}$
$\left(\frac{\partial p}{\partial \rho}\right)_s$	$\left(\frac{\partial p}{\partial \rho}\right)_T - \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial s}{\partial \rho}\right)_T \left(\frac{\partial s}{\partial T}\right)_\rho^{-1}$
$\left(\frac{\partial T}{\partial p}\right)_h$	$\left[\left(\frac{\partial p}{\partial T}\right)_\rho - \left(\frac{\partial p}{\partial \rho}\right)_T \left(\frac{\partial h}{\partial T}\right)_\rho \left(\frac{\partial h}{\partial \rho}\right)_T^{-1}\right]^{-1}$
$\left(\frac{\partial \rho}{\partial p}\right)_h$	$\left[\left(\frac{\partial p}{\partial \rho}\right)_T - \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial h}{\partial \rho}\right)_T \left(\frac{\partial h}{\partial T}\right)_\rho^{-1}\right]^{-1}$
$\left(\frac{\partial \rho}{\partial h}\right)_p$	$\left[\left(\frac{\partial h}{\partial \rho}\right)_T - \left(\frac{\partial h}{\partial T}\right)_\rho \left(\frac{\partial p}{\partial \rho}\right)_T \left(\frac{\partial p}{\partial T}\right)_\rho^{-1}\right]^{-1}$

The last relation will reduce into the relations given before if a , b and/or c agrees with x and/or y . It is also used by, e. g., Wagner and Kretzschmar, 2008. To derive it, the partial derivative is first written as Jacobian and then expanded (see, e. g., Crawford, 1949a; Carroll, 1965; Bauer, 1999).

As specific volume v is the inverse of density ρ , partial derivatives involving specific volume can be transformed using the relations

$$\left(\frac{\partial v}{\partial b}\right)_c = -\frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial b}\right)_c, \quad \left(\frac{\partial a}{\partial v}\right)_c = -\rho^2 \left(\frac{\partial a}{\partial \rho}\right)_c.$$

Using these relations, any partial derivative with respect to arbitrary properties can be expressed as a combination of partial derivatives with respect to the independent variables of the equation of state, i. e., temperature and density in the case of the Helmholtz energy EoS. For the mentioned derived properties and some partial derivatives for dynamic simulation, results of these transformations are summarized in Table 5.

Second order partial derivatives can be calculated in a two-step procedure; as an example the derivative $(\partial c_p / \partial p)_h$ is given: In the first step the derivative is transformed using

Table 6: Transformation of second order partial derivatives

Definition	Transformation
$\left(\frac{\partial^2 T}{\partial p^2}\right)_\rho$	$-\left(\frac{\partial^2 p}{\partial T^2}\right)_\rho \left(\frac{\partial p}{\partial T}\right)_\rho^{-3}$
$\left(\frac{\partial^2 T}{\partial \rho^2}\right)_p$	$-\left[\left(\frac{\partial^2 p}{\partial \rho^2}\right)_T \left(\frac{\partial p}{\partial T}\right)_\rho - \left(\frac{\partial p}{\partial \rho}\right)_T \left(\frac{\partial^2 p}{\partial T \partial \rho}\right)\right] \left(\frac{\partial p}{\partial T}\right)_\rho^{-2}$ $+ \left[\left(\frac{\partial^2 p}{\partial T \partial \rho}\right) \left(\frac{\partial p}{\partial T}\right)_\rho - \left(\frac{\partial p}{\partial \rho}\right)_T \left(\frac{\partial^2 p}{\partial T^2}\right)_\rho\right] \left(\frac{\partial p}{\partial T}\right)_\rho^{-3} \left(\frac{\partial p}{\partial \rho}\right)_T$
$\left(\frac{\partial^2 T}{\partial p \partial \rho}\right)$	$-\left[\left(\frac{\partial^2 p}{\partial T \partial \rho}\right) \left(\frac{\partial p}{\partial T}\right)_\rho - \left(\frac{\partial p}{\partial \rho}\right)_T \left(\frac{\partial^2 p}{\partial T^2}\right)_\rho\right] \left(\frac{\partial p}{\partial T}\right)_\rho^{-3}$
$\left(\frac{\partial^2 \rho}{\partial p^2}\right)_T$	$-\left(\frac{\partial^2 p}{\partial \rho^2}\right)_T \left(\frac{\partial p}{\partial \rho}\right)_T^{-3}$
$\left(\frac{\partial^2 \rho}{\partial T^2}\right)_p$	$-\left[\left(\frac{\partial^2 p}{\partial T^2}\right)_\rho \left(\frac{\partial p}{\partial \rho}\right)_T - \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial^2 p}{\partial T \partial \rho}\right)\right] \left(\frac{\partial p}{\partial \rho}\right)_T^{-2}$ $+ \left[\left(\frac{\partial^2 p}{\partial T \partial \rho}\right) \left(\frac{\partial p}{\partial \rho}\right)_T - \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial^2 p}{\partial \rho^2}\right)_T\right] \left(\frac{\partial p}{\partial \rho}\right)_T^{-3} \left(\frac{\partial p}{\partial T}\right)_\rho$
$\left(\frac{\partial^2 \rho}{\partial T \partial p}\right)$	$-\left[\left(\frac{\partial^2 p}{\partial T \partial \rho}\right) \left(\frac{\partial p}{\partial \rho}\right)_T - \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial^2 p}{\partial \rho^2}\right)_T\right] \left(\frac{\partial p}{\partial \rho}\right)_T^{-3}$
$\left(\frac{\partial c_p}{\partial T}\right)_\rho$	$\left(\frac{\partial^2 h}{\partial T^2}\right)_\rho + \left(\frac{\partial h}{\partial \rho}\right)_T \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial^2 p}{\partial T \partial \rho}\right) \left(\frac{\partial p}{\partial \rho}\right)_T^{-2}$ $- \left[\left(\frac{\partial^2 h}{\partial T \partial \rho}\right) \left(\frac{\partial p}{\partial T}\right)_\rho + \left(\frac{\partial h}{\partial \rho}\right)_T \left(\frac{\partial^2 p}{\partial T^2}\right)_\rho\right] \left(\frac{\partial p}{\partial \rho}\right)_T^{-1}$
$\left(\frac{\partial c_p}{\partial \rho}\right)_T$	$\left(\frac{\partial^2 h}{\partial T \partial \rho}\right) + \left(\frac{\partial h}{\partial \rho}\right)_T \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial^2 p}{\partial \rho^2}\right)_T \left(\frac{\partial p}{\partial \rho}\right)_T^{-2}$ $- \left[\left(\frac{\partial^2 h}{\partial \rho^2}\right)_T \left(\frac{\partial p}{\partial T}\right)_\rho + \left(\frac{\partial h}{\partial \rho}\right)_T \left(\frac{\partial^2 p}{\partial T \partial \rho}\right)\right] \left(\frac{\partial p}{\partial \rho}\right)_T^{-1}$
$\left(\frac{\partial c_p}{\partial p}\right)_h$	$\frac{\left(\frac{\partial c_p}{\partial T}\right)_\rho \left(\frac{\partial h}{\partial \rho}\right)_T - \left(\frac{\partial c_p}{\partial \rho}\right)_T \left(\frac{\partial h}{\partial T}\right)_\rho}{\left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial h}{\partial \rho}\right)_T - \left(\frac{\partial p}{\partial \rho}\right)_T \left(\frac{\partial h}{\partial T}\right)_\rho}$

the same relations as before, the result is given in the last line of Table 6. In the transformed expression, derivatives of c_p with respect to the independent variables of the EoS appear, which can be derived in the second step using the product rule and quotient rule.

4 Derivatives along the saturation line

The stable multi-phase equilibrium system is a mixture of two or more phases. The properties of such a system cannot be calculated directly from the equation of state, be-

cause the equilibrium conditions have to be taken into account. The conditions for equilibrium between the saturated liquid phase (') and the saturated vapour phase (") are:

$$\text{thermal equilibrium: } T' = T'' = T_\sigma$$

$$\text{mechanical equilibrium: } p' = p'' = p_\sigma$$

$$\text{diffusional equilibrium: } \varphi'_i = \varphi''_i$$

where the fugacity φ is considered once for each substance i that is involved in the phase equilibrium (see, e. g., O'Connell and Haile, 2005, section 7.3). By specifying temperature T or pressure p the equilibrium is determined and the corresponding properties of the saturated phases can be found by simultaneously solving the equilibrium conditions. Iterative procedures for the simultaneous solution are given in the literature, e. g., Span, 2000, Iglesias-Silva et al., 2003, or Akasaka, 2008. Analogous conditions exist for other equilibria, e. g., between multiple liquid or solid phases. The following text refers to the vapour-liquid equilibrium of pure substances only.

Once the equilibrium has been determined, the properties of the two phases, each at the saturation state, can be calculated using the single-phase formulations with temperature T and the saturated densities ρ' and ρ'' . The derived properties change discontinuously upon entering the two-phase region. Therefore, values for the derived properties at saturation that have been calculated using the single-phase formulations are limiting values coming from the single-phase region.

Saturation pressure p_σ and saturation temperature T_σ are coupled. The derivatives of pressure and temperature along the saturation line are given by the Clausius-Clapeyron equation:

$$\left(\frac{dp_\sigma}{dT}\right) = \frac{s'' - s'}{v'' - v'} = \frac{1}{T} \frac{h'' - h'}{v'' - v'}$$

$$\left(\frac{dT_\sigma}{dp}\right) = \frac{v'' - v'}{s'' - s'} = T \frac{v'' - v'}{h'' - h'}$$

Using the same rules for transformation as before, further derivatives *along* the saturation line can be calculated as combinations of the partial derivatives *at* saturation and the derivatives of saturation pressure and temperature, e. g.:

$$\left(\frac{dv}{dT}\right) = \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial v}{\partial p}\right)_T \left(\frac{dp_\sigma}{dT}\right)$$

$$\left(\frac{ds}{dT}\right) = \left(\frac{\partial s}{\partial T}\right)_p + \left(\frac{\partial s}{\partial p}\right)_T \left(\frac{dp_\sigma}{dT}\right)$$

$$\left(\frac{dh}{dp}\right) = \left(\frac{\partial h}{\partial p}\right)_T + \left(\frac{\partial h}{\partial T}\right)_p \left(\frac{dT_\sigma}{dp}\right)$$

$$\left(\frac{d\rho}{dp}\right) = \left(\frac{\partial \rho}{\partial p}\right)_T + \left(\frac{\partial \rho}{\partial T}\right)_p \left(\frac{dT_\sigma}{dp}\right)$$

To get the values along the saturated *liquid* line the partial derivatives must be calculated using the saturated liquid density ρ' while for derivatives along the saturated *vapour* line the saturated vapour density ρ'' is used.

The derivatives along the saturation line are needed to calculate derivatives in the two-phase region and they can be helpful in iterative procedures. Another usage example is the saturated liquid heat capacity $c_{\sigma'}$ which is defined as

$$c_{\sigma'} = T \left(\frac{ds'}{dT}\right)$$

5 Partial derivatives in the two-phase region

In the stable two-phase region both saturated phases are present simultaneously. The properties of each phase can be calculated using the single-phase formulations. The two-phase mixture can then be described using the vapour mass fraction

$$x = \frac{m''}{m' + m''} = \frac{\text{mass of vapour}}{\text{mass of liquid} + \text{mass of vapour}}$$

which becomes 1 for states on the saturated vapour line and 0 for states on the saturated liquid line. Using $m = m' + m''$ and $v = V/m$ the vapour mass fraction can be rewritten as

$$x = \frac{v - v'}{v'' - v'} = \frac{1/\rho - 1/\rho'}{1/\rho'' - 1/\rho'}$$

Solving for v yields

$$v = v' + x(v'' - v') = xv'' + (1 - x)v'$$

In the same way specific entropy s , enthalpy h , internal energy u and Gibbs energy g of the system can be calculated. Properties within the two-phase system will only be homogeneous if the two phases are mixed homogeneously. If the two phases are partly or completely separated the mixture is heterogeneous and the properties are also heterogeneous within the system. The properties calculated from the vapour mass fraction then only represent the system average and it depends on the application whether this average value or the properties of the two separate saturated phases should be used.

The derived properties listed in Table 4 should be used with care in the two-phase region. Some might show unexpected physical behaviour in the two-phase region, e. g. sound speed; others, e. g. isobaric heat capacity, are not defined mathematically due to the coupling of pressure and temperature:

$$\left(\frac{\partial p}{\partial a}\right)_T = \left(\frac{\partial T}{\partial a}\right)_p = 0, \quad \left(\frac{\partial a}{\partial T}\right)_p = \left(\frac{\partial a}{\partial p}\right)_T = \infty,$$

with a representing an arbitrary property.

Derivatives at constant pressure or constant temperature can be calculated from the properties at saturation:

$$\begin{aligned}\left(\frac{\partial s}{\partial h}\right)_T &= \left(\frac{\partial s}{\partial h}\right)_p = \frac{s'' - s'}{h'' - h'} = \frac{1}{T} \\ \left(\frac{\partial v}{\partial h}\right)_p &= \left(\frac{\partial v}{\partial h}\right)_T = \frac{v'' - v'}{h'' - h'} = \frac{1}{T} \left(\frac{dT_\sigma}{dp}\right) \\ \left(\frac{\partial \rho}{\partial h}\right)_p &= -\rho^2 \left(\frac{\partial v}{\partial h}\right)_p = -\frac{\rho^2}{T} \left(\frac{dT_\sigma}{dp}\right)\end{aligned}$$

Derivatives with respect to pressure or temperature can be calculated by using the two-phase definition of the properties and deriving according to the product rule:

$$\begin{aligned}c_v &= \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial (u' + x(u'' - u'))}{\partial T}\right)_v \\ &= \left(\frac{du'}{dT}\right) + \left(\frac{\partial x}{\partial T}\right)_v (u'' - u') + x \left(\left(\frac{du''}{dT}\right) - \left(\frac{du'}{dT}\right)\right)\end{aligned}$$

where

$$\begin{aligned}\left(\frac{\partial x}{\partial T}\right)_v &= \frac{-\left(\frac{dv'}{dT}\right)(v'' - v') - (v - v') \left(\left(\frac{dv''}{dT}\right) - \left(\frac{dv'}{dT}\right)\right)}{(v'' - v')^2} \\ &= \frac{\left(\frac{dv'}{dT}\right) + x \left(\left(\frac{dv''}{dT}\right) - \left(\frac{dv'}{dT}\right)\right)}{(v' - v'')} \\ &= \frac{x \left(\frac{dv''}{dT}\right) + (1 - x) \left(\frac{dv'}{dT}\right)}{(v' - v'')}\end{aligned}$$

follows from the definition of the vapour mass fraction and the quotient rule. Using the alternative definition of isochoric heat capacity gives

$$c_v = T \left(\frac{ds'}{dT}\right) + T \left(\frac{\partial x}{\partial T}\right)_v (s'' - s') + xT \left(\left(\frac{ds''}{dT}\right) - \left(\frac{ds'}{dT}\right)\right),$$

highlighting the relation between the saturated liquid heat capacity and the isochoric heat capacity in the two-phase region.

The same procedure can of course be applied to further derivatives, e. g., the derivative of density with respect to pressure at constant specific enthalpy. First, rewrite as derivative of specific volume

$$\left(\frac{\partial \rho}{\partial p}\right)_h = -\rho^2 \left(\frac{\partial v}{\partial p}\right)_h$$

then derive, as before, using the product rule

$$\left(\frac{\partial v}{\partial p}\right)_h = \left(\frac{dv'}{dp}\right) + \left(\frac{\partial x}{\partial p}\right)_h (v'' - v') + x \left(\left(\frac{dv''}{dp}\right) - \left(\frac{dv'}{dp}\right)\right)$$

where

$$x = \frac{h - h'}{h'' - h'}$$

and thus, using the quotient rule

$$\begin{aligned}\left(\frac{\partial x}{\partial p}\right)_h &= \frac{-\left(\frac{dh'}{dp}\right)(h'' - h') - (h - h') \left(\left(\frac{dh''}{dp}\right) - \left(\frac{dh'}{dp}\right)\right)}{(h'' - h')^2} \\ &= \frac{\left(\frac{dh'}{dp}\right) + x \left(\left(\frac{dh''}{dp}\right) - \left(\frac{dh'}{dp}\right)\right)}{(h' - h'')} \\ &= \frac{x \left(\frac{dh''}{dp}\right) + (1 - x) \left(\frac{dh'}{dp}\right)}{(h' - h'')}\end{aligned}$$

6 Summary

It has been shown, for pure fluids, how arbitrary derivatives of thermodynamic state properties can be calculated from a fundamental equation of state in a systematic way in the single-phase region, along the saturation line and within the two-phase region. For testing and validation, all derivatives mentioned in this article have been implemented in a fluid properties computer library (Thorade and Saadat, 2012).

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