

# Fundamental EoS Implementation for {Water+Ammonia} in Modelica

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## Abstract

The implementation of a library for the calculation of thermodynamic properties for the mixture {water + ammonia} based on a fundamental equation of state (EoS) for the Helmholtz free energy is developed and presented. The model uses the formulation of Tillner-Roth and Friend (1998a) in order to provide the best available single state thermodynamic data. The calculation of the vapour-liquid equilibrium (VLE) using the fundamental equation of state is examined. However due to difficulties found under certain pressure and temperature conditions, another method for calculating the VLE had to be used. The problems found included unreliable results and difficulties setting the initial values. Saturation temperature polynomials by Johnson et al. (2001) have been found to be faster and more reliable and have been implemented instead. It's possible to calculate thermophysical properties in single and two-phase region at pressures from the melting point up to 40 MPa.

*Keywords:* Ammonia + Water, fundamental EOS, thermodynamic properties, Helmholtz energy

## 1 Introduction

The description of the thermodynamic properties of the involved substances is crucial in modelling an industrial process. Today, the most accurate EoS available are fundamental EoS in terms of Helmholtz energy. Using such an EoS it is possible to calculate all thermodynamic state properties. In addition the fugacity coefficients used to receive the VLE-states are available through the partial derivatives of the Helmholtz energy. Another popular approach is the use of polynomial fitted VLE-data. These explicit equations are quick to solve and also invertible.

The comprehensive CoolProp library by Bell et al. (2014) (included in ExternalMedia) has an implementation of the mixture {water + ammonia} as an incompressible fluid using polynomials. The ammonia content is also restricted to 30 % which limits use in sorption devices. In these devices the refrigerant has ammonia contents above 90 %. A fundamental EoS in terms of

Helmholtz energy is implemented in the HelmholtzMedia library by Thorade (2012) for single substance working fluids.

Carluccio et al. (2014) presented a simulation model for gas absorption heat pumps using {water + ammonia}. For this model the thermodynamic properties were calculated using correlations presented by Xu and Goswami (1999) based on the work of Ziegler and Trepp (1984). The formulation of the latter is based on a Gibbs Free Energy fundamental EoS and the measurement data used are older than those used by Tillner-Roth and Friend.

## 2 Formulation of the Helmholtz energy fundamental EoS

Tillner-Roth and Friend (1998b) performed a comprehensive assessment of available measurements on thermodynamic properties of the mixture {water + ammonia}. Using a formulation of the Helmholtz energy this resulted in the best available EoS regarding the accuracy and domain of definition (Tillner-Roth and Friend, 1998a).

The Helmholtz energy  $f$  is a function of temperature  $T$ , specific volume  $v$  and mole fraction  $x$ . In order to represent all influences on the Helmholtz energy it is divided into several parts. At first it is separated in ideal  $\phi^\circ$  and residual  $\phi^r$  parts which both consist of a part for each substance and mixing terms. The Helmholtz energy is made dimensionless  $\phi$  using the specific gas constant  $R$  and the temperature  $T$  and calculated in Equation (1).

$$\frac{f}{RT} = \phi = \phi^\circ(\tau, \delta, x) + \phi^r(\tau, \delta, x) \quad (1)$$

The arguments of the function are also made dimensionless using normalization temperature  $T_n$  and volume  $v_n$  calculated in Equations (2). In the ideal-gas part  $T_n = 500\text{ K}$  and  $v_n = 15\text{ kmol/m}^3$  are chosen arbitrarily. For the residual part reducing functions containing four parameters are introduced. These are needed for an accurate representation but are not introduced here.

$$\tau = \frac{T_n}{T}, \quad \delta = \frac{v_n}{v} \quad (2)$$

As explained above the ideal part  $\phi^\circ$  is split into pure substance and mixing sub-parts. In Equation (3) the logarithmic terms represent the ideal mixing terms. The mixing part  $\Delta\phi^r$  of the residual part (Equation (4)) is fitted using up to 56 parameters.

$$\phi^\circ = (1-x)\phi_{01}^\circ + x\phi_{02}^\circ + (1-x)\ln(1-x) + x\ln x. \quad (3)$$

$$\phi^r = (1-x)\phi_1^r + x\phi_2^r + \Delta\phi^r \quad (4)$$

The modular structure allows the use of proven formulations for the residual parts of the pure substances. For water IAPWS from Wagner and Pruß (2002), which is already implemented in the Modelica Standard Library, is used. Ammonia properties are approximated with the formulation from Tillner-Roth et al. (1993).

All the parameters and equations, together with an assessment of the database may be found in the original article from Tillner-Roth and Friend (1998a).

## 2.1 Calculating Auxiliary Properties

In order to calculate any auxiliary property at first the Helmholtz energy with its arguments has to be known (see Section 4.3). To get the thermodynamic properties from the Helmholtz energy partial derivatives are used. The algorithms shown in Table 1 are derived from the total differential of the Helmholtz energy and the property in question. The process is described in detail in Thorade and Saadat (2013). Here one may also find a derivation of several partial derivatives of the Helmholtz energy in the one- and two-phase region.

As shown in Table 1, partial derivatives with respect to the molar fraction are only needed for the algorithms calculating the fugacity for both substances.

**Table 1.** Equations for auxiliary properties

Property	Equation
pressure	$p = RT\rho \left( 1 + \delta \frac{\partial \phi^r}{\partial \delta} \right)$
inner energy	$u = RT \left( \tau^\circ \frac{\partial \phi^\circ}{\partial \tau^\circ} + \tau \frac{\partial \phi^r}{\partial \tau} \right)$
enthalpy	$h = RT \left( 1 + \tau^\circ \frac{\partial \phi^\circ}{\partial \tau^\circ} + \tau \frac{\partial \phi^r}{\partial \tau} + \delta \frac{\partial \phi^r}{\partial \delta} \right)$
entropy	$s = R \left( \tau^\circ \frac{\partial \phi^\circ}{\partial \tau^\circ} + \tau \frac{\partial \phi^r}{\partial \tau} - \phi^\circ - \phi^r \right)$
specific heat	$c_v = -R \left( \tau^{\circ 2} \frac{\partial^2 \phi^\circ}{\partial \tau^{\circ 2}} + \tau \frac{\partial^2 \phi^r}{\partial \tau^2} \right)$
fugacity coef.	$\varphi_{ammonia} = \frac{\exp(\phi^r + \delta \frac{\partial \phi^r}{\partial \delta} - xF_\varphi)}{1 + \delta \frac{\partial \phi^r}{\partial \delta}}$
	$\varphi_{water} = \frac{\exp(\phi^r + \delta \frac{\partial \phi^r}{\partial \delta} - (1-x)F_\varphi)}{1 + \delta \frac{\partial \phi^r}{\partial \delta}}$
fugacity var.	$F_\varphi = \frac{\partial \phi^r}{\partial x} + \frac{\partial \delta}{\partial x} \frac{\partial \phi^r}{\partial \delta} + \frac{\partial \tau}{\partial x} \frac{\partial \phi^r}{\partial \tau}$

## 3 Vapour-Liquid Equilibrium

### 3.1 Solving the PDE in Modelica

The vapour-liquid equilibrium for the mixture {water + ammonia} is defined through the three equilibria:

$$\text{mechanical equilibrium: } p_{\text{vapour}} = p_{\text{liquid}} \quad (5)$$

$$\text{thermal equilibrium: } T_{\text{vapour}} = T_{\text{liquid}} \quad (6)$$

$$\text{chemical equilibrium: } \tilde{G}_{\text{NH}_3, \text{vapour}} = \tilde{G}_{\text{NH}_3, \text{liquid}} \quad (7)$$

$$\tilde{G}_{\text{H}_2\text{O}, \text{vapour}} = \tilde{G}_{\text{H}_2\text{O}, \text{liquid}} \quad (8)$$

For VLE-calculations equations (5) to (8) have to be used in combination with the EoS formulation of Helmholtz energy. To get thermodynamic information in the VLE-region temperature, specific volume and molar fraction for both phases are needed. With these values in hand the other state properties may be calculated using the algorithms from Section 2.1. Six variables are to be found and four equations given resulting in a algebraic equation system with a degree of freedom of two. In practice two variables out of temperature, pressure and molar fraction of the phases are used. Several approaches to solve the VLE in an efficient and robust way can be found in the literature, like in Privat et al. (2013). In this first approach however the set of equations are written with Modelica and the system solved providing two inputs variables and using standard compiler and solvers.

The chemical equilibrium in Equations (7),(8) may be converted to the chemical potential  $\mu$  for the species  $k$  using the definition of the partial molar Gibbs energy  $\tilde{G}$ . Equation (9) is converted into Equation (10) to enable the use of fugacity coefficients  $\varphi$  provided by the EoS

$$\mu_{k, \text{vapour}} = \mu_{k, \text{liquid}} \quad (9)$$

$$x_{k, \text{vapour}} \varphi_{k, \text{vapour}} = x_{k, \text{liquid}} \varphi_{k, \text{liquid}} \quad (10)$$

For a given couple of temperature and pressure the VLE has been computed using the PDE resulting from the EoS with a Modelica model solved with the DASSL solver. As shown In Figure 2 the solver is not able to find a solution under certain combinations of T and p.

### 3.2 Polynomial Saturation Curves

A widely used approach to approximate VLE-data is fitting with polynomial saturation curves. Patek and Klomfar (1995) introduced a methodology which is refined by Johnson et al. (2001). The measurement datasets used for the formulation of the Helmholtz energy are also used here which results in similar results. The temperature, pressure and molar fraction data is forming a three dimensional surface, which is fitted using a weighted least square algorithm. The result are saturation temperature curves  $T_{\text{phase}}(p, x)$  with the form of Equation (11) using

56 parameters.

$$T_{phase}(p, x) = t_0 \sum_i a_i x_{phase}^{q_i} (1 - x_{phase})^{r_i} \left[ \ln \left( \frac{p_0}{p} \right) \right]^{s_i} \quad (11)$$

The polynomials are build as Lagrange polynomials to ensure pure substance saturation lines equal to Equations (12) and (13).

$$T_{H_2O}(p) = 269.8p^{0.08839} + 52.79p^{0.3663} + 130.4 \quad (12)$$

$$T_{NH_3}(p) = 177.9p^{0.09397} + 40.28p^{0.3898} + 79.83 \quad (13)$$

The equations are taken from Reynolds (1979). Oscillation can be problematic in numeric algorithms. This behavior of the fitted polynomials was reduced near the pure substance data. Multiple new datasets are generated to punish oscillation in the least square method. The methodology in detail and the parameters of Equation (11) may be found in Johnson et al. (2001).

## 4 Modelica Implementation

The general implementation of the library `H2O_NH3_TillnerRoth` is shown in Figure 1 and is mostly based on the Modelica Standard Library. To calculate fluid properties the **model** `BaseProperties` may be used. Here all basic properties are included for easy use. All the functions can be accessed independently, too. The folder `VLE` includes the VLE computation using the polynomial saturation curves discussed in Section 3.2. Some tests may be carried out using the functions contained in the **package** `Test` (see Sec. 4.4).

The implemented library `H2O_NH3_TillnerRoth` provides functions and models for the calculation of thermodynamic properties and vapour-liquid equilibrium of ammonia-water mixtures. For the VLE calculation the library makes use of the polynomial saturation curves previously presented. It is also possible to solve the VLE using the Helmholtz energy fundamental EoS.

A new interface `Thermofluid` is introduced, that extends the standard `PartialMedium` interface. To ensure compatibility all of the defined functions and records are used. In `Thermofluid` all the newly introduced registers are implemented. For example the **record** `FluidConstants` is extended with the data, that are needed for the dimensionless expression of the variables in the fundamental equation of state, such as density and molar mass at critical points.

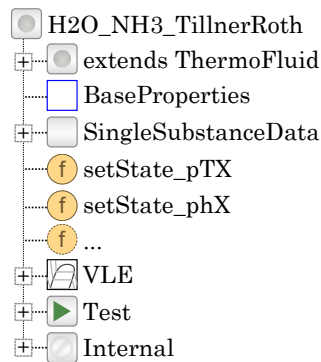


Figure 1. Basic structure

To calculate fluid properties in one phase several steps are taken successively:

1. At first the thermodynamic state vector (d,T,x) has to be determined. This is described in Section 4.3. The state vector is assigned to the **record** `ThermodynamicState`, which contains the arguments of the Helmholtz energy, in their mass based form.
2. As input for the Helmholtz energy EoS the state vector has to be made dimensionless in the **function** `taudeltaX_`.
3. Actual partial derivatives (Section 4.1) can now be calculated. The algorithms are found in the **package** `Internal.EOS` and assigned to the **record** `TauDeltaX`.
4. Lastly the high-level functions defined in the Modelica Standard Library access the derivatives to calculate the thermodynamic property as described in Section 2.1.

The implementation for the EoS is based on the 'HelmholtzMedia' library presented by Thorade (2012). Some modifications are needed however due to the fact that HelmholtzMedia was developed for single substances and not mixtures. This also adds an extra independent variable for the EoS, changing the definition of the thermodynamic state vector and the system of equations for the VLE.

### 4.1 Partial derivative calculation

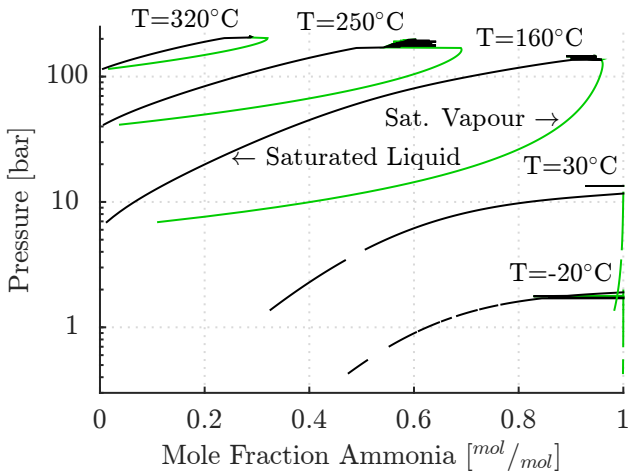
The partial derivatives of the formulation needed for the algorithms have been implemented using two different approaches. Firstly, the Modelica feature of automated symbolical derivatives is used. This is a very convenient solution, producing little program code and effort to implement. The implementation is described in Olsson et al. (2005) for single substance use. The partial derivative of the residual part of the Helmholtz energy  $\frac{\partial \phi^r}{\partial \delta}$  is calculated using

```
function dphir_ddelta = der(phir_, delta);
```

with the **function** `phir_` from Equation 4 and the argument `delta`.

However the use of this feature has not been shown as completely satisfactory. The calculation of the derivatives is not reliable since errors often appear caused by division by zero in logarithmic expressions. It was not possible to find a way to avoid these errors, because the algorithm used to automatically calculated the derivatives was not known, not manipulable and beyond the scope of this work.

Finally a second approach was used, implementing analytically determined derivatives. The formulation of



**Figure 2.** Solution of the VLE in Modelica for different temperatures

the Helmholtz energy is derivable analytically due to its structure as mostly a sum of small terms. With this second method the errors can be avoided through substituting the unfeasible terms with zero. The price is more complex Modelica code and the work load for the model maker associated with analytically solving the derivatives.

## 4.2 Vapour-Liquid-Equilibrium Calculation

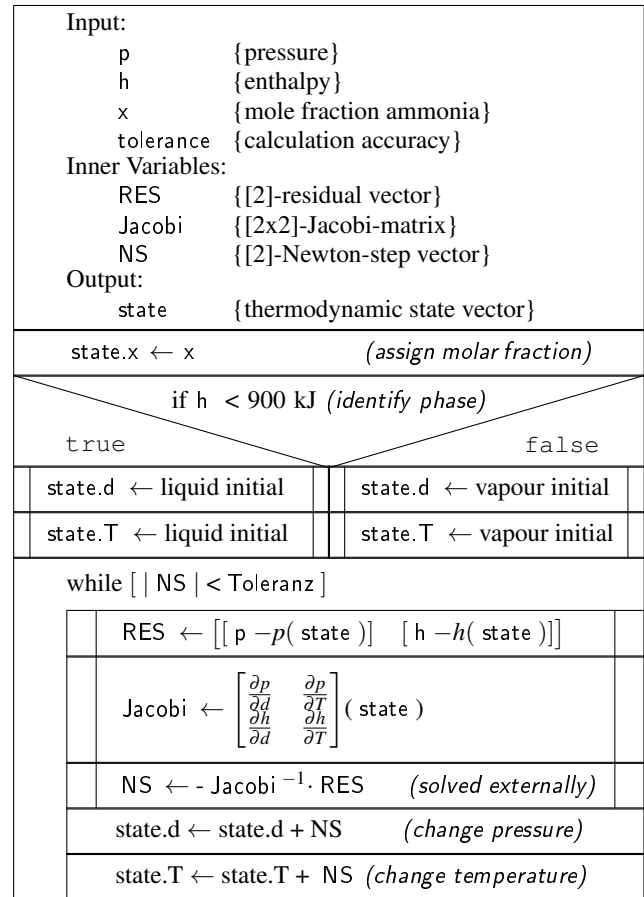
As shown in Figure 2, the use of the DASSL solver to solve the equation system of the VLE resulting from the EoS formulation of Helmholtz Energy is not successful in certain regions. Especially for low pressures (below 1 bar) and for mole fractions close to the single substances is not possible for the solver to find a solution.

In addition the solver is only able to solve the PDE if the given start values are very close to the solution. This can become a problem for dynamic simulations with big changes in pressure, temperature or mole fractions, since the start values have to be supplied to the model as parameters. Computed data from other components or former time steps is stored as variables. In the current version of Modelica parameters can't be calculated using variables. Not being able to use simulation data makes it very difficult to supply good start values to the VLE equation system.

For these reasons, the alternative implementation using the polynomial saturation curves is preferred, since it shows no convergence problems for the whole working region and the deviation of its results from those of the EoS implementation is in the range of measurement error reported by Tillner-Roth and Friend (1998a).

## 4.3 Finding the Thermodynamic State

As outlined by Thorade (2012) in engineering applications often the known variable combinations are (p,T,x)



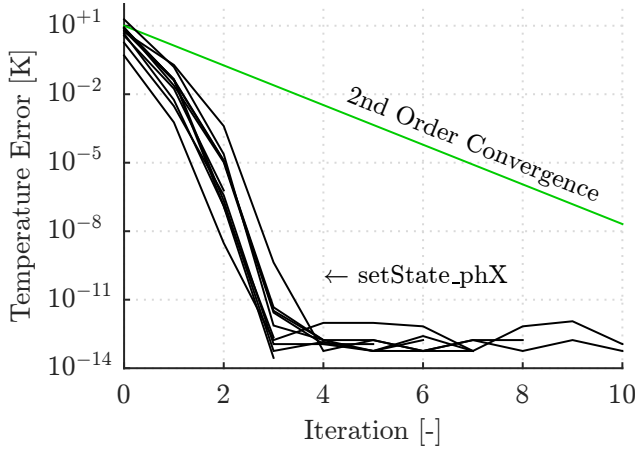
**Figure 3.** Nassi-Shneiderman-Diagram of setState\_phx

or (p,h,x) instead of (d,T,x), the arguments of the Helmholtz energy. This is particularly important for users of the Modelica Fluid library, since its connectors share the combination (p,h,x) between components.

In the Library H2O\_NH3\_TillnerRoth the functions setState\_pTx and setState\_phx are implemented. These functions iteratively determine a thermodynamic state (d,T,x) starting from (p,T,x) or (p,h,x).

The Nassi-Shneiderman-Diagram for the function setState\_phx is shown in Figure 3 as an example. After the unchanged mass fraction is assigned the phase needs to be determined. In the case of given (p,h,x) this can easily be achieved, because in the area of definition the enthalpy identifies the phase unambiguously. Afterwards a two-dimensional Newton-Raphson method is executed.

Firstly the input pressure is compared to the pressure computed by the current iteration of the state vector. Together with the analogue difference for the enthalpy the residual vector is assigned. In the Jacobi matrix the partial derivatives of pressure and enthalpy with respect to temperature and density are calculated using the current state vector. The equation  $NS = -Jacobi^{-1} \cdot RES$  is rearranged to  $Jacobi \cdot NS = RES$  and solved with the Gaussian elimination implemented in the Modelica Standard Library to receive the Newton step vector NS. Finally the



**Figure 4.** Temperature convergence of `getState_phx`

state variables temperature and density are changed.

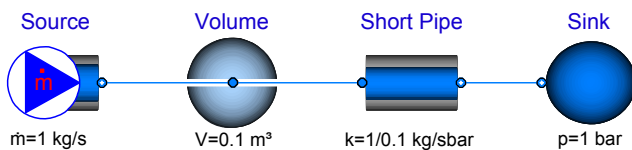
### Convergence behaviour

To test the reliability and speed of the `getState` functions convergence examinations are carried out. A list of 27 sample points in both phases and different temperatures and pressures was used. In Figure 4 the difference of the calculated temperature and the analytic solution is plotted on the iteration. It can be seen that the convergence is higher than the upper bound of the Newton-Raphson method, convergence of second order.

Having said that, for temperature errors below  $10^{-12}$  the method is not able to converge any more in some cases. These artefacts have been removed through a capping of the tolerance. In result the `getState` functions are able to find a solution in mostly three iterations with an error lower to the inaccuracies of the formulation in question.

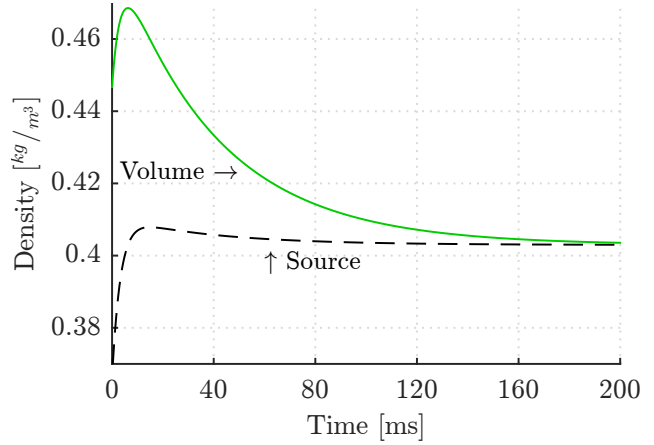
### 4.4 First Evaluation using PartialTestModel

A first test of the usability and performance of the Library was undertaken using the `PartialTestModel` from the Modelica Standard Library. The model shown in Figure 5 includes models for a source, volume, pipe and sink and follows a principle recommended by Tummescheit (2002). In Equation (14) the start conditions of the system is defined. For the source the values are slightly different (Eq. (15),(16)) which are then ad-



**Figure 5.** Diagram view of the `PartialTestModel`

vanced in the system through the mass flow.



**Figure 6.** Dynamic simulation of `PartialTestModel`: density

$$p_{start} = 1 \text{ bar}, \quad T_{start} = 200^\circ\text{C}, \quad x_{start} = 0.5 \quad (14)$$

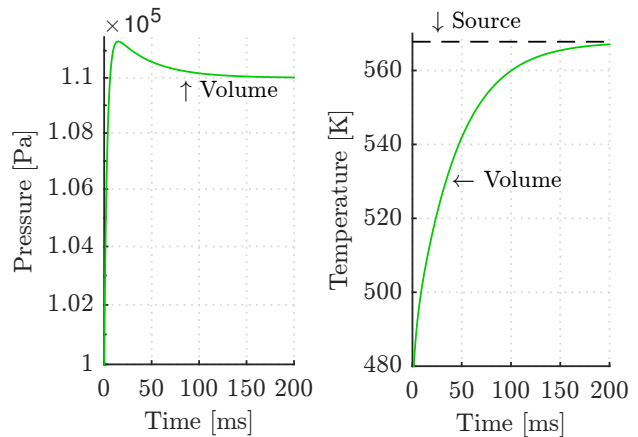
$$T_{Source} = 1, 2T_{start} = 294, 8^\circ\text{C} \quad (15)$$

$$x_{Source} = 0, 5x_{start} = 0, 25 \text{ kg/kg} \quad (16)$$

The results from Figure 6 and 7 show that the model is able to calculate thermodynamic states for dynamic changing conditions.

In Figure 6 the density in the simulated volume is plotted. The density of the fluid in the volume changes with changing pressure and temperature. The changes of pressure and temperature with time are shown in Figure 7.

The temperature of the volume changes from the starting  $200^\circ\text{C}$  since more and more fluid is flowing into the volume from the source with a constant temperature of  $\sim 300^\circ\text{C}$ . The pressure in the volume changes dynamically when fluid starts flowing until a stationary state is found (the source provides a constant mass flow rate). The density rises at the beginning as a consequence of the increasing pressure, but afterwards for constant pressure decreases with increasing temperature. The obtained results follow the expected behaviour for such a system.



**Figure 7.** Dynamic simulation of `PartialTestModel`: pressure and temperature

## 5 Summary and Outlook

A Modelica library for the calculation of thermodynamic properties of the mixture ammonia-water has been presented and discussed. The formulation of the Helmholtz energy fundamental equation of state using Modelica has been demonstrated. For the partial derivatives needed in the EoS, the automated symbolical derivation implemented in Modelica has been tested with not reliable results, and previously analytically solved differentials has been used instead.

For the solution of the vapour-equilibrium equations two alternative approaches have been tested. A first approach, solving the resulting PDE with Modelica has been found possible but inconvenient, since it requires quite accurate start values, takes long CPU-calculation times and is not able to solve the equation system under certain conditions. Instead, a second approach using polynomial saturation curves is preferred, and has been tested with regards of convergence using different methods.

In future works, the library will be extended to include calculation of non-state properties like surface tension, viscosity or thermal conductivity, that are relevant for the simulation of absorption heat pumps and chillers. Possible improvements can be made regarding the automatic recognition of the fluid phase to improve initialisation and simulation speed. An algorithm for the calculation of the VLE PDE could also be implemented.

A new Modelica Media connector for multiple phase mixtures (similar to FluidPort) would be very useful for heat transfer simulations, and would also require the adaptation of the presented library. The results obtained with this library are still to be compared with those obtained by the correlation equations implemented by Carluccio et al. (2014) or those obtained accessing external data base properties like REFPROP from Lemmon et al. (2013) or CoolProp from Bell et al. (2014).

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