Available online at www.sciencedirect.com
ScienceDirect
Fluid Phase Equilibria 250 (2006) 1–32
FLUID PHASE EQUILIBRIA
www.elsevier.com/locate/fluid

Mathematical and numerical analysis of classes of property models

Rafiqul Gani [a,*], Nuria Muro-Suñé [a], Mauricio Sales-Cruz [a], Claude Leibovici [b], John P. O'Connell [c]

[a] *CAPEC, Department of Chemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark*
[b] *CFL Consultant, Pau, France*
[c] *Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22911, USA*

Received 4 April 2006; received in revised form 24 August 2006; accepted 14 September 2006
Available online 19 September 2006

Abstract

A general analysis is presented to focus on the mathematical and numerical elements of property models for stand-alone results as well as within other calculations. This includes listing all of the equations that constitute a property model and articulating the sets of known and unknown variables for given problems. Ordering of equations is done to determine if a direct solution is feasible where the incidence matrix of unknown variables and equations can be written in tridiagonal form or if simultaneous or iterative solution of multiple equations is required. Example pure compound and mixture property models are: cubic equations of state; more advanced non-cubic equations of state; activity coefficient models; and models for polymer and electrolyte systems. Uses of this analysis are discussed for property calculations as a part of other calculations, such as for process models and parameter regression.

Keywords: Property models; Mathematical analysis; Numerical analysis; Thermodynamic consistency

1. Introduction

Property models are commonly used for synthesis, design, control and analysis of chemical processes and products. In many cases they are used as stand-alone (when property values needed for a specific problem are not available through a database, they need to be calculated through a model) or as part of a bigger model (when the property model is a subset of the total model equations as in a process simulation model). In either case, they are used in the so-called service role [1] where, given the values of a set of intensive variables (such as temperature, pressure and/or composition) and the chemical compound identities, the required properties are calculated. In this way, the property models are usually treated as *black-box* or *procedure* equations. That is, values for the known variables are transferred through an interface to a black-box or procedure, which returns calculated property values. Then, the model calculations form an inner calculation loop that is repeated for every request for property values by an outer calculation loop, which occurs when any of the intensive variables change. Although attempts have been made in the past to analyze the property model equations [2–4], the focus was on how to reduce the computational time per call of the property model rather than thorough analysis of the property model equations themselves. Other attempts have been made, for example, by Michelsen [5,6] and Hendriks [7] to reduce the number of equations to be solved per call of inner-loop property models, and Leibovici [8] to order the property model equations, e.g., cubic equations of state, into variant and invariant sets depending on the outer loop dependence on intensive variables.

From the points of view of more effective application and education, as well as a better understanding of property models, we believe a thorough mathematical and numerical analysis could be of value. For reliable and efficient usage, in addition to their principles, approximations, limitations and values, property models should be appreciated in terms of the equations that need to be

* Corresponding author. Tel.: +45 45252882; fax: +45 45932906.
E-mail address: rag@kt.dtu.dk (R. Gani).

0378-3812/$ – see front matter
doi:10.1016/j.fluid.2006.09.010

solved, the model parameters that need to be supplied, and the model (internal) variables that need to be calculated. This information can also help users to implement property models on their own for service, advice and solve roles [1]. Finally, such analysis should be valuable for utilizing third party software as well as implementation of property model exchange, e.g., CAPE-OPEN [9], when potential users know more about model content.

The objective of this paper is to present a systematic mathematical and numerical analysis that can be applied to a wide range of property models (also known as constitutive models). The analysis provides for each model a list of the set of independent (model) equations and their corresponding variables together with a classification of the variables as known and unknown variables. The known variables are further classified in terms of those fixed by the system, those fixed by the problem, those set by the property model and finally, those that are regressed or retrieved from model parameter tables. The set of unknown variables and the corresponding set of independent model equations are presented through an ordered incidence matrix of equations and (unknown) variables, which highlights the structure that elucidates issues in solving the equations. In particular, if the structure is lower tridiagonal, the solution approach is simpler than when the structure is not lower tridiagonal, in which case, simultaneous solution (or an extra iteration-loop) is necessary. The property models analyzed in this paper are cubic equations of state [10], advanced non-cubic equations of state: CPA [11–13]; PC-SAFT [14,15]; and SAFT [16], models for polymer systems: GC-Flory [17]; and models for electrolyte systems: UNIQUAC-Elec: [18,19]. Finally, these aspects of property models are discussed in connection with parameter regression and in the common process engineering calculations of two-phase separations and two-phase equilibrium.

2. Property model analysis

The systematic analysis performed for each property model consists of the following steps:

Step 1. List the independent set of equations representing the model for the desired property and all the variables found in the equations; classify the variables as scalars, vectors and matrices.
Step 2. Determine the degrees of freedom (DOF) by subtracting the number of equations from the number of variables. Based on the DOF, select the variables that need to be specified and classify them as those fixed by the problem, fixed by the system, fixed by the property model and adjustable (regressed) model parameters. The remaining variables would typically be the remaining state conditions, properties and intermediate values.
Step 3. Establish an incidence matrix of equations and all variables (except those fixed by the system and the property model). If the case has relatively few variables, this may be done visually by putting equations in columns and variables in rows and putting a * on the column–row index where a variable appears in an equation.
Step 4. Eliminate the columns for variables that have been selected as specified variables (i.e., variables set by the problem). The incidence matrix must then become square.
Step 5. Order the equations so that a lower tridiagonal form will appear, if possible. (Standard equation ordering techniques exist in computer-aided modeling tools [24] to obtain the ordered equation set.)

a. If the incidence matrix shows a lower tridiagonal form, then all the equations can be solved sequentially (one unknown for each equation) corresponding to the order giving the lower tridiagonal form. Expect some of the equations to be non-linear, requiring iterative solution.
b. If there are elements in the upper tridiagonal portion of the matrix, equations will need to be solved simultaneously and/or iteratively.

Note that steps 3–5 may also be combined by directly generating the ordered incidence for the square system. In the text below, some common property models are analyzed according to the systematic analysis given above. We do not give the model derivations since these can be found in the original references. Only the set of equations representing the property model are given and analyzed.

In the model equations and their analysis below, a vector will be represented by an underlined variable name (for example, x), a matrix will be represented by an underlined bold variable name (for example, $\boldsymbol{u}$). An element of a vector or a matrix will be indicated by subscripts (for example, x_i or u_{ij}). In this case, unless otherwise indicated, variables will be single-valued. The notation we have used is typically that of the papers cited. This means that the same quantity may have different symbols for different models and vice versa. We have denoted in the text those variables that might not be obvious, but the reader should consult the original references for symbols of uncertain meaning.

2.1. Cubic equations of state: SRK EOS

We consider the SRK cubic equation state in its most commonly used form [10]. First we will consider the pure compound property, followed by the compound properties in a mixture.