

IMPLEMENTING SAFT-BASED THERMODYNAMICS IN PROCESS MODELLING TOOLS

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Abstract

This paper considers the robust and efficient software implementation of the SAFT-VR equation of state in the context of general-purpose process modelling tools. Mixtures of arbitrary numbers of associating and non-associating components are handled.

Keywords

SAFT, Process modelling, Dynamic simulation.

Introduction

Most process modelling and simulation activities today employ well-established equations of state (EOS), such as Soave-Redlich-Kwong and Peng-Robinson, for physical property calculations. Albeit appropriate for small and roughly spherical molecules, these cannot offer the necessary accuracy for complex systems. During the last decade, much research effort has been invested in deriving equations of state based on a more rigorous statistical mechanical framework. In principle, these can lead to improved predictive capabilities even for systems and/or ranges of conditions for which relatively limited experimental data are available.

A number of these new equations of state are based on SAFT (Statistical Associating Fluid Theory) and have proven remarkably successful at modelling associating (hydrogen-bonded) fluids such as aqueous systems, refrigerants or surfactants and non-spherical systems like polymers. Implementations of variants of the SAFT EOS, such as HR-SAFT (Huang and Radosz, 1990) and PC-SAFT (Gross and Sadowski, 2001), are currently in use in commercial modelling and simulation tools. However, these tend to be limited, e.g. they do not include the association contributions to the free energy where

arguably both the main advantage and most of the complexity of SAFT resides.

This paper considers the implementation of the SAFT-VR EOS (Gil-Villegas *et al.*, 1997) as a software component able to provide computational services of thermophysical property calculations in process modelling tools both for associating and non-associating molecules. The software is able to handle mixtures of any number of species with any number of associating sites providing accurate, efficient and robust operation.

The SAFT-VR Equation of State

The SAFT EOS thermodynamic model attempts to correct the ideal gas behaviour by assuming that the excess energy of a fluid comprises different contributions due to hard-sphere effects, attractive and repulsive forces (described by the negative part of an intermolecular potential), chain formation and association phenomena like hydrogen-bonding (for details see the review by Müller and Gubbins, 2001). The overall formulation is given in terms of the system's Helmholtz free energy, A , as a function of temperature T , volume V and molar composition, \underline{N} . Other physical properties are calculated

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from the partial derivatives of A via standard thermodynamic relations, e.g. $P = -\partial A / \partial V$, $S = -\partial A / \partial T$, $\underline{\mu} = -\partial A / \partial \underline{N}$.

SAFT-VR is an improved version of the original EOS which replaces the hard-sphere potential with a square-well intermolecular potential. This modification allows the equation to describe non-conformal effects of matter. More specifically, molecules are modelled as chains of m hard spheres of diameter σ . The spheres exhibit attractive interactions of energy $-\varepsilon$ at distances ranging from σ to $\lambda\sigma$ where $\lambda > 1$ is an additional “range” parameter. Where hydrogen-bonding effects are present, a number of association sites of distinct types are placed on each sphere at a cut-off range r to interact via an energy ε^{ab} . SAFT-VR has proven to be quite successful in phase equilibrium and physical property calculations of highly non-ideal fluids including refrigerants, aqueous mixtures and polymers (see Economou, 2001).

Some issues in the implementation of SAFT EOS

Notwithstanding their differences, all variants of the SAFT EOS need to address certain common key issues. One of these is the computation of the contribution to the function $A(T, V, \underline{N})$ arising from the association interaction. This involves the solution of a set of nonlinear algebraic equations of the form:

$$X_{ia} = \frac{1}{1 + \sum_{j=1}^{N_c} \sum_{b=1}^{NST_j} \alpha_{ijab} X_{jb}}, \quad \begin{array}{l} \forall i = 1, \dots, N_c, \\ a = 1, \dots, NST_i \end{array} \quad (1)$$

where N_c is the number of species in the mixture, NST_i is the number of distinct types of association sites in species i , and X_{ia} is the fraction of sites of type a in species i that are not associated in the current mixture. For the purposes of the solution of the above equation, the quantities α_{ijab} are known constants (which can be computed from the given T, V, \underline{N}). We have devised a robust and efficient hybrid method for determining the solution X_{ia} . This involves a small number (typically 2-3) of successive substitution iterations, followed by a sequence of Newton iterations. A small number (typically 5-10) of the latter is necessary to satisfy the equations to machine accuracy.

A second issue is the computation of the ideal contribution to $A(T, V, \underline{N})$. This appears to have received little attention to date as it does not affect the values of chemical potentials used for phase equilibrium calculations which have been the main practical focus of SAFT to date. However, the ideal term is needed for computing other important properties such as internal energy, enthalpy and entropy. Our work has considered two approaches for the computation of the ideal term. One is based on deriving the Helmholtz free energy from

empirical polynomials for specific heat capacity $C_p(T)$ (cf. Reid *et al.*, 1987). Perhaps more consistent with SAFT’s claims to a more fundamental molecular basis is the second approach based on a general statistical mechanical formulation that takes into account the translational, rotational and vibrational modes of molecular motion. Our trials with a range of simple molecules have found the latter to be a much more accurate and reliable method with larger area of validity. However, its use is limited by the availability of the necessary constants derived from infrared or Raman spectroscopy.

Implementation of SAFT-VR

The SAFT-VR equation of state has been implemented as a general-purpose FORTRAN90 subroutine named `saftVRprops` which can be applied to mixtures of any number of species, each of which may include any number of association sites. `saftVRprops` receives as inputs the mixture temperature T (K), volume V (m^3) and molar composition \underline{N} (mol) and returns the Helmholtz free energy A (J) and its partial derivatives $\partial A / \partial V$ (J/m^3), $\partial A / \partial T$ (J/K), $\partial A / \partial N_i$ (J/mol). Partial derivatives are computed analytically, with the contributions of the association term being obtained from the exact sensitivities of (1).

The basic `saftVRprops` routine is wrapped within another subroutine, `saftVR` which returns commonly used physical properties such as pressure P (Pa), Gibbs free energy G (J), internal energy U (J), enthalpy H (J), entropy S (J/K), chemical potentials μ_i (J) and fugacity coefficients ϕ .

The SAFT Parameter File

`saftVRprops` requires knowledge of a number of molecular model parameters relating to the species in the mixture and the interactions among the various sites. This information is provided by the user in a SAFT Parameter File (SPF) of the following form:

- Number of species in mixture
- Pure species parameters: For each species i :
 - molecular weight, MW_i
 - ideal term parameters:
 - If spectral data are available for species i :
 - $z=1$ for nonlinear molecules, else 0
 - atoms per molecule, s
 - number of molecular symmetry, ω
 - rotational constants, $\Theta_r, \Theta_s, \Theta_t$ (cm^{-1})
 - vibrational constants, Θ_j (cm^{-1}), $j=1, \dots, 3s-5z$
 - If no spectral data are available for species i :
 - $C_p(T)$ cubic polynomial coefficients ($\text{J}/\text{mol.K}$)

- SAFT-VR parameters
 - $m_i, \sigma_i(m), \lambda_{iij}, \varepsilon_{iij}/k_B$ (K)
 - Number of site types NST_i
 - For each type site a , number of sites η_{ia}
 - $\varepsilon_{iia}^{ab}/k_B$ (K), $r_{iia}^a(m)$, $\forall a, b=1, \dots, NST_i$
- Species parameter terminator “0 0 0 0”
- Species interaction parameters: For (some) species pairs i, j :
 - Lorentz-Berthelot mixing rules parameters $\gamma_{ij}^{\lambda}, \gamma_{ij}^{\varepsilon}$
 - for (some) pairs of site types (a, b) $\varepsilon_{ijab}^{ab}/k_B$ (K), r_{ijab}^a (m)
- Terminator of molecular description “0 0 0”

Figure 1 presents a sample SPF for a binary mixture involving hydrogen fluoride and water¹. Lines 2-14 provide parameters for pure HF and lines 15-27 for water. The ideal terms for both molecules are computed using empirical $C_p(T)$ temperature polynomials (lines 4-5 and 17-18). Each molecule comprises a single hard sphere segment (lines 6 and 19) and has two distinct types of associating sites (lines 10 and 23). In the HF case, there is a single site of each type (lines 11-12) while water has two sites of each type (lines 24-25).

Lines 28-40 define species interaction parameters, each defined over two lines. The first line specifies the species i, j involved in the interaction and the kind of parameter being specified (where: 1 $\equiv\gamma^{\lambda}$, 2 $\equiv\gamma^{\varepsilon}$, 3 $\equiv\varepsilon^{ab}/k_B$, 4 $\equiv r^a$). The second line specifies the value of the interaction parameter; for parameters of type 3 and 4, the types of the association sites involved are also specified. For example, line 29 indicates that a parameter γ^{ε} relating to species 1 (=HF) and 2 (=water) is to be specified; then line 30 provides its value. Also, line 35 indicates that a parameter r^a is to be specified, and line 36 states that its value is 2.6Å and clarifies that this relates to the interaction between association sites of type 1 on HF and 2 on water. We note that, in general, parameters may be provided for only a subset of possible binary interactions. All interactions not specified explicitly are taken to be zero.

The SPF provides a complete and non-redundant description of a mixture in the context of the SAFT-VR EOS. It is designed so that, in the future, it can be generated automatically by a user interface drawing data from databanks of pure species and binary interaction parameters.

```

1 2                                     # Number of components
2 2                                     # Pure component parameters for HF
3 20.0140                                'MW
4 0                                       'Spectra data are not available
5 2.9066d1 6.611d-4 -2.032d-6 2.504d-9    'Cp constants
6 1.040                                  'SPHEPES
7 3.06937d-10                            'SIGMA
8 1.7502d0                                'LAMDA
9 121.717d0                               'EPSILON/K
10 2                                       'ntyp_site
11 1 1                                     'sites: no of sites
12 2 1
13 1 2 1810.67d0 3.06936995815494d-10 'KHB and Rc
14 0 0 0 0
15 # Pure component parameters for H2O
16 18.0164d0                              'MW
17 0                                       'Spectra data are not available
18 3.224d1 1.924d-3 1.055d-5 -3.596d-9    'Cp constants
19 1.040                                  'SPHEPES
20 3.03612d-10                            'SIGMA
21 1.840                                  'LAMDA
22 253.288d0                              'EPSILON/K
23 2                                       'ntyp_site
24 1 2
25 2 2                                     'sites: no of sites
26 1 2 1365.86 2.10099504d-10 'KHB and Rc
27 0 0 0 0
28 # Interaction parameters for HF/H2O
29 1 2 1
30 -1.634636390002164d-5
31 2 2
32 -0.43351994316703d0
33 1 2 3
34 1855.42d0 1 2
35 1 2 3
36 1855.42d0 2 1
37 1 2 4
38 2.600275426730523d-10 1 2
39 1 2 4
40 2.600275426730523d-10 2 1
41 0 0 0 ' End SPF

```

Figure 1. SAFT-VR Parameter File (SPF) for the mixture HF-H₂O

Interfacing to gPROMS

In order to be able to test our implementation of SAFT-VR within realistic process models, we have interfaced it to the commercial gPROMS process modelling tool² using the latter’s Foreign Object Interface (Kakhu *et al.*, 1998). More specifically, the FORTRAN90 code described above has been wrapped within a foreign object named SAFTVR. Written in C++, SAFTVR supports the following methods:

```

ChemicalPotential(T,V,N)
Enthalpy(T,V,N)
Entropy(T,V,N)
FugacityCoefficient(T,V,N)
GibbsEnergy(T,V,N)
HelmholtzEnergy(T,V,N)
InternalEnergy(T,V,N)
NumberOfComponents()
Pressure(T,V,N)

```

Whilst far from comprehensive, the above set is sufficient to implement some basic process models.

Use of SAFT-VR in dynamic process simulation

As an illustration of the use of SAFT-VR in relatively complex process simulation applications, we consider the dynamics of a flash unit for vapour-liquid separation. The

¹ The parameter values appearing in this file have been taken from Grice (1999) and from unpublished data by S.J. Grice, A. Galindo and G. Jackson.

² <http://www.psenterprise.com/gPROMS>

unit has a volume of 0.1m^3 and is fed with a mixture of 70% hydrogen fluoride (HF) and 30% water (H_2O) at a rate of 2 mol/min and temperature 370.5K. The system operates initially at steady state for 10 min and is then subjected to the following external manipulations:

- Heat the system until the liquid phase disappears.
- Stop heating and continue operation for another 40min.
- Start cooling the system until liquid reappears.
- Continue running for a further 40min; then stop.

The left plot in Figure 2 shows the variation of the external heat load and temperature, while the right plot shows the variation of the liquid and vapour molar holdups. It can be seen that the initial increase of the heat load causes the liquid phase to disappear after about 20 min of operation. Liquid re-appears once the heating stops after about 60 min of operation.

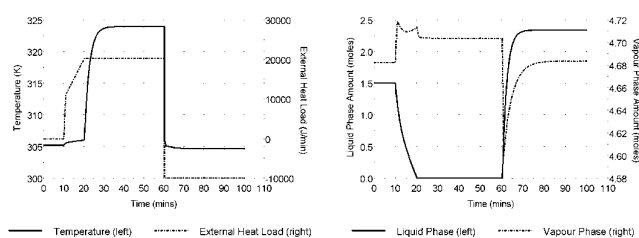


Figure 2: Dynamics of vapour-liquid separation of HF- H_2O mixtures.

Concluding remarks

This paper has presented a generic software implementation of the SAFT-VR equation of state in a form that can be used within process modelling tools. The implementation is applicable to mixtures of any number of components, each involving any number of associating sites. The efficiency and (numerical) accuracy of our implementation permit its use within sophisticated model-based applications, such as dynamic simulation and optimisation, that go well beyond the simpler steady-state flowsheeting calculations where SAFT has been applied until now.

The use of SAFT EOS is predicated on the availability of a relatively large number of parameters. Interestingly, a side-benefit of the incorporation of SAFT within integrated environments such as gPROMS is that SAFT itself can now benefit from the services that these packages provide for model development and validation. These include the derivation of optimal estimates of its parameters from experimental data, the analysis of the statistical significance of these estimates, and the optimal design of further experiments for increased parameter precision.

Finally, recent developments in open software architectures, and in particular, the CAPE-OPEN initiative (Braunschweig *et al.*, 2000), provide a mechanism for making our SAFT implementation available within any

process modelling environment providing a CAPE-OPEN compliant thermodynamics “socket”³.

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³ See <http://www.colan.org>.