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A molecular-based equation of state for process engineering

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Abstract

We outline here some of the steps we are taking towards the development of reliable tools for quantitative predictions of thermodynamic properties of complex fluids with equations based on statistical mechanics. The long term objective is to provide a user-friendly computer code and a wide database of molecular parameters for different compounds, able to be implemented in a process simulator. We have observed that the keys of the success when using molecular modelling tools for predictions rely on the selection of the appropriate model, representative of the molecular structure, and the use of physically meaningful molecular parameters.

Keywords: molecular modelling, SAFT-type equations, quantitative predictions.

1. Introduction

The optimization and design of existing and new processes and materials in the chemical process industry require accurate models for thermodynamic properties and phase equilibria predictions of pure compounds and their mixtures, over a wide range of thermodynamic conditions. Traditional approaches such as empirical equations, cubic equations of state or activity coefficient models have proved to be adequate for some systems, but only for a limited range of conditions and/or compounds. They drastically fail outside the range for which they were fitted, or for complex systems, when usually more accurate data is needed for process design. In fact, it has been proved that, especially for the case of complex fluids and/or extreme conditions, only equations which explicitly consider the underlying molecular nature of the system from its inception are accurate enough for prediction purposes. These new types of equations

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belong to what is generally called molecular-based equations of state, developed from Molecular Modelling techniques.

The Molecular Modelling term refers to an approach in which a system is modelled starting from a potential energy of interaction for the molecules. The model is solved using methods based on Statistical Mechanics. These techniques can be separated in two groups: molecular simulation (Monte Carlo and Molecular Dynamics) and analytical theories. Since the theories and the simulations start from the same intermolecular potential, and hence, no fitted parameters are needed, a direct comparison between an (approximate) theory and the (exact) simulations shows the accuracy of the theory, before any parametrization and application of the theory to the particular experimental system. An additional advantage of molecular-based equations versus macroscopic equations is that the different microscopic contributions that control the macroscopic properties are explicitly considered when building the theory. In this sense, non-ideal contributions such as multipolar moments or molecular shape can be introduced in the development of the equation. In addition, the parameters are few in number, have a physical meaning and are independent of the fitting conditions. These molecular bases provide the equation with a reliable predictive and extrapolative power.

One of the most popular equations developed from this approach is the SAFT equation of state (from the Statistical Associating Fluid Theory), originally developed by Chapman et al. (1988, 1990). The most popular version of this equation, both in academia and industry, is a slightly different version, developed by Huang and Radosz (1990). These authors parameterized the equation for several fluids and mixtures, showing its applicability for real engineering applications from its development. Other recent modifications of SAFT include the SAFT-VR equation of Jackson and co-workers (Gil-Villegas et al., 1997), the PC-SAFT equation of Sadowski and co-workers (Gross and Sadowski, 2001) and the soft-SAFT equation of Vega and co-workers (Blas and Vega, 1997, 1998; Pàmies and Vega, 2001). All these modifications seek for improvements of the underlying model, and most of them replace the original hard-sphere reference fluid and an attractive perturbation term by an attractive and repulsive interaction unique term. A discussion of the different versions of SAFT, and their applications and limitations, can be found in two recent reviews on the subject (Müller and Gubbins, 2001; Economou, 2002). The success of SAFT, with more than 250 papers published in the last fifteen years, is making it a standard equation for engineering purposes.

Besides its impressive range of applications and the potentiality of the SAFT approach, one of its main present limitations is the transferability of the developed codes for different applications. The inherent difficulty of the theory itself, and the complexity of the equations behind it, had lead to the development of different codes from different research groups, focused on specific applications, instead of developing them in a more general framework. In this sense, our objective is to develop a general code, friendly, multioptional, and modular, and a wide database of molecular parameters for several compounds and their mixtures, ready to be implemented in a process simulator. This is a long term project in which the different steps should be clearly defined and tested.

The purpose of the present work is to briefly show some of the steps we are taking towards the development and applications of soft-SAFT and its code implementation.

2. The soft-SAFT equation of state

For details on the applications and limitations of SAFT-type equations the reader is referred to two excellent reviews (Müller and Gubbins, 2001; Economou, 2002). We just retain here the main features relevant for this work.

SAFT equations are usually written in terms of the residual Hemholtz free energy, where each term in the equation represents different microscopic contributions to the total free energy of the fluid. For associating chain systems the equation is written as:

$$a^{res} = a^{ref} + a^{chain} + a^{assoc} \quad (1)$$

where a^{res} is the total residual Helmholtz free energy density of the system. The superscripts *ref*, *chain* and *assoc* refer to the contributions from the monomer, the formation of the chain, and the association, respectively.

In the soft-SAFT equation of state (EOS) (Blas and Vega, 1997,1998; Pàmies and Vega, 2001), the reference term is a LJ monomer fluid, which accounts both for the repulsive and attractive interactions of the monomers forming the chain. We use the accurate EOS of Johnson et al. (1993). The chain and association terms come from Wertheim's theory (1984, 1986a,b), and they are formally identical in the different versions of SAFT. Details on the equations can be found in the original papers.

One of the several advantages a molecular-based equation offers is the way in which it can be extended, in a systematic manner. As a Helmholtz energy equation, soft-SAFT can directly provide phase equilibria properties. However, as any other analytical equation, soft-SAFT is unable to accurately describe the long-range fluctuations near the critical region, unless a specific treatment is included. The equation has been modified to overcome this limitation by combining it with the renormalization group theory. This produces a crossover equation, accurate far from and close to the critical point (Llovell et al., 2004). In addition, the theory can be systematically extended to calculate other thermodynamic properties. For instance, a combination of soft-SAFT with the density gradient theory of van der Waals can be used to obtain phase equilibria as well as interfacial properties, including surface tension, a key property for design purposes (Pàmies, 2003; Duque et al., 2004). Interfacial properties can be predicted from the molecular parameters obtained by fitting vapour-liquid properties.

Besides thermodynamic properties, the equation is also able to provide structural properties, such as the number of molecules forming a given aggregate. This is of great importance for the case of micellar systems, such as surfactants and copolymers. The performance of the equation for aggregate formation was compared versus simulation results for model surfactants depending on the molecular architecture (Herdes et al., 2004). The equation gives quantitative predictions for thermodynamic properties and the qualitative trend of the size of the aggregates with pressure and temperature.

3. The soft-SAFT code

Keeping in mind that our long term objective is to develop a code *implementable* in a process simulator, we have developed a multioptional, user-friendly code, in which different types of mixtures, molecular architectures, different types of properties and other features can be studied systematically. The program is written using *Fortran 77* in

a modular manner. It has a single, easy-to-use input file, and a number of output files depending on the type of calculation performed. A list of the current features includes:

- Application to pure/binary mixtures of associating and non-associating molecules:
  - fluid phase equilibria (two and three coexisting phases) and single phase properties (subcritical or supercritical)
  - critical properties of pure fluids and binary mixtures (crossover treatment)
  - interfacial properties of planar interfaces
  - derivative properties for pure fluids and mixtures: heat capacities, compressibilities, Joule-Thomson coefficients, speeds of sound.
- Available models:
  - reference fluid of LJ monomers and dimers with van der Waals one-fluid mixing rules and generalized Lorentz-Berthelot combining rules
  - multipolar interactions: dipolar and quadrupolar terms
  - several self-association and cross-association models up to 4 association sites
- Additional features
  - parameters optimization to the given experimental data. Calculation of deviations
  - generation of isotherms, isobars and isopleths for equilibrium calculations in binary mixtures
  - automatic search for appropriate initial values (guesses) for the determination of coexisting densities
  - inclusion of correlations for the molecular parameters of several families of compounds. This permits direct predictions without the need of fitting from experimental data

The use of the program for thermodynamic property calculations is not restricted to soft-SAFT. Any other equation of state can be implemented into the code as a subroutine. For additional details on the development of the code and some of its applications up to date the reader is referred to the Ph.D. Dissertation of Pàmies (2003).

As an example of output data from the soft-SAFT program, figure 1 shows the reduced values of thermodynamic properties for the LJ spherical fluid, including both, single phase and equilibrium curves.

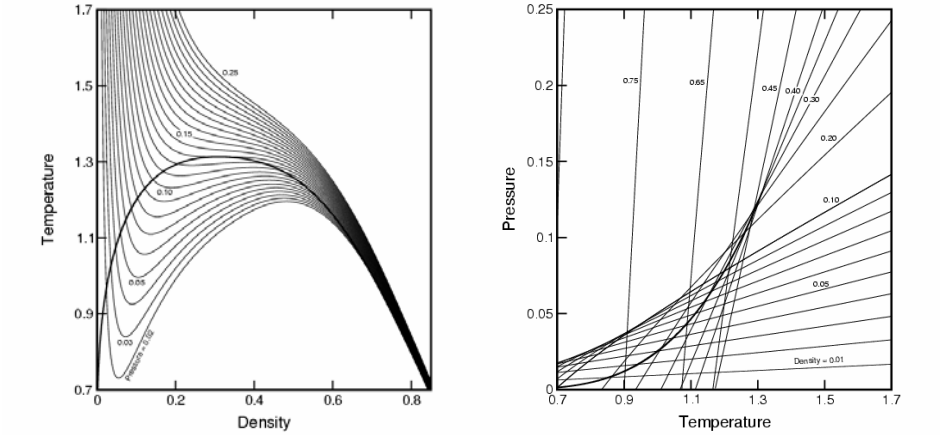

Figure 1: Temperature-density and pressure-temperature plots for the LJ fluid as obtained from the soft-SAFT code

4. Implementation of the equation to real fluids

As with any other theoretical tool, the performance of the soft-SAFT equation should be always checked before implemented for production data. The way in which the accuracy of the equation is tested differs from traditional equations: since the equation has a molecular basis, a direct comparison with molecular simulations is possible. In this case, no adjustable parameters are needed, and the comparison shows the accuracy of the equation for the given property. This is a great advantage versus other approaches in which the fitted parameters can screen some inaccuracies of the equation.

The application to experimental systems proceeds as follows: first, a molecular model for the compounds is proposed, for instance, n-alkanes are modelled as *m* tangent LJ spheres of diameter σ and energy of interaction ε. Each LJ site represents a group of atoms in the molecule (CH_3 or CH_2 in this case). Hence, the molecular parameters of the n-alkane model are *m*, σ and ε; n-alkanols are modelled in a similar manner, with two additional parameters, the volume and the energy of association of the associating sites, mimicking the –OH groups. The molecular parameters of the compounds are obtained by fitting to experimental data, typically from vapour-liquid equilibrium. Usually, a correlation of these molecular parameters with the molecular weight is obtained; in this case, the equation is able *to accurately predict* the behaviour of a chemical family (i.e. alkanes, alkanols, ketones, etc.) from a limited set of experimental data. Depending on the mixture, pure component parameters can be used to directly predict the behaviour of the mixtures. When the mixture deviates from ideality, two additional parameters, *independent* of the thermodynamic conditions, are fitted. These mixture parameters are obtained from a single set of binary data and are used to predict the properties of the system at any thermodynamic condition. Ternary and multicomponent mixtures are also predicted from the binary parameters.

As an example of the transferability of the parameters, figure 2 shows predictions for vapour-liquid equilibrium data for the binary mixture ethane-eicosane at 340 and 450K. The molecular parameters of n-eicosane were obtained from a correlation of the molecular parameters with the molecular weight obtained just by fitting the first eight members of the series (Pàmies and Vega, 2001).

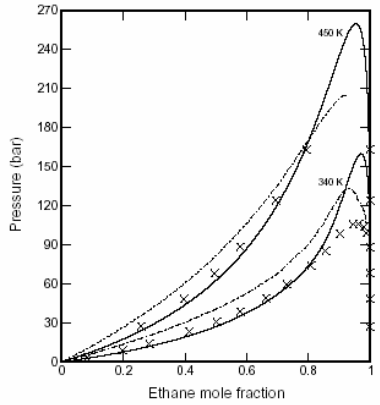

Figure 2: Px,y diagram for a mixture of ethane and n-eicosane. The crosses represent the experimental data of Peters et al. (1987), the full line the soft-SAFT predictions, and the dashed line the Peng-Robinson equation as performed from a process simulator (HYSYS plant 2.1).

5. Summary and future directions

The impressive amount of published works in which molecular-based equations of state are applied, especially SAFT-type equations, and the accurate predictions they provide, show, by themselves, the applicability of this approach for engineering applications. In most of these studies predictions from the equation are compared to the best available model in a process simulator for the studied systems, showing a better performance in most of the cases. The key of the success of this approach relies on the molecular nature of the equation, which allows modifying systematically the underlying model, explicitly accounting for the molecular features. In addition, a careful fitting of the molecular parameters, taking care of their physical meaning and their transferability, strengthens this approach, providing a reliable tool for predictions and extrapolations.

The future of molecular-based equations needs to deal with the development of user friendly codes, the extension of the database of available molecular parameters for different species and mixtures, and the extension of the equation itself to predict other needed thermodynamic and structural properties.

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