



# An examination of the excess thermodynamic properties of flexible molecules from a molecular modelling perspective



María Carolina dos Ramos<sup>a</sup>, Ana Villegas Páez<sup>b,c</sup>, Manuel M. Piñeiro<sup>d</sup>, Felipe J. Blas<sup>b,c,\*</sup>

<sup>a</sup> Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235, United States

<sup>b</sup> Departamento de Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Huelva, E21071 Huelva, Spain

<sup>c</sup> Centro de Física Teórica y Matemática FIMAT, Universidad de Huelva, E21071 Huelva, Spain

<sup>d</sup> Departamento de Física Aplicada, Universidade de Vigo, E36310 Vigo, Spain

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## ABSTRACT

Excess thermodynamic properties provide fundamental information on the intermolecular interactions in multicomponent fluid mixtures. However, very often only phase equilibria is used to test the accuracy of any theory or molecular model describing the solution thermodynamic behaviour. Although this approach is valid and often sufficient, some situations require stronger tests to determine whether a model and/or theory can provide a realistic description of a particular system. Excess properties estimation is a valuable test for this purpose because excess properties are very sensitive to the molecular model details. The goal of this work is to show how simple models, with a reduced number of molecular parameters, are able to predict accurately excess thermodynamic properties. We concentrate on binary mixtures formed by different models of flexible molecules. In particular, we focus on two general models: the fully-flexible tangentially bonded Lennard–Jones chains model described with the SAFT VR [J. Chem. Phys. 106 (1997) 4168] approach, and the united-atom model combined with Monte Carlo simulation, in both cases applied to the description of short chain alkane mixtures (from methane to propane). While the first model does not consider intramolecular interactions and the bond length equals the monomer size, the second one incorporates a more realistic description. Although the molecular models are relatively simple, they are able to describe most of the microscopic features of real chainlike molecules. The predictions obtained from SAFT-VR and simulation are compared with available experimental data, and the agreement is good for a wide range of thermodynamic conditions. In addition to the vapour–liquid equilibria, both theory and simulation are able to characterize the most relevant features of two important excess thermodynamic properties, excess volume and enthalpy.

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## 1. Introduction

The determination (either experimental or theoretical) of thermophysical properties of fluid solutions is a classical research domain. In this general framework, the determination of the deviation from ideal solution behaviour, through the determination of the so-called excess properties, has been one of the most active areas. From an experimental perspective, if we take into account that the natural thermodynamic ensemble corresponding to the experimental setup of most fluid solution experiments is the isothermal-isobaric (or NPT) ensemble, and so the corresponding thermodynamic potential is the Gibbs free energy ( $G$ ), the set of excess properties related in this case include [1] excess Gibbs free

energy,  $G^E$ , entropy,  $S^E$ , volume,  $V^E$ , heat capacity,  $C_p^E$ , and enthalpy,  $H^E$ .

The study of excess thermodynamic properties of fluid mixtures has been an extremely active field of research, if the number of related publications in literature is evaluated. There are several reasons for this. First, from an experimental point of view two of the excess properties, namely excess volumes (volume change on mixing) and excess enthalpies (heats of mixing) are easily accessible from an experimental point of view, using different volumetric or calorimetric techniques. The widespread use of dilatometers and vibrating tube densimeters have contributed to the publication of a huge body of work concerning multicomponent mixtures excess volumes, and the same applies, although to a lesser extent, to the various types of calorimetric devices that allow to determine the heat exchanged during a fluid solution process. In addition, these properties can be measured to a great degree of accuracy, and have been widely used to explore non-ideality in mixtures. The differences of sign and shape observed experimentally for

\* Corresponding author. Tel.: +34 959 219796; fax: +34 959 219777.

E-mail address: [felipe@uhu.es](mailto:felipe@uhu.es) (F.J. Blas).

these properties have been attributed to the combination of different molecular scale effects, ranging from geometrical effects, including free volume effects or creation or disruption of order, to energetic effects arising mostly from the differences in the mutual interactions between alike and/or different molecules. Thus, excess properties have been readily used as a probe to discuss molecular interactions.

From a different perspective, the sometimes subtle trend of these properties, and their interpretation as fingerprint of real fluid behaviour represents a challenge for any fluid state theory. Quite often the explanation given for the observed experimental results relies only on qualitative argumentations and many of them have become common place repeated many times with scarce rigorous support. The relative simplicity of the experimental determination of these properties is in clear contrast with the difficulty associated to their proper theoretical representation. In fact, these properties represent a difficult test for any theoretical method, because for instance an acceptable description of the density of a given fluid mixture, with deviations below 1% from experimental data, may lead to an erratic or even completely wrong estimation of the corresponding excess volume. This is the reason why excess properties have been so often used as benchmark for all type of fluid solution models (there are several excellent reviews in literature concerning liquid state thermodynamic theories, as the books by Prausnitz et al. [2] or Sandler [3]). In the literature, different theoretical approaches based on the lattice fluid theory, combined with the two-liquid mixture approximation, have been extensively used in the past to estimate excess properties. The comprehensive textbook of Prausnitz et al. [2] describes in detail the foundations of fluid lattice theories, that led to different models as NRTL, UNIQUAC, DISQUAC or UNIFAC. All these theories share many features, representing semi-empirical approaches that have been used to correlate large bodies of mixture experimental phase equilibria and excess properties data. The main limitation of these theories is that the characteristic correlation parameters, although often determined using a group contribution scheme, do not have a solid physical ground. In addition, these models consider ideal volumetric behaviour on mixing, so they can not describe excess volumes. When using this type of traditional approaches, the success or not of the excess magnitude representation depended on the fitting of parameters of mixing, the use of more or less developed mixing rules, or other phenomenological schemes. In these cases, there is little to be learned from the empirical approaches used, the determined parameters have limited meaning, and neither the theoretical schemes, determined parameters or conclusions may be transferred to the estimation of the same property for other systems, or to the calculation of other different fluid properties or phase equilibria. Over the years, many other theories describing condensed fluid phases have been presented, improving by far the estimative ability of more traditional approaches. Despite this, there has not been a systematic comparison of the new approaches performance when applied to the estimation of real solution excess properties, and only a few studies have addressed this issue (see e.g. Blas [4], Dominik et al. [5], Kleiner et al. [6])

In principle, any thermodynamic equation of state (EoS) or thermodynamic model able to describe the involved thermodynamic potential (Gibbs free energy) can be used for this purpose, and even the simplest cubic EoS serves to obtain excess magnitude estimations, but usually with poor results, as it could be expected a priori. In this context, the evaluation of the ability of recent models and updated approaches to the estimation of excess properties appears as an interesting objective. The evaluation of the performance of a model or theoretical technique to the estimation of these excess properties serves also as a rigorous consistency test, that may be combined with other results obtained for phase equilibria, homogeneous or inhomogeneous fluid properties, transport properties,

or whatever thermodynamic functions feasible to be calculated. As an example of this type of test, Blas [4] used a combination of the well known soft-SAFT molecular EoS and MC simulation to determine the excess properties (excess volumes and enthalpies) of tangentially bonded chains of segments, evaluating the influence of chain length, and diameter and energetic ratios.

In this context, alkanes represent an interesting case study of homologous family, at first sight due to their practical applications, as they are present in many industrial processes. They are for instance the basic compounds of a very wide range of oil derivatives, from natural gas to heavy oils. Moreover, the fact that their mutual interactions are rather weak, because coulombic interactions can be considered negligible, is also an interesting feature because the excess properties of their solutions are very small if compared with other more interactive molecules. In the particular case of light alkanes, with short chain lengths, the molecules are so similar to each other that resolving the distinctive features of their excess properties is a demanding test for any theory.

Although many classical phenomenological approaches have provided a description of the liquid state, and the excess thermodynamic properties in particular, from a theoretical point of view, the most important theoretical developments in the field of flexible molecules in the liquid state have been achieved in the last 30 years, since the formulation of the so-called first-order thermodynamic perturbation theory (TPT1) of Wertheim [7–10]. The original Wertheim's theory is a Statistical Mechanics approach to account for the thermodynamic properties of hard spherical associating fluids. One of the major extensions, proposed by Wertheim [11,12], Jackson et al. [13], and Chapman et al. [14] allows for the use of this theoretical approach to analyse chainlike molecules. The Statistical Associating Fluid Theory (SAFT) is a formalism based on Wertheim's theory that, in general, combines a chain reference contribution with an associating perturbation term (for systems with specific interactions, i.e., hydrogen bonding, reactive systems, etc.) to analyse complex-chain and associating fluids. The original SAFT EoS was proposed by Chapman et al. [15,16] and has since been extended and used to predict the phase behaviour, among other thermodynamic properties, of a wide variety of pure components and their mixtures. A number of different versions of SAFT have been used during last two decades, including the Soft-SAFT, SAFT-VR or PC-SAFT, among many others, for predicting the thermodynamic and phase behaviour properties of many different model and real complex mixtures. The reader is referred here for more information to the existing comprehensive reviews on the SAFT approach and its capabilities [17–21].

As an alternative route, both Monte Carlo (MC) and Molecular Dynamics (MD) molecular simulation (MS) techniques have been widely used, combined with different molecular models, as theoretical approaches to estimate the thermodynamic behaviour of alkanes. The remarkable practical relevance of alkanes in Chemical Engineering, and the fact that they may be described using relatively simple molecular models makes them an attractive target for this type of calculation methods. A survey of literature shows that their study can be dealt from different levels of molecular structure complexity. Ungerer et al. [22] have recently published a review including a description of different models used to describe hydrocarbons using molecular simulation, with a clear focus on practical applications in Petrophysics. Not intending to be rigorous, a few existing models may be cited in a brief summary of the main features that, combined, lead to the different existing descriptions.

Linear alkanes are usually considered as heteronuclear chains of segments whose mutual pair interactions are represented by an effective Lennard–Jones pair potential. Each of these segments may represent either a single atom or a functional group embodying several atoms. The latter scheme is denoted as United-Atom (UA) approach. OPLS (Jorgensen et al. [23]), TraPPE (Martin and

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