An Examination of the Excess Thermodynamic Properties of Flexible Molecules from a Molecular Modelling Perspective

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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**, 4168 (1997)] 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 more 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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I. 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 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 diamater 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 analyze 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 analyze 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 Siepmann[24]), NERD (Nath *et al.*[25]) or Vega and López-Rodríguez[26] are samples of force fields that follow this philosophy and have met great success in a wide range of practical applications. All these cited UA models consider the centre of forces coincident with the spherical segment centre, but a displacement from this centre leads to the anisotropic united atoms (AUA) models, as the one proposed by Ungerer *et al.*[27]

If each hydrocarbon atom is represented as a single segment, the molecular model is denoted as All-Atom (AA) or hydrogen explicit. An example is the OPLS-aa, by Kaminski *et al.*[28] or also the TraPPE Explicit Hydrogen[29]. Although more realistic, the multiplication of the number of segments leads to a considerable increase of computing times, which makes many calculations non feasible. In addition to this complexity, OPLS-aa includes also point electric charges on each segment, which contributes also to increase remarkably CPU time requirements.

The intramolecular configuration of these chains may be treated with different degrees of detail, ranging from completely rigid geometries[26] to freely jointed spheres in fully flexible chains. A common intermediate option is the flexible chain including angular potentials controlling the bending and torsion between segment bonds[23,30]. The bonds distances between segments may be considered as well fixed or variable through an harmonic stretching potential.

This short description may serve to introduce the variety of approaches already used to study the alkane series using MS. Most of these studies have dealt with phase equilibria estimation as main goal. The usual method to determine the characteristic parameters of any of the molecular models cited relies on the comparison with experimental phase equilibria data, focusing mainly in the vapour-liquid region, and the saturation condition properties.

The evident reason for this is that most of the practical applications of these models entail phase equilibria determination as a primary objective.

Despite this, the alkane molecular models cited have proved to be very versatile also when applied to the determination, for instance, of bulk fluid response functions, as Joule-Thomson coefficients or heat capacities, either for pure fluids or mixtures[31–34]. These authors have determined derivative properties combining Fluctuation Theory and NPT MC simulation. These properties are related to the second derivatives of the thermodynamic potential, so they are very sensitive to the model characteristic parameters, but the results obtained can be considered satisfactory, supporting the reliability of the existing models. Remarkable results have been obtained also in the calculation of alkane interfacial properties,[35,36], transport and viscoelastic properties[37,38], or even solid-fluid equilibrium[39,40]. The use of these models in these different contexts raises the issue of parameter transferability, physical soundness of parameter determination or the location of global minima in multiparametric landscapes for a given objective function.

Nevertheless, and despite this important body of work, little attention has been paid so far to the analysis of the performance of these models on excess properties determination, and the influence that each of the characteristics of molecular structure may reflect on these properties. Isothermal-isobaric (NPT) MC simulation is a useful route for determining excess molar volumes and enthalpies. The calculation of excess molar volumes is straightforward from the determination of pure and fluid mixture densities. Excess enthalpies can be determined as well, but the nature of the calculated magnitude during MC must be carefully considered[22]. A number of studies have been published dealing with the estimation of heats of mixing of liquid binary mixtures using MS[41–49], but none of them considered mixtures of alkanes. Ramos-Estrada *et al.*[50] performed Molecular Dynamics (MD) calculations of mixture density for n-pentane + n-octane with the aim to compare with experimental data at temperatures ranging from 278.15 to 363.15 K and atmospheric pressure, but they did not calculate the excess magnitude nor provided the detailed numerical results to do so.

The main goal of this work is to predict the behaviour of some excess properties of mixtures containing light alkanes. We use two different but complementary approaches, SAFT-VR and MC, to predict the excess volume and heat for methane (1) + ethane (2), + propane (2), and + n-butane (2), and ethane (1) + propane (2) binary systems. In addition to that, the SAFT-VR approach is also used to predict the phase behaviour of the mixtures considered at the same (T,p) conditions at which excess properties are determined. This allows to test the accuracy of the molecular approaches used in this work in predicting its thermodynamic behaviour. It is important to mention here that excess properties are generally more sensitive to the molecular details than phase equilibria. We have used previously this approach to assess the accuracy of SAFT[4,51–53] describing excess properties of chainlike systems.

The rest of the paper is organized as follows. We present first the SAFT theory and the molecular model used in section II, and then describe the MS technique used in section III. The obtained results are described and discussed in section IV and finally the conclusions are presented in section V.

II. SAFT THEORY AND MOLECULAR MODEL

In this work we have considered n-alkane molecules, which constitute the simplest homologous series of real molecules that exhibit chainlike molecular behaviour. The approach used here is similar to that used in a previous work (dos Ramos and Blas[53], where *Soft*-SAFT was used to describe the excess properties of alkanes, focusing in that case on longer chain molecules and very asymmetric mixtures). Now, mixtures of shorter chain molecules are the objective, trying to establish the performance of the method for very symmetric mixtures of small and nearly identical molecules. Thus, following the same approach proposed by different authors [54–56], the short n-alkanes are modeled with a simple united atom approach, in which m_i hard-sphere attractive segments of equal diameter σ_{ii} are bonded tangentially to form the molecules. Attractive intermolecular and intramolecular interactions between two arbitrary segments i and j of the same and/or different chain are described via a square-well (SW) potential, which is given by

$$u_{ij}(r_{ij}) = \begin{cases} +\infty & \text{if } r_{ij} < \sigma_{ij} \\ -\epsilon_{ij} & \text{if } \sigma_{ij} \leq r_{ij} \leq \lambda_{ij}\sigma_{ij} \\ 0 & \text{if } r_{ij} > \lambda_{ij}\sigma_{ij} \end{cases} \tag{1}$$

where r_{ij} is the distance between two segments, σ_{ij} defines the contact distance between segment type i and segment type j, and λ_{ij} and ϵ_{ij} are the range and depth of the potential well for the i-j interaction, respectively.

The original version of the SAFT-VR approach is used to deal with mixtures of short n-alkanes. Since this theory has already been presented and used[54,55], here we only give a brief overview of the main expressions. The SAFT equation is written in terms of the Helmholtz free energy. In the case of mixtures of non-associating homonuclear molecules the thermodynamic potential can be expressed as a sum of three microscopic contributions: an ideal contribution A^{IDEAL}, a monomer term A^{MONO} that takes into account the attractive and repulsive forces between the segments that form the molecules, and a chain contribution A^{CHAIN} that accounts for the connectivity of segments within the molecules. The Helmholtz free energy is then written as

$$\frac{A}{Nk_{\text{B}}T} = \frac{A^{\text{IDEAL}}}{Nk_{\text{B}}T} + \frac{A^{\text{MONO}}}{Nk_{\text{B}}T} + \frac{A^{\text{CHAIN}}}{Nk_{\text{B}}T} \tag{2}$$

where N is the total number of molecules, T is the temperature, and k_{B} is the Boltzmann constant.

The monomer contribution is written in terms of the Helmholtz free energy per segment of the mixture a^M as

$$\begin{aligned} \frac{A^{MONO}}{Nk_BT} &= \left(\sum_{i=1}^{n} m_i x_{si}\right) \frac{A^M}{N_s k_B T} = \\ &= \left(\sum_{i=1}^{2} m_i x_{si}\right) \left(a^{HS} + \beta a_1 + \beta^2 a_2\right) = \\ &= \left(m_1 x_{s1} + m_2 x_{s2}\right) \left(a^{HS} + \beta a_1 + \beta^2 a_2\right) \end{aligned} \tag{3}$$

where $\beta = (k_BT)^{-1}$, m_i and x_{si} are the chain length and the molar fraction of segments type i, respectively; the index i runs from 1 to n, with n the number of components in the mixture, which in this case is equal to 2. a^{HS} is the residual free energy per segment in a mixture of hard spheres obtained from the expression of Boublík[57] (equivalent to that of Mansoori *et al.*[58]). The mean-attractive energy associated to the first-order perturbation term, a_1, is treated in the context of the M1Xb mixing rules[54,55], and the second-order perturbation term a_2 is obtained from a_1 using the local compressibility approximation for mixtures[59–61].

The chain contribution to the Helmholtz free energy takes into account the chain formation of n-alkanes. In particular, we have used the original expression of the SAFT-VR approach[54,55] to describe the chain contribution, which in the case of a binary mixture formed by homonuclear chains is given by:

$$\frac{A^{\mathrm{CHAIN}}}{Nk_{\mathrm{B}}T} = \sum_{i=1}^{n} x_i\,(1-m_i)\ln y_{ii}^{\mathrm{SW}}(\sigma_{ii}) = x_1\,(1-m_1)\,\ln y_{11}^{\mathrm{SW}}(\sigma_{11}) + x_2\,(1-m_2)\,\ln y_{22}^{\mathrm{SW}}(\sigma_{22}) \tag{4}$$

where x_1 and x_2 are the compositions of the mixture ($x_1+x_2=1$), and m_1 and m_2 represent the chain length of components 1 and 2, respectively. $y_{ii}^{\mathrm{SW}}(\sigma_{ii})$ is the cavity correlation function of the reference SW fluid mixture between the segments of type i. The cavity function can be expressed in terms of the corresponding pair radial distribution function at the contact value, which within the SAFT-VR framework is given by a high-temperature expansion. For further details see the seminal works of Jackson and co-workers[54,55]. The rest of thermodynamic properties, such as the chemical potentials μ_i, and pressure P, can be easily obtained from the Helmholtz free energy using standard thermodynamic relations.

As other versions of SAFT, the original SAFT-VR approach needs a number of molecular parameters to describe the thermodynamic properties of real substances. In this work, each n-alkane molecule is characterised by four molecular parameters, the segment size (σ_{ii}), the square-well dispersive energy parameter (ϵ_{ii}), the range of the attractive interactions (λ_{ii}), and the chain length (m_1 or m_2). The potential model parameters σ_{ii}, ϵ_{ii} and λ_{ii} values for the n-alkanes have been extracted from McCabe and Jackson[56]. In addition to that, we have used the simple empirical relationship proposed previously in literature[62,63], which relates the number of spherical segments in the model chain to the number of carbon atoms C in the alkanes, $m=(1/3)(C-1)+1$. Table I lists the molecular parameters used in this work to describe each component.

Since we are dealing with mixtures of homonuclear chains, a number of cross or unlike parameters need to be specified. The Lorentz combining rule is used for the unlike hard-core diameter

$$\sigma_{ij} = \frac{\sigma_{ii}+\sigma_{jj}}{2} \tag{5}$$

while the unlike dispersive energy of the system is defined by the usual Berthelot combining rule,

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \tag{6}$$

The unlike range parameter of the mixtures is obtained from the following equation

$$\lambda_{ij} = \frac{\lambda_{ii}\sigma_{ii}+\lambda_{jj}\sigma_{jj}}{\sigma_{ii}+\sigma_{jj}} \tag{7}$$

It is important to recall again that our goal is not to provide a detailed account of the excess thermodynamic properties neither the phase behaviour of these mixtures but only to give a general overview of the properties exhibited by these model mixtures.

III. MOLECULAR SIMULATION

In this work, isothermal-isobaric (or NPT) MC MS have been carried out for several short-alkane mixtures using the TraPPE model[24]. A detailed description of the technique can be found elsewhere[64–66]. The open source Towhee[67,68] code has been used to perform the MC simulations. Simulations for pure methane, ethane, propane, and n-butane and their binary mixtures are performed in order to check the accuracy of the model in predicting excess molar volumes and enthalpies by comparing the results obtained to available experimental data. Pure fluid simulations are carried out using cubic simulation boxes applying the usual periodic boundary conditions and minimum image convention for $N = 1000$, 800, 500, and 400 molecules of methane, ethane, propane, and n-butane, respectively. In the case of mixtures, systems formed by 800 (methane (1) + ethane (2) and + propane (2)) and 500 (methane (1) + n-butane (2) and ethane (1) + propane (2)) molecules are used to study mixture properties.

Simulations are organized in cycles, each of them consisting of a series of N move attempts. The type of movement is chosen randomly at every MC step. In the case of pure methane, only two types of moves are considered, i.e., volume change, which is chosen with a probability equal to $1/N$, and particle displacement. For systems containing longer alkanes, rotation and Configurational Bias (CB) chain regrowth moves are also used. In this case, the probabilities chosen for each movement, i.e., volume change, CB chain regrowth, displace, and rotation moves are $P_{\mathrm{vol}} = 1/N$, $P_{CR} = 0.1 - 1/N$, and $P_{\mathrm{disp}} = P_{\mathrm{rot}} = 0.45$, respectively. Maximum molecule displacements, rotation angle and box-volume change are chosen in such a way that a $30 - 50\%$ acceptance probability is obtained during the run. Unlike parameters between Lennard-Jones chemical units forming alkanes are determined using the classical Lorentz-Berthelot rules. Finally, a constant 16 Å cut-off radius, combined with the usual homogeneous long-range correction for the potential tail, are used to speed up the calculations.

Initial configurations of the molecules in the simulation box are obtained through a low-density simple cubic regular lattice arrangement. The system is then allowed to equilibrate during 10^5 MC cycles. In addition to that, a production run of 2×10^5 MC cycles is also used to determine the properties of interest. This production run is divided into 10 blocks. This allows to estimate the statistical uncertainty of the molar volume and internal energy through block averaging. The statistical error is estimated as twice the standard deviation of the average values of the magnitude in each block.

Excess molar properties are evaluated using the usual relationships[69]. Since the calculation of the excess volume and enthalpy are similar, we show here only the calculation method for the excess molar enthalpy of a fluid, h. This magnitude may be expressed as:

$$h = u_{\mathrm{ext}} + u_{\mathrm{int}} + k + PV \tag{8}$$

where u stands for internal energy, due to the addition of intermolecular (ext) and intramolecular (int) interactions, and k is the kinetic energy of the molecules, which is not computed using MC. Thus, only part of the intramolecular energy is considered, so what is actually calculated is the so-called configurational enthalpy $\hat{h}$, defined as:

$$\hat{h} = u_{\mathrm{ext}} + \bar{u}_{\mathrm{int}} + PV \tag{9}$$

where $\bar{u}_{\mathrm{int}}$ is the part of the intramolecular internal energy that is explicitly accounted for.

This configurational enthalpy $\hat{h}$ differs from the enthalpy h by part a term e'^{id}, that includes the implicit intramolecular contribution and the kinetic energy:

$$h = \hat{h} + e'^{id} \tag{10}$$

Bearing this in mind, the molar excess enthalpy can be determined with the usual relation:

$$h^E = \hat{h} - \sum_{i=1}^{n} x_i \hat{h}_i \tag{11}$$

The uncertainties of the derived properties may be determined by error propagation, but the nature of excess properties makes this method of little use in the case of mixtures of alike molecules. Let's recall that either excess molar volume or enthalpy are properties of small absolute value obtained as the difference of quite large mixture and pure component values, so the individual uncertainties add up to a value that may even exceed the excess property value itself. A study of the influence of correlation between simulation run length and excess properties uncertainty might be helpful to elucidate the reliability of this calculation. In this case, we have decided to present the numerical values of density, configurational enthalpy, and their uncertainties determined by block averaging in Table II, and to plot the determined excess values without error bars.

IV. RESULTS AND DISCUSSION

We have applied the cited theoretical approaches to predict the excess thermodynamic functions of short linear alkanes binary mixtures. In particular, we focus on the excess molar volume and enthalpies of methane (1) + ethane (2), + propane (2), and + butane (2), and ethane (1) + propane (2) binary systems. In this case, we have paid special attention at the temperature and pressure conditions at which experimental data are available. In addition to that, we have also determined the phase equilibria at similar (T,P) conditions. This allows establishing the ability of the theory and the molecular model used in simulation for predicting both properties.

A. Methane (1) + ethane (2) binary mixture

We first consider the simplest binary mixture of short alkanes, i.e., the methane (1) + ethane (2) system. Before studying the excess properties, we have determined the phase equilibria at similar temperatures at which excess properties are evaluated. Figure 1 shows the Px slice of the phase diagram of methane (1) + ethane (2), at two different (low) temperatures, as predicted by SAFT-VR. The experimental data taken from literature at the same conditions are also displayed for comparison. As shown, SAFT-VR is able to provide an excellent description of the phase behaviour of the system at low temperatures. We should mention that theoretical results obtained from SAFT-VR are pure predictions since no binary parameters have been fitted.

Before presenting the results corresponding to the excess properties, it is important to recall the coordinates of the triple and boiling point (at atmospheric pressure) of the pure components that form the mixture in order to locate the thermodynamic coordinates at which the excess properties are evaluated. The low temperatures considered in the next figure (Figure 2) correspond to values above the experimental triple temperature[70], $T_t = 90.67 \pm 0.03$ K, and below the boiling temperature[70], $T_b = 111.0 \pm 2$ K, of the most volatile component (methane). Therefore, the system at 91.5 and 103.99 K (at 0.101 MPa) exhibits a homogeneous liquid phase over the whole composition range. Temperature 112.0 K (and pressure 0.101 MPa) is within the error reported of the experimental boiling temperature, and hence, the theoretical results for the system at these conditions will also exhibit a homogeneous liquid phase. On the other hand, at all temperatures considered in Figure 2 (b) and (d), the methane (1) + ethane (2) system lies above the critical point of pure methane[70], $T_c = 190.6 \pm 0.3$ K, and the boiling temperature of pure ethane[70], $T_b = 184.6 \pm 0.6$ K, so the system is in vapour phase.

Figure 2 shows the excess volume (V^E) and enthalpy (H^E) of the methane (1) + ethane (2) binary mixture, at atmospheric pressure. As can be seen, we have also included the MC results obtained (see Table II). Excess volume is an indicator of the degree of non-ideality on mixing between different species. The sign and shape of this property is due to two different contributions, one energetic depending of the difference in the interactions between different molecules, and another structural due to steric hindrance effects in the mixture caused by the arrangements of the involved molecular geometries. Figure 2a shows negative values of V^E in the whole composition range. All the curves exhibit clearly non-symmetric shapes, with a minimum displaced towards rich compositions of the more volatile component (methane). This property increases in magnitude, i.e., it becomes more negative, as the temperature is increased from 91.5 K to 112.0 K. Both MC and SAFT-VR results capture the essential features exhibited by the excess volume of this mixture. As can be seen, MC results are able to describe quantitatively the experimental data taken from the literature at the conditions considered here, while SAFT-VR overestimates the value of the excess volume.

Figure 2b shows the excess volume of the same binary mixture, methane (1) + ethane (2), but now at 0.101 MPa and higher temperatures, from 282.20 to 303.20 K. At these (T,p) conditions, excess volumes obtained from MC and SAFT-VR show positive values. Unfortunately, no experimental data from the literature is available. As temperature increases excess volume shift towards lower values. The SAFT-VR estimations underestimate remarkably the values obtained from MC.

It is very interesting to compare the behaviour of V^E at low (Figure 2a) and high (Figure 2b) temperatures. As can be seen, three interesting differences can be pointed out. First, V^E changes from negative values at low temperatures to positive values at higher temperatures. Second, the excess volume of mixing at high temperatures is an order of magnitude larger than that corresponding to low temperatures. And third, the excess volume, as a function of molar fraction, is a more symmetric function at higher temperatures. These differences are not unexpected since at lower temperatures the system exhibits a liquid phase where attractive interactions are relevant, while at higher temperatures the system is in vapour phase, in which repulsive interactions are predominant. Unfortunately, the large excess volume values predicted by MC in the gas region are not realistic if we take into account the asymmetry of the results and the large values obtained if compared with SAFT-VR estimations. Nevertheless, two facts should be considered. First, the molecular parameters of methane and ethane used were originally obtained by fitting simulation results to saturated liquid densities. As a consequence, the estimation of the liquid densities along the vapour-liquid phase envelope is better than those corresponding to the gas phase. Second, although the density estimation is still rather accurate for pure fluids, the densities of both components, methane and ethane, at the conditions studied are so close to each other that a variation in the mixture density within the statistical uncertainty obtained from MC produces a large variation in the excess volume. Due to that, the predictions presented in Figure 2b must be considered only qualitative in this case.

Concerning excess enthalpy, Figures 2c and 2d show the comparison of experimental literature values and the estimations obtained in this work. Let us recall that the excess enthalpy or heat of mixing is usually considered as the result of the difference in the strength of the interactions between unlike molecules in a solution. When a mixture of non-polar molecules is considered, the main energetic interaction between molecules is due to the so-called dispersive interactions, accounted for in this case by the interactions between individual segments in the SAFT-VR approach and the Lennard-Jones intermolecular potential in the case of MC. Other possible contributing interactions, as those between induced dipoles, are very weak in the case of short alkanes. In our particular case, the methane (1) + ethane (2) binary mixture constitutes a representative case of mixture formed by similar non-polar molecules. For this type of mixtures, it is very well known that interactions between unlike molecules are weaker than those between the same molecules (see for instance refs.[2,71]). As a consequence of this, the mixture exhibits positive heats of mixing, i.e., endothermic behaviour.

As said before, since methane and ethane are very similar molecules with weak interaction between both components, the mixture exhibits very low H^E values, specially in the vapour phase (see Figures 2c and 2d). As shown, the SAFT-VR approach is able to provide the correct picture of the excess heat as a function of composition. Although quantitative agreement is found at high temperatures (Figure 2d), only qualitative agreement is found at very low temperatures (Figure 2c). In the case of MC results, as it happened previously for V^E, H^E is calculated as the difference of two large quantities, producing very low values that are in the limit of sensitivity of the calculation method, with inaccurate results, specially in the vapour phase.

B. Methane (1) + propane (2) binary mixture

We now consider the effect of increasing the number of carbon atoms of one of the components on the phase equilibria and excess properties by changing ethane by propane. Figure 3 shows the Tx slice of the phase diagram of the methane (1) + propane (2) binary system at 0.101 MPa. As it can be seen, the SAFT-VR approach is able to provide an excellent description of the Tx diagram of the mixture. Although the theory overestimates the compositions of the vapour phase, especially at high temperatures, it is able to reproduce quantitatively the phase behaviour at the liquid phase. It is important to underline again that SAFT-VR results are pure predictions obtained from the values of the pure compound molecular parameters without need of further fitting.

Figures 4a and 4b show the excess volume of the methane (1) + propane (2) binary system at 0.101 MPa. We first consider the excess molar volume values at low temperatures (Figure 4a). The V^E curves are negative over the whole composition range and exhibit the same qualitative shape than in the previous system (see Figure 2a). As the chain length increases from ethane to propane, the V^E becomes more negative and the minimum of the curve shifts slightly towards methane-rich compositions. The theory is able to capture the essential features of this property, although it underestimates (overestimates in absolute value) both experimental and MC data. At the low temperatures considered in Figure 4a (91.5, 103.99, and 112 K), the methane (1) + propane (2) system is below both boiling points of pure components (111.0 ± 2 K[70] for methane and 231.1 ± 0.2 K[70] for propane) and therefore the system exhibits a homogeneous single liquid phase. As temperature increases above the boiling temperatures of both components (but still below the critical temperatures of methane, 190.6±3 K, and propane, 305.3±3 K), the excess volume curve changes, similarly to what happened in the previous mixture, and exhibits large positive values (see Figure 4b) with a nearly symmetric and quadratic shape with the maximum located at approximately equimolar compositions. Note that SAFT-VR estimations are now in better agreement with MC results, if compared with the previous case. Now, the difference in densities between both compounds is larger, and results obtained from MC are closer to literature experimental data since fluctuations associated to the calculated excess volume (due to statistical uncertainty) are lower. In addition, a temperature increase produces a decrease of the excess volume, although the shape of the curve is nearly identical. It is also interesting to mention that SAFT-VR predicts an increase of the excess volume values of nearly 300% when passing from methane (1) + ethane (2) to methane (1) + propane (2). This may be due to the increase of the asymmetry in size of the molecules , as it has been demonstrated previously for the case of binary mixtures of fully-flexible Lennard-Jones chains[4].

Figures 4c and 4d show the comparison between the literature experimental H^E values and the estimations. At low (liquid phase) and high (vapour phase) temperatures, the experimental (endothermic) H^E values are larger than those corresponding to the more symmetric methane (1) + ethane (2) mixture. Both SAFT-VR and MC are able to estimate the correct sign of the property. Unfortunately, both SAFT-VR and MC predictions are inaccurate in the liquid region, as it happened for the first mixture studied..

C. Methane (1) + n-butane (2) binary mixture

We have considered an additional increase of the asymmetry of the system, with the case of methane (1) + n-butane (2) binary mixture. Figure 5 shows the Tx slice of the phase diagram at 0.101 MPa. SAFT-VR estimations give a nice general picture of the phase behaviour at these conditions[72], using again only pure compound parameters. As before, the composition of the less volatile component of the mixture in the gas phase is slightly underestimated. However, estimations are able to reproduce the phase envelope of the liquid phase along the whole temperature range.

Figure 6a shows the excess volume of the system as obtained from SAFT-VR and MC at two different temperatures. Unfortunately, experimental data are scarce. To our knowledge, there is no experimental data at the selected conditions (0.1 MPa and 277 and 394.30 K), that have been chosen to keep the parallelism between both excess properties, as previously. Now, excess volume is nearly symmetric and the absolute value increases with the chain length of the second component.

Unfortunately, only the H^E data published by Hutchings *et al.*[73] is available in literature, and Figure 6b, shows that both theory and simulation are able to estimate it with good qualitative agreement. Although, in general, MC and SAFT-VR underestimate experimental data, both approaches are able to reproduce the most important features of this property.

D. Ethane (1) + propane (2) binary mixture

Finally, we have studied the ethane (1) + propane (2) binary mixture. This is an interesting case of study, first considered experimentally by Ott *et al.*[74] These authors measured both V^E and H^E at temperatures ranging from 273.15 to 373.15 K and pressures from 5 to 15 MPa. These conditions of temperature and pressure comprise an interesting combination of liquid and supercritical conditions for ethane and propane. As previously noted, the critical coordinates of ethane are $T_c = 305.3\,\mathrm{K}$ and $P_c = 4.91\,\mathrm{MPa}$, while those of propane are $T_c = 369.9\,\mathrm{K}$ and $P_c = 4.25\,\mathrm{MPa}$. This means that at 348.15 K, pure propane is liquid while ethane is supercritical. At these conditions, and due to the vicinity to the critical point, the estimation of excess properties is a remarkable challenge. On one hand, SAFT-like theories have been combined with different crossover treatments to take into account the long-range critical fluctuations and MC techniques are known to present finite size effects in the immediacy of the critical region due to the limited size of the simulating boxes.

In order to understand the behaviour obtained from theory and simulation we have obtained the vapour-liquid phase equilibria envelope of the mixture at 345.15 K, which is the temperature at which we have determined the excess properties of the system from SAFT-VR and MC and compared these predictions with the experimental data of Ott *et al.* As plotted in Figure 7, SAFT-VR predicts vapour-liquid phase separation at 5 MPa, as indicated by the corresponding (red) tie line, while the system exhibits a homogeneous liquid phase at higher pressures, i.e., above the critical pressure of the mixture at this temperature ($\sim 7.5\,\mathrm{MPa}$) and particularly at 15 MPa.

Figures 8a and 8b show the experimental data and estimations corresponding to the excess properties at these conditions. At 15 MPa, in the liquid region of the phase diagram, both V^E and H^E are negative and present low absolute values. In particular, SAFT-VR and MC estimations are very accurate when compared with experimental data (agreement can not be distinguished in the figure due to the scale used to represent the excess volume at both pressures). But the most interesting behaviour exhibited by the system, and predicted nicely by both approaches, corresponds to the results at 5 MPa. The figure shows that as the mixture concentration increases from $x_1 \sim 0$ (pure propane) to $x_1 \sim 0.35$, both V^E and H^E present very large negative values. Suddenly, both properties go through a discontinuous jump, indicated by straight lines in the figures, and for compositions in the range $x_1 \sim 0.43 - 1$, both excess properties become positive yielding a sigmoid behaviour. The discontinuity is a consequence of the transition from the liquid to the vapour side of the phase envelope at this pressure, as it has been shown previously on the Px slice of the phase diagram (see Figure 7). Taking into account the scenario at which these properties are calculated and that no mixing parameters have been fitted during the calculations, the estimations of both SAFT-VR and MC are remarkable. This includes not only the correct determination of the property values, but also the accurate location of the phase transition. The fact that neither combining parameters nor any critical region treatment have been iconsidered to obtain these estimations may be recalled again. This is a consequence of the physical soundness and wide range of applicability of the otherwise rather simple alkane molecular models considered.

Just as a hint to understand the difficulty of dealing with these excess properties in this near critical range, the approach presented in this work may be compared to the description by Kiselev and Rainwater[75]. These authors developed a scaling-law crossover thermodynamic model to describe excess properties of critical and supercritical binary mixtures. In their study the authors included, among others systems, the theoretical predictions of several thermodynamic properties of the ethane (1) + propane (2) binary mixture and the comparison with the experimental data of Ott *et al.*[74]. Their approach, which is very rigorous from a formal point of view and highly reliable as it includes critical effects, provides very accurate results. Unfortunately, it needs the mixture excess critical compressibility factor as input data, and several fitting parameters. The fact that the theoretical approaches used in this work provide results not too far away from these much more sophisticated theoretical model is to be highlighted as a proof of their reliability as estimative tools and their ability to describe the various trends and scenarios described using a very simplified molecular description.

V. CONCLUSIONS

The performance of the SAFT-VR molecular EoS and MC MS combined with an United-Atom molecular model for estimating excess thermodynamic properties (excess volume and enthalpy) of short flexible linear chain molecules has been tested. The homologous family of alkanes has been selected as benchmark to obtain quantitative results by comparing with experimental data when available. The study has been focused on the shortest chain molecules of this homologous family, because these molecules are very similar to each other, their densities are very close, their mutual energetic interactions are very weak, and the estimation of their phase equilibria and excess properties represents a demanding test for any theoretical approach. In this context, the choice of these short chain molecules represents a non favourable estimation scenario for any molecular theory. Bearing this in mind, the binary mixtures methane (1) + ethane (2), + propane (2), and + n-butane (2), and ethane (1) + propane (2) have been studied. For both theoretical approaches, the alkane molecular models, including their characteristic parameters values, were taken from literature. The mixture behaviour is purely predicted with the use of the Lorentz-Berthelot combining rules without the use of any additional fitting of mixing parameters. This allows to evaluate the soundness of the theories to describe real solutions and raises also the issue of the reliability of the available molecular parameters.

We have used both SAFT-VR and MC to predict the excess volume and enthalpy at different pressures and temperatures. In addition, we have also determined the phase behaviour at the same conditions using SAFT-VR. Both approaches are able to provide a qualitative description of the most important features of the excess properties. It is important to mention that SAFT-VR is able to predict quantitatively the phase behaviour of the systems for which experimental data are available. On the contrary, neither SAFT-VR nor MC are able to predict quantitatively both excess properties at all (T,p) conditions considered. However, a number of important features are predicted in a qualitative way. In particular: (1) the transition from small asymmetric negative excess volume values in the liquid region of each mixture to large positive symmetric representations of this magnitude in the vapour phase region; (2) the small positive values of the heat of mixing for both liquid and vapour regions of the mixtures, including the fact that changing from liquid to vapour conditions makes this property decrease by an order of magnitude; (c) the correct influence of chain length and temperature on the trends of both properties; and (d) the most convincing result underlining the robustness and versatility of both theories is the ability in locating the crossing of the vapour-liquid boundary for the ethane (1) + propane (2) mixture, and the accuracy in the estimation of the change of sign and absolute value of the excess properties, both in the liquid and supercritical regions.

Unfortunately, results are not quantitative in some cases, specially for mixtures formed by very similar molecules (e. g. methane (1) + ethane (2)). This fact is more evident for the estimation of excess enthalpies. In the case of MC simulation, the calculation method used, through the NPT ensemble, reaches the limit of sensitivity for these very symmetric mixtures of molecules, in which the very close densities, and the fluctuations within the statistical errors of density or internal energy, produce large variations in the excess properties. The results obtained improve their accuracy as the mixture becomes more asymmetric. Despite these quantitative differences, the success in the description of the trends of both excess properties for the family of molecules analyzed using simplified molecular models, containing only pure molecular parameters without further adjustment or not considering explicitly the effects of fluctuations near the critical region, deserves consideration. In summary, the results shown in this work represent a demonstration of the rigour and theoretical soundness of both theoretical approaches when applied to predict excess thermodynamics properties of these mixtures of short and alike chain molecules interacting via Lennard-Jones potentials. It is clear that further studies concerning the same study of excess properties described using molecular models involving more complex interactions would be desirable. An example of this might be the analysis of the excess properties of mixtures including associative molecules, as for instance alkanols, that would allow to discuss the ability of the representation of either hydrogen bonding and polarity effects through a simplified representation of point charges in MS, or the performance of different association schemes for SAFT EoS in this particular application. In any case, excess properties estimation is clearly an additional and revealing test to assess the performance of any fluid state thermodynamic theory, that should be used more often that it is actually done.

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REFERENCES

[1] J.-P. Hansen and I. R. McDonald. *Theory of Simple Liquids.* Academic Press, London, Academic Press, London, (1986).

[2] J. M. Prausnitz, R. N. Lichtenthaler, and E. G de Azevedo. *Molecular Thermodynamics and Phase Equilibria Calculations.* Prentice Hall, New Jersey, 1999.

[3] S. I. Sandler. *Models for Thermodynamics of Fluid-Phase Equilibria, 3rd Ed.* Marcel Dekker Inc., New York, 1994.

[4] F. J. Blas. *J. Phys. Chem. B*, 104:9239, 2000.

[5] A. Dominik, W. G. Chapman, M. Kleiner, and G. Sadowski. *Ind. Eng. Chem. Res.*, 44:6928–6938, 2005.

[6] M. Kleiner, F. Tumakaka, and G. Sadowski. *Structure and Bonding*, 131:75–108, 2009.

[7] M. S. Wertheim. *J. Stat. Phys.*, 35(19), 1984.

[8]M. S. Wertheim. *J. Stat. Phys.*, 35:35, 1984.

[9]M. S. Wertheim. *J. Stat. Phys.*, 42:459, 1986.

[10]M. S. Wertheim. *J. Stat. Phys.*, 42:477, 1986.

[11]M. S. Wertheim. *J. Chem. Phys.*, 85:2929, 1986.

[12]M. S. Wertheim. *J. Chem. Phys.*, 87:7323, 1987.

[13]G. Jackson, W. G. Chapman, and K. E. Gubbins. *Mol. Phys.*, 65:1, 1988.

[14]W. G. Chapman, G. Jackson, and K. E. Gubbins. *Mol. Phys.*, 65:1057, 1988.

[15]W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz. *Fluid Phase Equil.*, 52:31, 1989.

[16]W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz. *Ind. Eng. Chem. Res.*, 29 (8):1709, 1990.

[17]E. A. Müller and K. E. Gubbins. *Ind. Eng. Chem. Res.*, 40:2193, 2001.

[18]I. G. Economou. *Ind. Eng. Chem. Res.*, 41:953, 2002.

[19]P. Paricaud. *Fluid Phase Equilib.*, 194:87, 2002.

[20]S. P. Tan, H. Adridharma, and M. Radosz. *Ind. Eng. Chem. Res.*, 47:8063, 2008.

[21]C. McCabe and A. Galindo. *Applied Thermodynamics of Fluids (Chapter 8), pages 215-279.* The Royal Society of Chemistry, 2010.

[22]P. Ungerer, B. Tavitian, and A. Boutin. *Applications of Molecular Simulation in the Oil and Gas Industry.* Ed Technip, Paris, 2005.

[23]W. L. Jorgensen, J. D. Madura, and C. J. Swenson. *J. Am. Chem. Soc.*, 106:6638, 1984.

[24]M. G. Martin and I. J. Siepmann. *J. Phys. Chem. B*, 102:2569–77, 1998.

[25]S. K. Nath, F. A: Escobedo, and J. de Pablo. *J. Chem. Phys.*, 108:9905–11, 1998.

[26]C. Vega and A. López-Rodríguez. *J. Chem. Phys.*, 10:4223–33, 1996.

[27]P. Ungerer, C. Beauvais, J. Delhommelle, A. Boutin, B. Rousseau, and A. H. Fuchs. *J. Chem. Phys.*, 112:5499–510, 2000.

[28]G. Kaminski, E. M. Duffy, T. Matsui, and W. L. Jorgensen. *J. Chem. Phys.*, 98:13077, 1994.

[29]J. Potoff and J. I. Siepmann. *AIChE J.*, 47:1676–82, 2001.

[30]P. van der Ploeg and H. J. C. Berendsen. *J. Chem. Phys.*, 94:3721, 1982.

[31]V. Lagache, P. Ungerer, A. Boutin, and A. H. Fuchs. *Phys. Chem. Chem. Phys.*, 3:4333–9, 2001.

[32]V. Lagache, P. Ungerer, and A. Boutin. *Fluid Phase Equilib.*, 220:220–4, 2004.

[33]D. Bessières, S. L. Randzio, M. M. Piñeiro, Th. Lafitte, and J.-L. Daridon. *J. Phys. Chem. B*, 110:5659–64, 2006.

[34]D. Bessières, M. M. Piñeiro, G. S. de Ferron, and F. Plantier. *J. Chem. Phys.*, 133:074507, 2010.

[35]M. A. Amat and G. C. Rutledge. *J. Chem. Phys.*, 132:114704, 2010.

[36]E. Müller and A. Mejía. *J. Phys. Chem. B*, 115:12822–34, 2011.

[37]C. Nieto-Draghi, P. Ungerer, and B. Rousseau. *J. Chem. Phys.*, 125:044517, 2006.

[38]H. C. Tseng, J. S. Wu, and R. Y. Chang. *J. Chem. Phys.*, 129:014502, 2008.

[39]A. P. Malanoski and P. A. Monson. *J. Chem. Phys.*, 110:664–75, 1999.

[40]M. Cao and P. A. Monson. *J. Chem. Phys.*, 120:2980–8, 2004.

[41]R. Chitra and P. E. Smith. *J. Chem. Phys.*, 114(426-35), 2001.

[42]G. Milano and F. Müller-Plathe. *J. Phys. Chem. B*, 108:7415–23, 2004.

[43]D. González-Salgado and I. Nezbeda. *Fluid Phase Equilib.*, 240:161–6, 2006.

[44]H. Yu, D.P. Geerke, H. Liu, and W.F. van Gunsteren. *J. Comput. Chem.*, 27(1494-504), 2006.

[45] J. P. Carvalho, J. P. P. Ramalho, and L. F. G. Martins. *J. Phys. Chem. B*, 111:6437–43, 2007.

[46] Y. Zhong, G.L. Warren, and S. Patel. *J. Comput. Chem.*, 27:1142–52, 2008.

[47] G. Guevara-Carrión, C. Nieto-Draghi, J. Vrabec, and H. Hasse. *J. Phys. Chem. B*, 112:1664–74, 2008.

[48] Q. Zhang, X. Zhang, and D. Zhao. *J. Mol. Liq.*, 145:67–81, 2009.

[49] L. Zoranic, R. Mazighi, F. Sokolic, and A. Perera. *J. Chem. Phys.*, 130:124315, 2009.

[50] M. Ramos-Estrada, G. A. Iglesias-Silva, K. R. Hall, and F. Castillo-Borja. *J. Chem. Eng. Data*, 56:4461–5, 2011.

[51] F. J. Blas. *Mol. Phys.*, 100:2221, 2002.

[52] F. J. Blas and I. Fujihara. *Mol. Phys.*, 100:2823, 2002.

[53] M. C. dos Ramos and F. J. Blas. *J. Phys. Chem. B*, 109:12145, 2005.

[54] A. Gil-Villegas, A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson, and A. N. Burgess. *J. Chem. Phys.*, 106(10):4168, 1997.

[55] A. Galindo, L. A. Davies, A. Gil-Villegas, , and G. Jackson. *Mol. Phys.*, 2:1998, 93.

[56] C. McCabe and G. Jackson. *Phys. Chem. Chem. Phys.*, 1(9):2057, 1999.

[57] T. J. Boublík. *J. Chem. Phys.*, 53:471, 1970.

[58] G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland. *J. Chem. Phys.*, 54(1523), 1971.

[59] J. A. Barker and D. J. Henderson. *J. Chem. Phys.*, 47(8):2856, 1967.

[60] J. A. Barker and D. J. Henderson. *J. Chem. Phys.*, 47(11):4714, 1967.

[61] J. A. Barker and D. J. Henderson. *Rev. Mod. Phys*, 48(4):587, 1976.

[62] A. L. Archer, M. D. Amos, G. Jackson, and I. A. McLure. *Int. J. Thermophys.*, 17(1):201, 1996.

[63] G. Jackson and K. E. Gubbins. *Pure Applied Chemistry*, 61(6):1021, 1989.

[64] M. P. Allen and D. J. Tildesley. *Computer Simulation of Liquids.* Oxford Univ. Press, Oxford, 1987.

[65] D. Frenkel and B. Smit. *Understanding Molecular Simulation, 2nd Ed.* Elsevier, San Diego, 2002.

[66] D. P. Landau and K. Binder. *A Guide to Monte Carlo Simulation in Statistical Physics, 2nd Ed.* Cambridge Univ. Press, Cambridge, 2005.

[67] Towhee, http://towhee.sourceforge.net.

[68] M. G. Martin and J. I. Siepmann. *J. Phys. Chem. B*, 103:4508–17, 1999.

[69] J. S. Rowlinson and F. L. Swinton. *Liquids and Liquid Mixtures, 3rd Ed.* Butterworth Scientific, London, 1982.

[70] *NIST Chemistry Webbook*, http://webbook.nist.gov/chemistry/.

[71] J. M. Smith, H. C. Van Ness, and M. M. Abbott. *Introduction to Chemical Engineering Thermodynamics, 6th Ed.* McGraw Hill, New York, 2001.

[72] K. Watanabe, M. Kuroki, M. Ogura, and I. Saito. *Teion Kogaku*, 4:292, 1969.

[73] D. J. Hutchings, E. J. Lewis, and C. J. Wormald. *J. Chem. Thermodynamics*, 10:559, 1978.

[74] J. B. Ott, P. R. Brown, J. D. Moore, and A. C. Lewellen. *J. Chem. Thermodynamics*, 29:149, 1997.

[75] S. B. Kiselev and J. C. Rainwater. *J. Chem. Phys.*, 109:643, 1998.

[76] E. J. S. Gomes de Azevedo and J. C. G. Calado. *Fluid Phase Equilib.*, 49:21, 1989.

[77] R. C. Miller and L. A. K. Staveley. *Adv. Cryog. Eng.*, 21:8, 1976.

Table I. Optimized intermolecular potential parameters for the short linear alkanes used in the SAFT-VR approach[56].

Substance	m	λ	σ (Å)	ϵ/k_B (K)
methane	1.0000	1.444	3.670	168.8
ethane	1.3333	1.449	3.788	241.8
propane	1.6667	1.452	3.873	261.9
n-butane	2.0000	1.501	3.887	256.3

Table II. Density (ρ) and configurational entalphy ($\hat{h}$) values determined through NPT MC simulations for the binary mixtures studied. Estimated uncertainties are shown between parenthesis.

x_{C1}	ρ (kg/m^3)	$\hat{h}$ (kJ/mol)	ρ (kg/m^3)	$\hat{h}$ (kJ/mol)
methane (1) + ethane (2), $P = 0.101$MPa				
	T = 103.99 K		T = 303.20 K	
0.00	639(1)	−14.95(4)	1.200(3)	2.479(6)
0.25	600(2)	−13.07(6)	1.058(2)	2.489(7)
0.50	554(1)	−11.20(5)	0.918(2)	2.497(5)
0.75	498(1)	−9.32(3)	0.777(1)	2.504(4)
1.00	432.2(6)	−7.49(1)	0.639(1)	2.501(5)
methane (1) + propane (2), $P = 0.101$MPa				
	T = 90.68 K		T = 303.20 K	
0.00	734(1)	−20.72(4)	1.776(3)	3.674(8)
0.25	691(1)	−17.48(4)	1.489(4)	3.390(8)
0.50	634(2)	−14.28(5)	1.203(2)	3.098(6)
0.75	558(2)	−11.09(5)	0.921(2)	2.802(6)
1.00	451.1(5)	−7.91(1)	0.639(1)	2.502(4)
methane (1) + n-butane (2), $P = 0.101$MPa				
	T = 277.0 K		T = 394.3 K	
0.00	2.625(9)	6.77(2)	1.808(4)	9.83(2)
0.25	2.127(3)	5.672(6)	1.476(3)	8.190(7)
0.50	1.645(3)	4.551(8)	1.147(2)	6.548(5)
0.75	1.172(9)	3.42(6)	0.8197(8)	4.897(4)
1.00	0.704(2)	2.267(6)	0.4944(9)	3.241(6)
ethane (1) + propane (2), $T = 348.15$K				
	P = 5 MPa		P = 15 MPa	
0.00	409(7))	−7.1(2)	464(3)	−8.62(8)
0.25	323(12)	−6.1(3))	429(1)	−7.6(1))
0.50	112(2)	−0.56(7)	400(2)	−6.90(4)
0.75	87.8(9)	0.20(4)	368(1)	−6.13(3)
1.00	67.5(4)	0.69(2)	306(4)	−4.79(9)

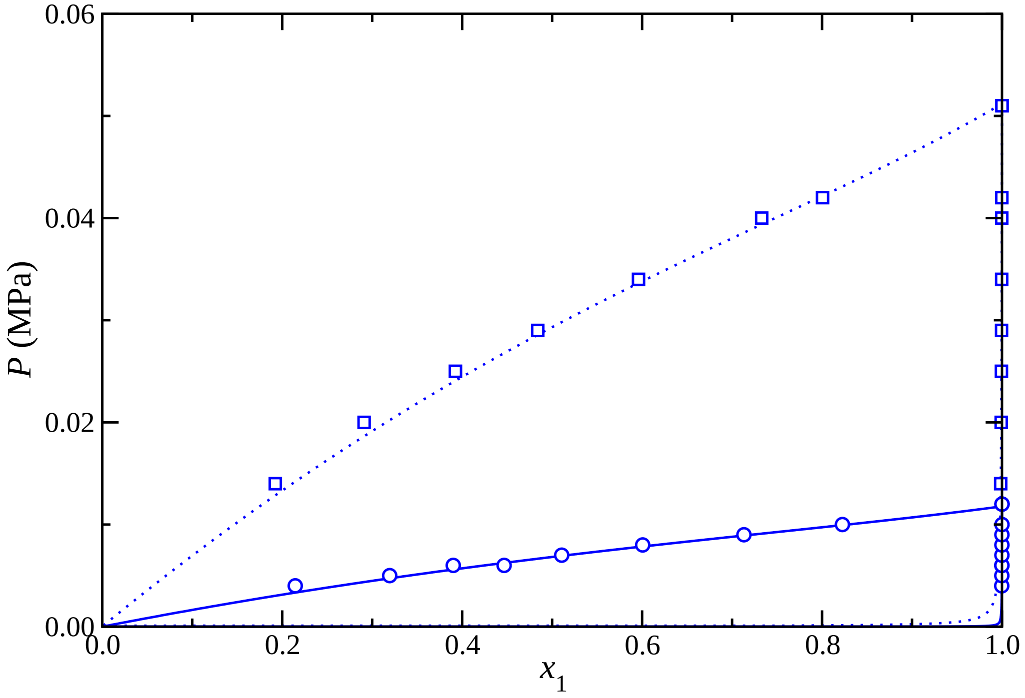

Figure 1. Px slice at 90.69 K (continuous curve and open circles) and 103.99 K (dotted curve and open squares) for methane (1) + ethane (2) binary system compared with the SAFT-VR predictions. The symbols correspond to the experimental coexistence curves[72,76] and the curves to the theoretical predictions.

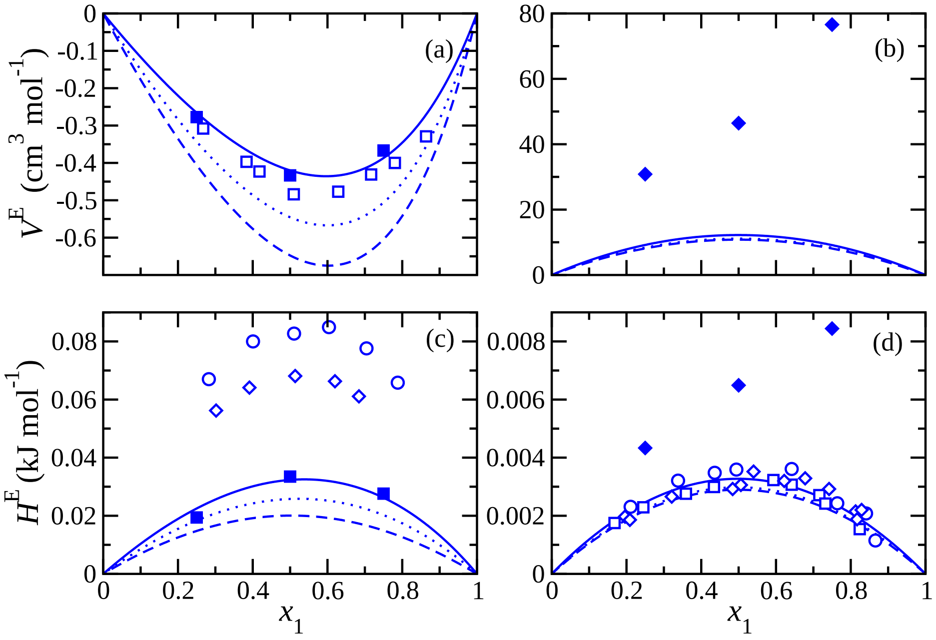

Figure 2. Excess molar properties of the methane (1) + ethane (2) binary mixture at 0.101 MPa. Open symbols are experimental data, curves correspond to SAFT-VR estimations, and filled symbols to simulation results. Excess molar volumes correspond to: (a) 91.50 K (continuous curve), 103.99 K (dotted curve, open[76] and filled squares), and 112.00 K (dashed curve); (b) 282.20 K (continuous curve), 298.20 K (dotted curve), and 303.20 K (dashed curve and filled diamonds). Excess molar enthalpies correspond to: (c) 91.50 K (continuous curve and open circles[77]), 103.99 K (dotted curve and filled squares), and 112.00 K (dashed curve and open diamonds[77]); (d) 282.20 K (continuous curve and open circles[73]), 298.20 K (dotted curve and open squares[73]), and 303.20 K (dashed curve, open[73] and filled diamonds).

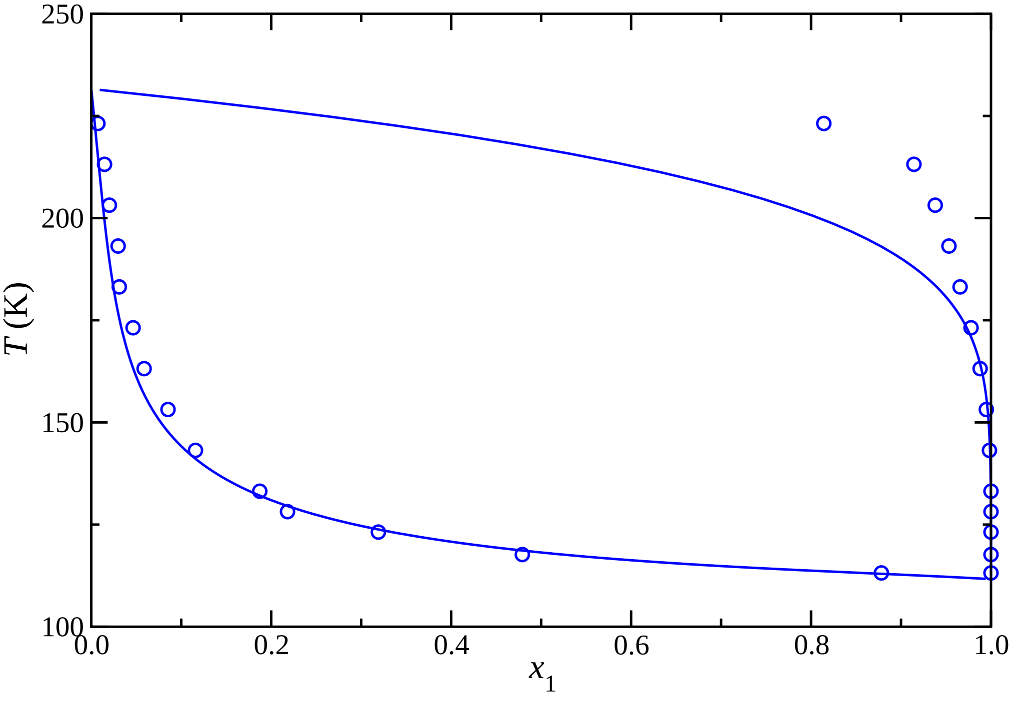

Figure 3. Tx slice at 0.101 MPa for methane (1) + propane (2) binary system compared with the SAFT-VR predictions. The symbols correspond to the experimental coexistence curves[72,76] and the curves to the theoretical predictions.

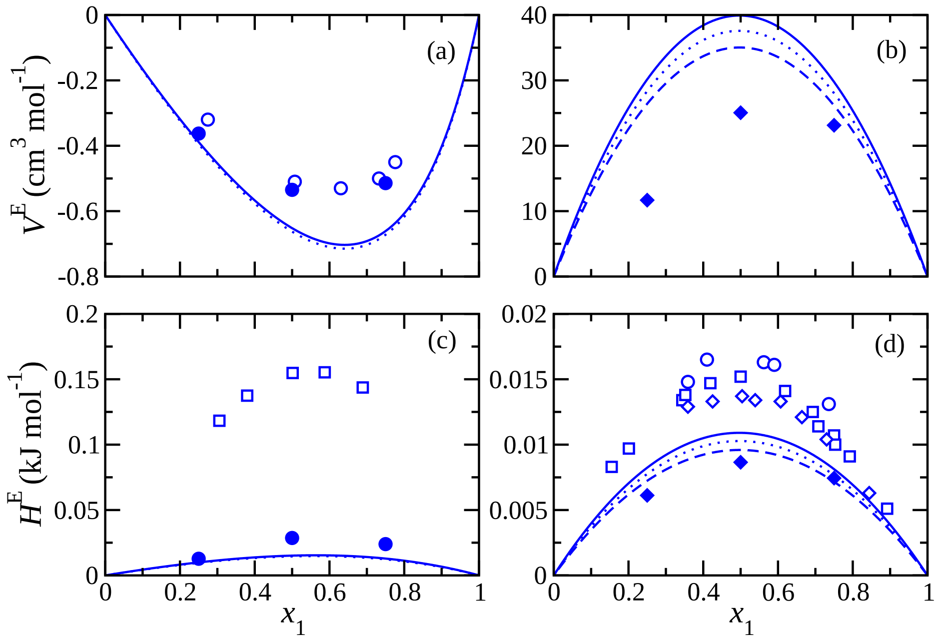

Figure 4. Excess molar properties of the methane (1) + propane (2) binary mixture at 0.101 MPa. Open symbols are experimental data, curves correspond to SAFT-VR estimations, and filled symbols to simulation results. Excess molar volumes correspond to: (a) 90.68 K (continuous curve, open[76] and filled circles) and 91.50 K (dotted line); (b) 281.20 K (continuous curve), 290.70 K (dotted curve), and 302.20 K (dashed curve and filled diamonds). Excess molar enthalpies correspond to: (c) 90.68 K (continuous curve and filled circles) and 91.50 K (dotted curve and open squares[77]); (d) 282.20 K (continuous curve and open circles[73]), 298.20 K (dotted curve and open squares[73]), and 303.20 K (dashed curve, open[73] and filled diamonds).

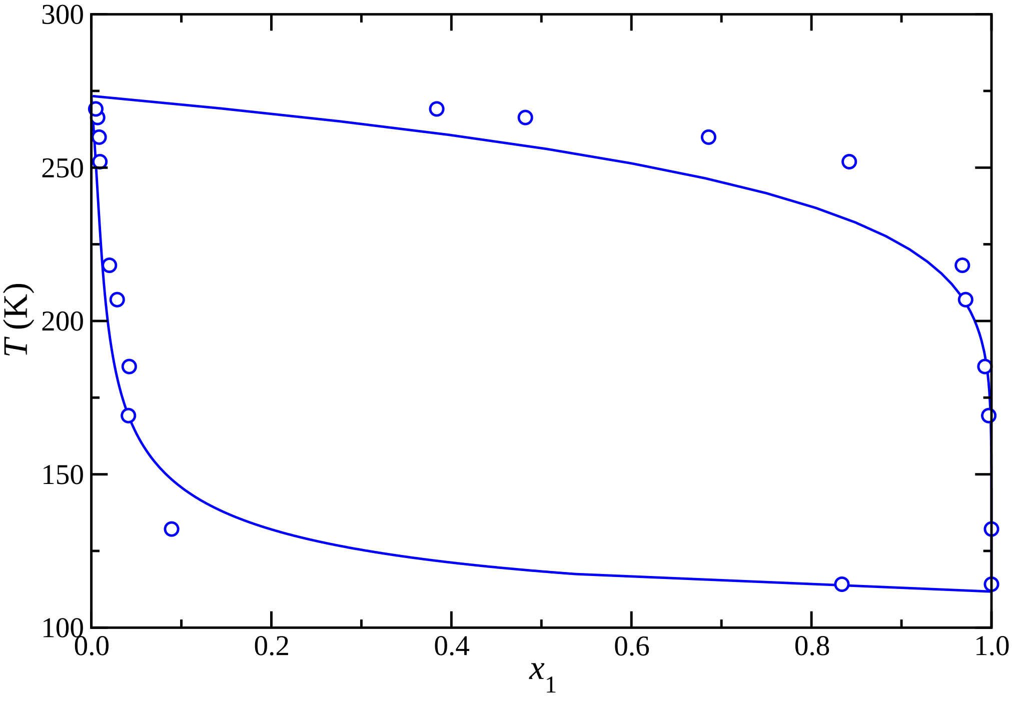

Figure 5. Tx slice of phase diagram corresponding to the vapour-liquid equilibria of the methane (1) + n-butane (2) binary system at 0.101 MPa. The curves correspond to the theoretical SAFT-VR predictions and symbols to the experimental data from Watanabe *et al.*[72]

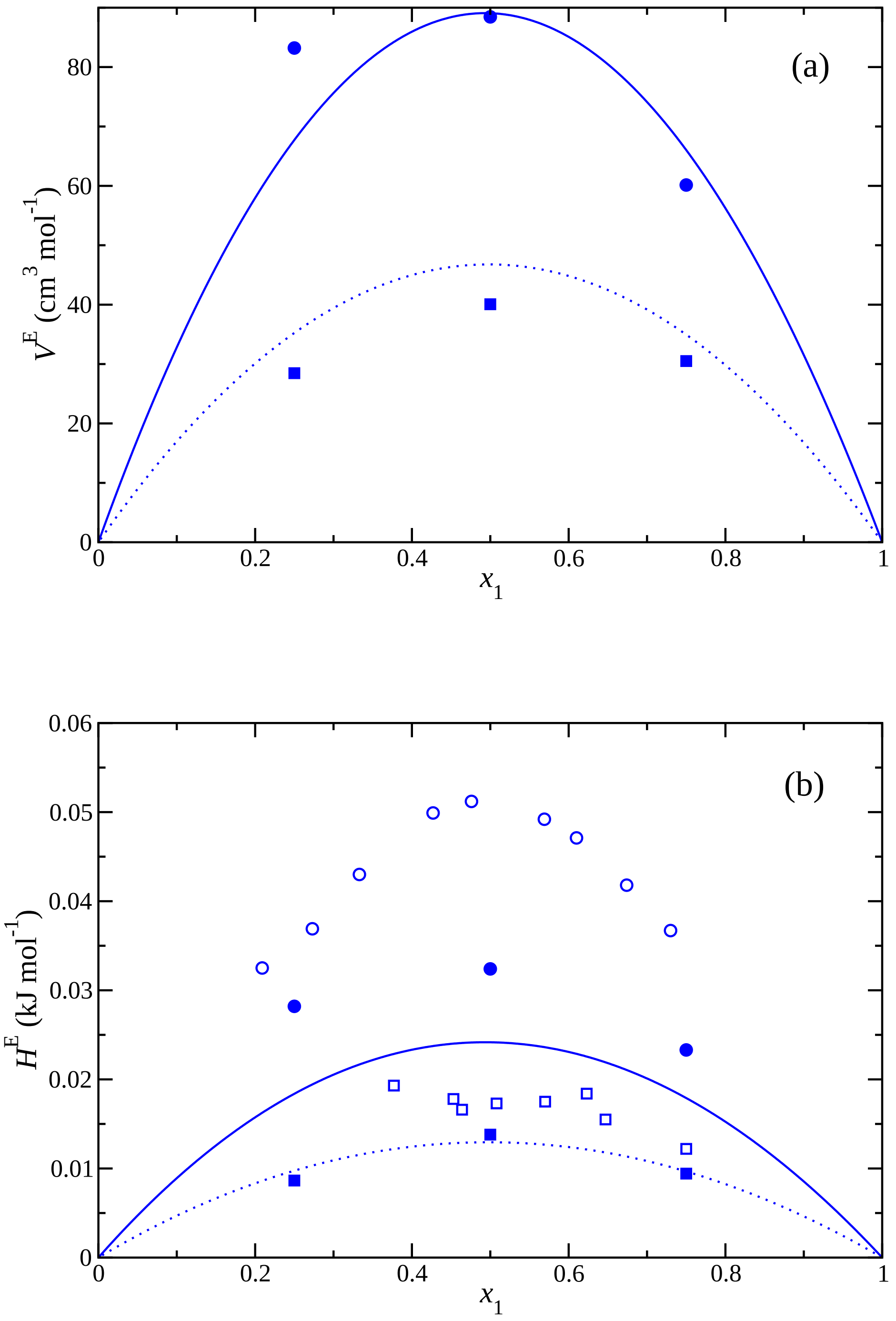

Figure 6. Excess molar properties of the methane (1) + n-butane (2) binary mixture at 0.101 MPa. Open symbols are experimental data, curves correspond to SAFT-VR predictions, and filled symbols to simulation results. Excess molar volume (a) and excess molar enthalpy (b) at 277.0 K (open circles[73], filled circles, and continuous curve) and 394.30 K (open squares[73], filled squares, and dotted curve).

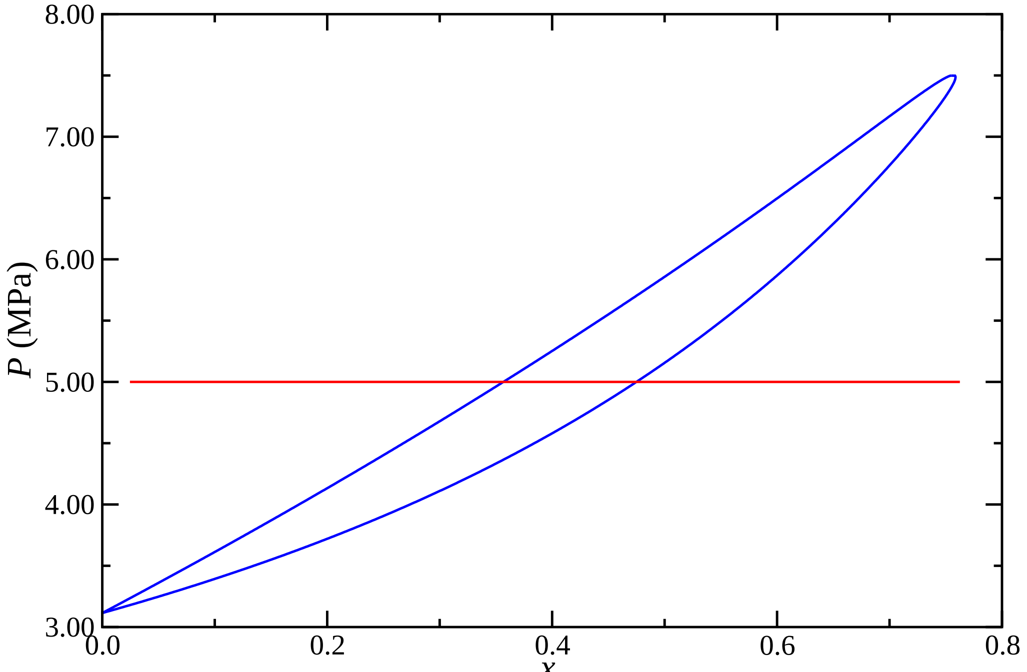

Figure 7. Px slice at 348.15 K for ethane (1) + propane (2) binary system obtained from the SAFT-VR approach. The horizontal line at 5 MPa, pressure at which the experimental excess properties have been estimated, has been plotted as a guide to the eye, showing the phase separation at compositions $x_1 = 0.375$ (liquid) and $x_1 = 0.475$ (vapour).

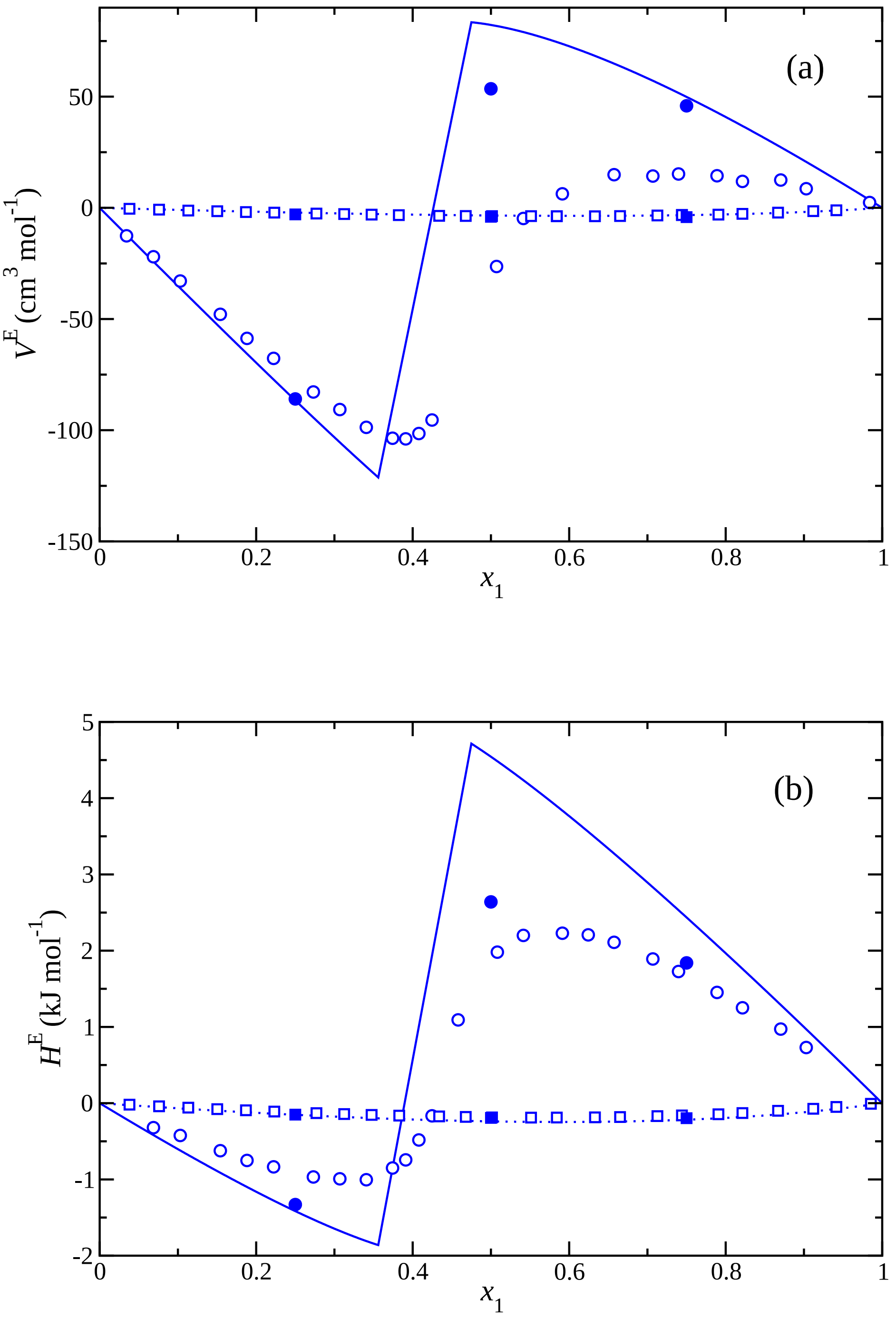

Figure 8. Excess molar properties of the ethane (1) + propane (2) binary mixture at 348.15 K. Open symbols are experimental data, curves correspond to SAFT-VR predictions, and filled symbols to simulation results. Excess molar volume (a) and excess molar enthalpy (b) at 5 MPa (open circles[74], filled circles, continuous curves) and 15 MPa (open squares[74], filled squares, and dotted curves).