Thermodynamic characterization of pure perfluoroalkanes, including interfacial and second order derivative properties, using the crossover soft-SAFT EoS

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ABSTRACT

Highly fluorinated molecules have proved to be versatile compounds that can be used for a large number of applications in different research fields including medicine, industry and environment. In this work we have used the soft-SAFT equation of state in its most general form, namely with the inclusion of a renormalization-group treatment and in combination with the van der Waals density gradient theory, to characterize several perfluorinated compounds in a systematic manner, and with the same tool. For this purpose, densities, vapour pressures, surface tensions, heat capacities and speed of sound were evaluated at different thermodynamic conditions including the critical region. The molecular parameters of the equation were obtained by fitting to vapour–liquid equilibrium data and used, in a transferable manner, to calculate the remaining properties. The specific renormalization-group treatment allowed quantitative agreement with experimental data far from and close to the critical point, with a unique set of parameters. The density gradient theory treatment enabled a precise evaluation of the surface tension, reproducing the low values experimentally observed. The transferability power of the equation allowed not only a very good description of phase and interfacial properties, but also a good accuracy when calculating derivative properties in one-phase equilibrium regions, in a purely predictive manner.

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1. Introduction

Fluorinated compounds have been a subject of study for more than 60 years. They were first synthesized during the World War II, as part of the Manhattan project, when scientists were looking for a material that was able to resist to chemical attack and with long-term thermal stability at high temperatures to serve as coating for volatile elements in radioactive isotope production. The importance of the inclusion of fluorine atoms in organic molecules is well documented from the number of publications/year regarding fluorinated compounds. Among them, perfluoroalkanes are probably the most commonly employed in industry. They are synthetic fluorinated hydrocarbons produced by replacing the hydrogen by fluorine atoms in organic compounds. These compounds are used in different fields like medicine, environment and industry and the number of their applications increases every year. They can be used as substitutes for chlorinated solvents, as co-solvents in supercritical extraction, as medium in two-phase reaction mixture and as refrigerants, among other applications.

From a chemical point of view, fluorine's high ionization potential and relatively low polarizability lead to weak intermolecular forces [1] which, together with the strong intramolecular bonds, are responsible for the unique properties that characterize these compounds [2]. As a result, perfluoroalkanes present the highest solubility towards gases known among organic liquids [3], an exceptional chemical and biological inertness, and excellent spreading characteristics. In addition, because of their low surface tension and refractive index, high viscosity, and gas solubility, most of the technological applications of perfluorinated alkanes occur at the interface. Understanding the structure and thermodynamic properties of the free surface of fluorocarbons is an area of fundamental and current interest with numerous technological implications [4]. It is widely accepted that the van der Waals interactions between highly fluorinated molecules are usually very small when compared to the corresponding non-fluorinated molecules. Therefore, the difference between the free energy of fluorinated molecules at the surface and in the bulk is also small,

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justifying the low surface tensions of perfluoroalkanes when compared with their corresponding alkanes and partially fluorinated compounds.

The obvious interest in perfluoroalkanes has given rise, as a consequence, to a considerable amount of papers devoted to the study of their thermodynamic properties. Some of the recent theoretical studies are based on refined molecular-based equations of state, being SAFT (the Statistical Associating Fluid Theory) one of the most applied ones, as a consequence of its success in both academic and industrial environments. SAFT [5] is an equation of state (EoS) fully based on statistical mechanics concepts. The equation, originally coming from Wertheim's theory [6–8] it is written as a perturbation theory, where the Helmholtz energy is calculated considering that the effects of molecular shape and interactions on the thermodynamic properties can be separated and quantified, given specific contributions to the total free energy. Different versions of SAFT, most of them dealing with a more refined reference term, have appeared in the late 90s, being the most popular ones soft-SAFT [9], SAFT-VR [10] and PC-SAFT [11]. The key of the success of SAFT-based equations for describing complex fluids is their physical interpretation of the system: the equation is constructed based on the intermolecular forces present into the systems, with molecular parameters with physical meaning and transferable. This theory has been proved to quantitatively predict thermodynamic properties, phase equilibrium of multi-component mixtures and solubilities in a broad range of systems (see, for instance, the review by Müller and Gubbins [12]). The success of this equation is demonstrated by the publication of more than 500 scientific articles in this field since its development, as well as the adoption of the equation by some process simulators.

Regarding the application of SAFT-based equations to fluorinated compounds, several works have been published using different versions of SAFT. The SAFT-VR version [10] was first used to describe the first four members of the linear perfluoroalkanes family. Some later works [13–16] completed the series till perfluorodecane. In previous works, we used the soft-SAFT equation [9] to calculate the phase equilibria of the first eight members of the linear perfluoroalkanes family, and some aromatics like perfluorobenzene and perfluorotoluene [3,17], as well as the behaviour of mixtures of perfluoroalkanes with other compounds. The PC-SAFT EoS [11] has also been recently used to estimate the phase equilibria diagrams of the first 5 members of the family [18] with correlated molecular parameters used to calculate heavier compounds.

Although all these works provided good agreement with experimental data, it is important to notice that in the above mentioned models, no special attention was given to the critical region of the phase diagram. It is known that classical thermodynamic models fail in this specific region because in their original development the long-wavelength density fluctuations that characterize the near-critical region are not explicitly taken into account. This matter can be solved by the addition of a specific treatment coming from the renormalization group (RG) theory [20,21] into any classical EoS. This treatment, usually called *crossover* (as there is a crossover between the classical and the non-classical behaviour) takes into account the inherent fluctuations of the critical region and corrects the prediction of the original equation, capturing the critical point without affecting calculations away from it. As we are interested in accurately characterizing fluorinated compounds for a wide range of conditions and properties, the use of a crossover equation is needed in order to precisely describe the near-critical region. To our knowledge, this is the first time a crossover equation is applied to perfluoroalkanes.

Another key point in the characterization of fluorinated compounds is the evaluation of their interfacial properties. The surface tension is a macroscopic thermodynamic property that is intimately associated to the microscopic structuring of molecules in the vapour–liquid interface. It is related to the difference between the intermolecular interaction in the bulk and at the surface as well as to molecular ordering and structuring. This was recently confirmed by the study of Sakka and Ogata [22], which reported the parachor parameter for different highly and partially fluorinated compounds, concluding that the former presented lower and constant parachor values suggesting a systematic stabilization due to the structuring of the molecules. It was demonstrated very recently that at the surface the chain segments are found to point perpendicular to the surface with the $-CF_3$ end groups at the surface. The amount of surface orientation of the chains strongly depends on temperature and also on chain length, where at a given temperature the ordering increases with increasing chain length [23]. Predicting the surface properties of fluorinated materials before their synthesis can provide the means to tailor their surface properties for specific applications.

Different methods/models can be used to correlate and/or predict the surface tension of heterogeneous fluids, such as the parachor method [24,25], the corresponding states principle [26], the perturbation theory [27], the density functional theory [28–31] and the density gradient theory [32,33]. The density gradient theory (DGT), based on van der Waals work [34], and widespread by Cahn and Hilliard [36], relates an EoS to interfacial properties. The theory explicitly considers the local free energy density within the interface, hence providing a route to obtain density profiles across the interface and the interfacial thickness, which cannot be calculated by empirical methods [37]. The theory results from a truncation of a general Landau expansion of the free energy in terms of the density profile where the free energy of a homogeneous theory is evaluated for every local density value, and extended by means of a term with a squared gradient of the density profile. This theory converts statistical mechanics of inhomogeneous fluids into a non-linear boundary value problem that can be solved to compute the density and the stress distributions at the interface [32]. The inputs to the gradient theory are the Helmholtz free energy density of the homogeneous fluid and the influence parameter of the inhomogeneous fluid. An advantage of this approach is that it is straightforwardly applicable to any EoS.

The coupling of DGT in SAFT-type equations has already been reported and proved to be successful when applied to the calculation of surface tension of model [32,38,39] and real fluids [37]. Although DGT has been largely applied to several systems, with special attention to alkanes [26,32,33,37], less work has been done in what concerns the modelling of the interfacial tensions of highly fluorinated compounds, despite its importance. Recently, Tsige and Grest [23] studied the surface properties of various perfluorinated alkanes by molecular dynamics simulations using two all-atom force fields. These authors obtained good predictions for liquid densities and surface tensions for short chains but the results were less accurate for longer chains at higher temperatures. Moreover, only a limited temperature range was investigated and no information was given about the behaviour of the models near to the critical point. Oliveira et al. [40] coupled DGT with the CPA EoS to describe the surface tensions of a broad range of homologue families of non-associating (*n*-alkanes and *n*-fluoroalkanes) and associating components (*n*-alkanols). The authors used a quadratic correlation of the influence parameter in *Tr* obtaining accurate estimations of surface tensions in the 0.45 < *Tr* < 0.85 range.

Finally, almost no modelling work on the derivative properties of perfluoroalkanes has been done until now. This is one of the stringiest tests that can be done to any equation of state, as these properties are second order derivatives from the Helmholtz energy of the system and are very sensitive to errors. The most interesting contribution related to the present work was done by Jin et al. [41] who measured heat capacities of heavy perfluoroalkanes from the solid till the gas phase. By considering previously

measured data for light perfluoroalkanes, they established some heat capacity temperature-dependent correlations for the CF_2 and CF_3 groups. To our knowledge, no estimation of derivative properties has been performed using either a classical or a molecular-based EoS.

In this work, we use the soft-SAFT EoS [9] improved with a crossover term [42] based on Wilson's renormalization group (RG) theory [20,21] and combined with the Cahn–Hilliard DGT to characterize a wide selection of fluorinated compounds. The approach is similar to the work of Fu [43], where he employed the original SAFT EoS [5] with the same RG theory and DGT treatment to study the vapour–liquid equilibria and surface tension of the first ten members of the n-alkanes family. In the work presented here, phase equilibrium, interfacial tension, heat capacities, compressibility and speed of sound of linear and aromatic perfluoroalkanes were calculated in a wide range of temperature and pressure, and compared to experimental data. The characterization was done systematically, with particular emphasis on the equation parameters transferability. Molecular parameters were optimized for phase equilibrium calculations and then transferred to evaluate surface tension and derivative properties. The rest of the paper is organised as follows: the next section is devoted to a brief description of the different modelling tools and treatments that are used in this work, with appropriate references for further details. Section 3 includes results concerning the throughout characterization of perfluoroalkanes and other fluorinated compounds while Section 4 gives the main conclusions of this work.

2. Model

2.1. The soft-SAFT equation of state

All SAFT-type equations are written as a sum of contributions to the total energy of the system, in which the molecular effects are separated and quantified. Soft-SAFT [9] mainly differs from the original SAFT in the reference term, which is a Lennard Jones (LJ) fluid, instead of a hard sphere plus a perturbative attractive term. The LJ fluid accounts for both the repulsive and attractive interactions of the monomers forming the chain in a single term. Hence, the Helmholtz free energy density of these systems is given as:

$$a_0 = a^{id} + a^{ref} + a^{chain} \tag{1}$$

where a^{id} states for the ideal term, a^{ref} refers to the Helmholtz energy density of the reference LJ fluid and a^{chain} is the chain term coming from the TPT1 approximation of Wertheim's theory. Further details regarding the theory and its implementation have been widely revised and can be found in the literature [44–47].

Linear perfluoroalkanes can be described as non-associating homonuclear chains and hence the system is characterized with the terms provided in Eq. (1). The characterization of perfluorobenzene and perfluorotoluene includes the modelling of the experimentally observed quadrupole moment [48]. The framework of SAFT offers the possibility of adding a new term into the equation to explicitly consider quadrupolar interactions. Eq. (1) is rewritten as:

$$a_0 = a^{id} + a^{ref} + a^{chain} + a^{polar} \tag{2}$$

The polar term is calculated by mean of an expansion of the Helmholtz energy in terms of the perturbed quadrupole-quadrupole potential with the Padé approximation proposed by Stell et al. [49].

2.2. Renormalization group theory corrections

Although the original soft-SAFT provides an excellent overall description of bulk properties of perfluoroalkanes, it still fails in

the critical region, due to its classical formulation [17]. Hence, in order to capture the non-classical behaviour in the near-critical region it is thus necessary to couple it with a theory that explicitly considers these fluctuations. The implementation of a crossover treatment based on the renormalization group theory developed by Wilson [20,21] was done using a numerical approach proposed by White [50] and applied to the soft-SAFT equation of state by Llovell et al. [42]. The contribution of the long-wavelength density fluctuations is taken into account through the phase-space cell approximation [42,50]. In a recursive manner, the Helmholtz free energy per volume of a system at density ρ is described as [51,52]:

$$a_n(\rho) = a_{n-1}(\rho) + da_n(\rho) \tag{3}$$

being

$$a_0(\rho) = a^{\text{soft-SAFT}} \quad (classical) \tag{4}$$

where a is the Helmholtz free energy density and da_n the term where long-wavelength fluctuations are accounted for in the following way:

$$da_n(\rho) = -K_n \ln \frac{\Omega_n^s(\rho)}{\Omega_n^l(\rho)} \tag{5}$$

being $\rho = \min(\rho, \rho_{\max} - \rho)$ where $\rho_{\max}$ is the maximum possible molecular density and it depends on the selected model. In this work it was defined as:

$$\rho_{\max} = \frac{1}{mN_A\sigma^3} \tag{6}$$

Ω^s and Ω^l represent the density fluctuations for the short-range and long-range attraction, respectively, and K_n is a coefficient:

$$K_n = \frac{k_B T}{2^{3n}L^3} \tag{7}$$

where T is the temperature and L the cut-off length.

$$\Omega_n^\beta(\rho) = \int_0^\rho \exp\left[\frac{-G_n^\beta(\rho, x)}{K_n}\right] dx \tag{8}$$

$$G_n^\beta(\rho, x) = \frac{\bar{a}_n^\beta(\rho + x) + \bar{a}_n^\beta(\rho - x) - 2\bar{a}_n^\beta(\rho)}{2} \tag{9}$$

The superindex β refers to both long (l) and short (s) range attraction, respectively, and G^β is a function that depends on the evaluation of the function $\bar{a}$, calculated as:

$$\bar{a}_n^l(\rho) = a_{n-1}(\rho) + \alpha(m\rho)^2 \tag{10}$$

$$\bar{a}_n^s(\rho) = a_{n-1}(\rho) + \alpha(m\rho)^2 \frac{\phi w^2}{2^{2n+1}L^2} \tag{11}$$

where m is the LJ segment parameter, ϕ an adjustable parameter, α is the interaction volume with units of energy volume, and w refers to the range of the attractive potential. For the LJ fluid, α and w are given by

$$\alpha = \frac{16\pi\varepsilon\sigma^3}{9} \tag{12}$$

$$w^2 = \frac{9\sigma^2}{7} \tag{13}$$

For a detailed explanation about the previous procedure and some numerical aspects, the reader is referred to Ref. [42].

2.3. The density gradient theory (DGT)

Once an accurate model for the whole phase equilibrium envelope is constructed, we can proceed to the study of interfacial properties, as the success of the description will depend on the underlying theory for the bulk. Interfacial properties also require

a specific theory to be coupled to soft-SAFT, as the Helmholtz free energy of the system becomes a functional of the density $\rho(r)$ in the interface. The density gradient theory (DGT) approach was selected for this purpose. DGT was firstly proposed by van der Waals [34,35] and rediscovered by Cahn–Hilliard theory [36]. It describes the thermodynamic properties of a system with an interface between two fluid phases. In the interface between the liquid and the gas phase of a pure substance in thermodynamic equilibrium, the density, ρ, varies continuously from the bulk liquid density, ρ_L, to the vapour density, ρ_V. The assumption that the density gradient is small compared to the reciprocal of the intermolecular distance allows the treatment of the density, ρ, and its derivatives, as independent variables. This means that the total Helmholtz energy, A, of a system with an interface can be obtained by expanding the Helmholtz energy, A, in a Taylor series around the equilibrium bulk state. Following Cahn and Hilliard [36] one finds for the Helmholtz energy:

$$A[\rho(r)] = \int dr \left\{ a(\rho(r)) + \frac{c}{2}[\nabla\rho(r)]^2 \right\} \tag{14}$$

where a is the Helmholtz free energy density of the bulk phases, $\rho(r)$ is the molecular density profile, and c includes the direct correlation function among the molecules, although it is usually treated as an adjustable parameter, the so-called influence parameter. For a planar interface, the functional minimization of Eq. (14) for phase coexistence conditions leads to the following expression for the surface tension:

$$\gamma = \int_{\rho_v}^{\rho_l} d\rho \sqrt{2c\Delta\omega(\rho)} \tag{15}$$

where the integration takes place from the vapour bulk densities to the liquid one and $\Delta\varpi$ is the excess grand free energy density:

$$\Delta\varpi(\rho) = a(\rho) - \mu\rho + p/k_BT \tag{16}$$

where p and μ are the equilibrium pressure and chemical potential, k_B is Boltzmann's constant and T is the temperature. The density profiles can be obtained by inversion of the following expression:

$$z = z_0 + \int_{\rho(z_0)}^{\rho(z)} d\rho \sqrt{\frac{c}{2\Delta\varpi(\rho)}} \tag{17}$$

where z_0 is some arbitrarily chosen position.

2.4. Thermodynamic derivative properties

The thermodynamic characterization of perfluoroalkanes can be completed with the calculation of some derivative properties. These are second order derivatives obtained from the main thermodynamic function. They can be obtained by derivation with respect to the temperature and density, and all of them are connected by straightforward mathematical relationships. They represent a strong test for any equation of state, as they are very sensitive to errors in the model. In this work we focus in the most important derivative properties namely, the heat capacity, the compressibility and the speed of sound. All the mathematical expressions for their calculation and the way to proceed from the original soft-SAFT are described in previous works [42,53].

3. Results and discussion

The main results for the application of the generalized soft-SAFT equation to the main thermodynamic properties of perfluoroalkanes as compared to available experimental data are presented in this section. Results are divided into three main blocks: phase equilibria, interfacial properties and second order thermodynamic properties.

Table 1
Optimized molecular parameters for linear (C_1–C_8) and aromatic perfluoroalkanes (C_6F_6 and C_7F_8). See text for details.

Molecular formula	m	σ (Å)	ε/k_B (K)	ϕ	L/σ
CF_4	1.025	4.152	182.0	5.00	1.04
C_2F_6	1.390	4.335	203.8	5.50	1.10
C_3F_8	1.750	4.400	216.0	6.12	1.16
C_4F_{10}	2.134	4.430	222.5	6.63	1.22
C_5F_{12}	2.470	4.460	229.0	7.10	1.27
C_6F_{14}	2.750	4.475	234.0	7.45	1.33
C_7F_{16}	3.160	4.485	236.5	7.72	1.38
C_8F_{18}	3.510	4.500	239.0	8.10	1.43
C_6F_6	3.148	3.655	257.0	7.75	1.35
C_7F_8	3.538	3.770	255.0	8.55	1.44

The inclusion of the crossover treatment requires the adjustment of two additional parameters, the cut-off length L, related to the maximum wavelength fluctuations that are accounted for in the uncorrected free energy and ϕ, the average gradient of the wavelength function [51]. Llovell et al. [42] applied the crossover soft-SAFT to linear alkanes treating both L and ϕ as adjustable parameters. These authors tested the accuracy of the crossover soft-SAFT equation by comparison with molecular simulations of LJ chains and did several studies about the influence of both values ϕ and L in predicting the phase envelope when compared to simulation data. The model was then applied to experimental systems of chainlike molecules, the n-alkane series, providing a set of transferable parameters equally accurate far from and close to the critical region. The same procedure was used for studying the n-alkanol series [53]. This is the approach we have followed in this work.

As in previous works [3,54,55], n-perfluoroalkanes are described as homonuclear chainlike molecules, modelled as m LJ segments of equal diameter σ, and the same dispersive energy ε, bonded tangentially to form the chain. According to the crossover model, these three molecular parameters plus the crossover parameters ϕ and L, are enough to describe all thermodynamic properties. To minimize the number of adjusted parameters, the L/σ ratio used in the present work was transferred from the n-alkane series [42]. It was assumed that L depends proportionally on the segment diameter of perfluoroalkanes in the same way as it does for n-alkanes. This hypothesis is based on the analogy in the structures between alkanes and perfluoroalkanes. Their difference in terms of critical volumes (within a ratio of 3:2) is taken into account in the σ value. A new set of parameters, obtained by fitting experimental saturated liquid densities and vapour pressures is presented in Table 1. With this set, crossover soft-SAFT is able to simultaneously describe the vapour–liquid equilibrium diagram far from and close to the critical region. As for other chemical families we have found a linear correlation between the optimized parameters for the first eight members of the perfluoroalkanes series and the number of carbons in the molecule, given by

$$m = 0.689 + 0.352\,CN \tag{18}$$

$$m\sigma^3 = 43.05 + 34.65\,CN \tag{19}$$

$$m\varepsilon/k_B = 98.29 + 92.55\,CN \tag{20}$$

$$m\phi = 1.08 + 3.33\,CN \tag{21}$$

$$mL/\sigma = 0.11 + 0.12\,CN \tag{22}$$

where CN represents the number of carbons in the linear molecular chain.

The correlation coefficients for each of the linear relations is higher than 0.995 in all cases. As stated, the reduced L parameter (L/σ) used is the same as for the equivalent compound in the n-alkanes series. The molecular parameters show the expected trends

Table 2
Critical constants for linear (C_1–C_9) and aromatic perfluoroalkanes. Comparison between experimental data and predictions given by the soft-SAFT EoS with and without crossover.

Compound	T_c (K)			P_c (MPa)			ρ_c (mol/L)		
	Exp	Soft-SAFT	Crossover soft-SAFT	Exp	Soft-SAFT	Crossover soft-SAFT	Exp	Soft-SAFT	Crossover soft-SAFT
CF_4	227.6	249.6	227.6	3.74	4.55	3.65	7.16	6.86	8.23
C_2F_6	292.8	314.0	292.4	3.04	3.72	2.96	4.51	4.44	5.17
C_3F_8	345.1	370.1	344.6	2.67	3.26	2.56	3.34	3.18	3.81
C_4F_{10}	386.4	417.5	386.8	2.31	2.93	2.19	2.52	2.46	2.92
C_5F_{12}	421.9	460.7	421.6	2.04	2.67	1.94	2.11	1.99	2.40
C_6F_{14}	448.8	498.4	448.2	1.88	2.43	1.78	1.65	1.65	2.00
C_7F_{16}	474.8	533.3	474.2	1.62	2.23	1.51	1.51	1.40	1.78
C_8F_{18}	498.5	559.7	497.0	1.55	2.05	1.36	1.39	1.21	1.52
C_9F_{20} [a]	524.0	583.3	517.5	1.56	1.88	1.27	–	1.06	1.47
C_6F_6	516.7	555.84	516.2	3.23	4.44	3.03	2.98	2.67	3.36
C_7F_8	534.5	578.67	534.6	2.71	3.64	2.60	2.34	2.08	2.70

[a] Critical values extrapolated from the correlations obtained for the linear perfluoroalkane series from C_1 to C_8.

corresponding to their physical meaning: the value of the LJ diameter, σ, obtained for the perfluoroalkanes molecules is higher than the corresponding one obtained for alkanes [42] for the same carbon number, capturing the larger size of the fluorine atom when compared to the hydrogen atom. Moreover, the energy parameter, ε, is slightly lower in the case of perfluoroalkanes simulating the lower interactions that are reported in the literature for these compounds due to strong repulsive forces originated by the large electron density involving the fluorine atom. Finally, the crossover ϕ parameter is slightly smaller in the case of perfluoroalkanes when compared with the corresponding alkanes [42]. It is believed that this is the way the model captures the higher density and low compressibility that perfluoroalkanes exhibit in the critical region.

The experimental critical temperature, pressure and density and those predicted from the original soft-SAFT and crossover soft-SAFT for the first eight members of the perfluoroalkane series are presented in Table 2. Experimental data was taken from the works of Smith and Srivastava [56] and Vandana et al. [57]. While the original soft-SAFT overestimates the critical temperature and pressure, as expected, crossover soft-SAFT is able to predict the critical properties with high accuracy. However, as already observed by other authors using a similar approach, the critical density is still slightly overestimated. Using the correlations from Eqs. (18) to (22), the parameters for perfluoro-n-nonane were calculated and from them, the critical properties of this compound were also estimated. Results are also presented in Table 2. Agreement between experimental and predicted values is fairly good especially knowing that, as stated by Vandana et al. [57], the experimental critical properties for perfluoro-n-nonane might be slightly over estimated. Fig. 1 compares results of VLE calculations with experimental data taken from the literature [19,55,58] for the eight first members of the n-perfluoroalkane series when the crossover treatment is included. Agreement is excellent in all cases, including the critical region. The vapour pressures for the same members of the series are depicted in Fig. 2. Again, excellent agreement is obtained in all cases.

One of the main advantages of having a molecular-based equation for these systems is that once the molecular parameters are obtained from vapour–liquid equilibrium data, they can be used to calculate other thermodynamic properties for which experimental data is more difficult to obtain. If experimental data is available, the comparison of the experimental results with those obtained from the model reinforces the transferability of the molecular parameters, or highlights the need for further improvements. In this work we use the molecular parameters obtained by fitting vapour–liquid equilibria to calculate the interfacial properties of perfluoroalkanes with the same soft-SAFT model. As some of the most important applications of perfluoroalkanes are related to interfacial proper-

ties, having an accurate knowledge of the interface width will help to optimize some of their applications.

When applying DGT to calculate interfacial properties, the influence parameter needs to be optimized for each pure compound using experimental surface tension data. For this purpose we have used all available data, including data measured close to the critical region. The fitted values are well correlated using the following parabolic function:

$$c_{\text{perfluoroalkane}} = 1.403 \times 10^{-20} \, CN^2 + 5.064 \times 10^{-20} \, CN$$
$$- 1.295 \times 10^{-20} \tag{23}$$

where c is expressed in $\text{J m}^5/\text{mol}^2$.

The results obtained when using the crossover soft-SAFT EoS combined with the DGT to describe the surface tensions of linear series of perfluoroalkanes are given in Fig. 3. The results are excellent especially if we bear in mind that surface tension experimental data for perfluoroalkanes found in the literature present a significant dispersion in most cases [58–60]. When crossover soft-SAFT is used in combination with DGT, the surface tension is well described for the whole range of temperatures including the critical region, following the asymptotic behaviour in the neighbourhood
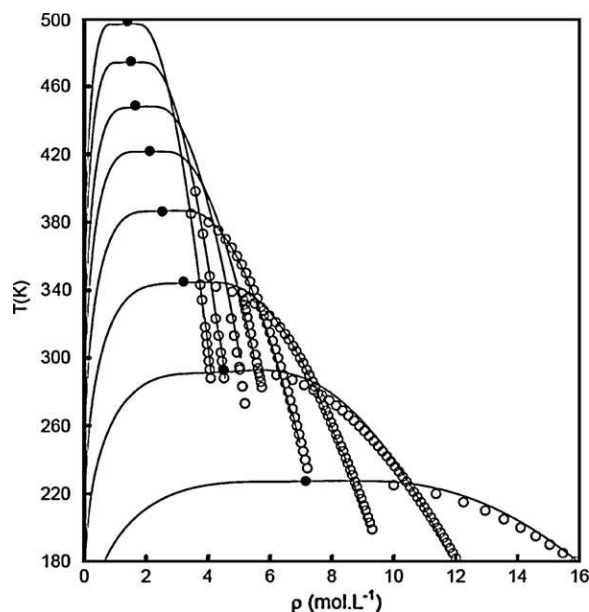

Fig. 1. Temperature–density diagram for the first eight members of the n-perfluoroalkane series from C_1 to C_8. Symbols represent the experimental data and solid lines the results obtained with crossover soft-SAFT.
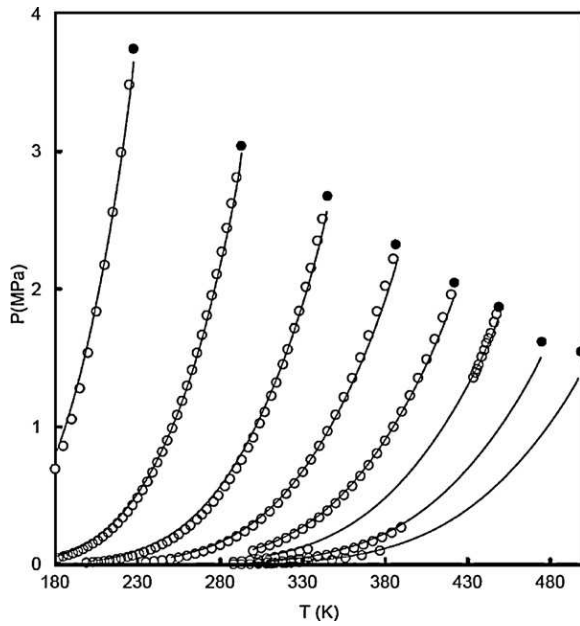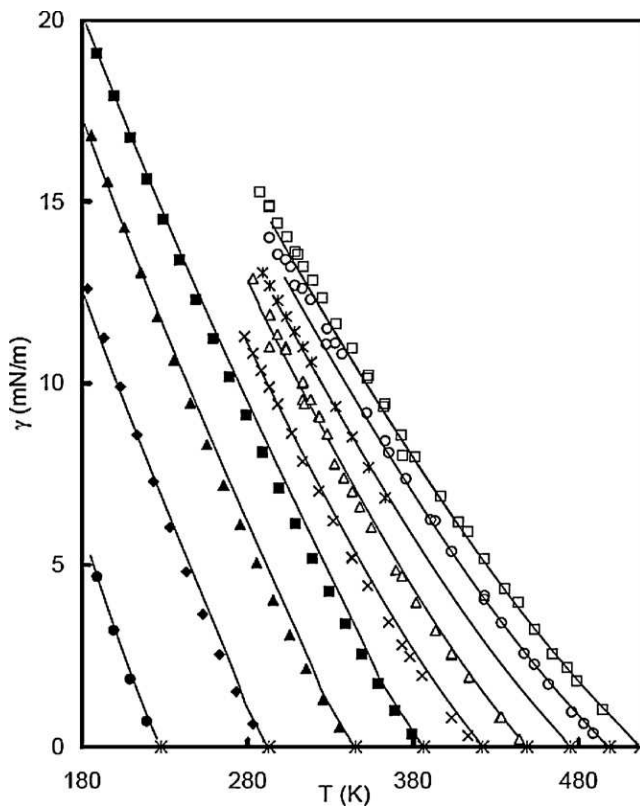
Fig. 2. Temperature–vapour pressure diagram for the first eight members of the *n*-perfluoroalkane series from C_1 to C_8. Symbols represent the experimental data and solid lines the results obtained with crossover soft-SAFT.

Fig. 3. Vapour–liquid interfacial tensions (IT expressed in mN m^{-1}) of *n*-perfluoroalkanes from C_1 to C_9. Symbols represent experimental data and lines correspond to crossover soft-SAFT combined with the DGT approach. The asterisk represents the critical temperature of the pure compounds. Experimental data was taken from Refs. [58–60].
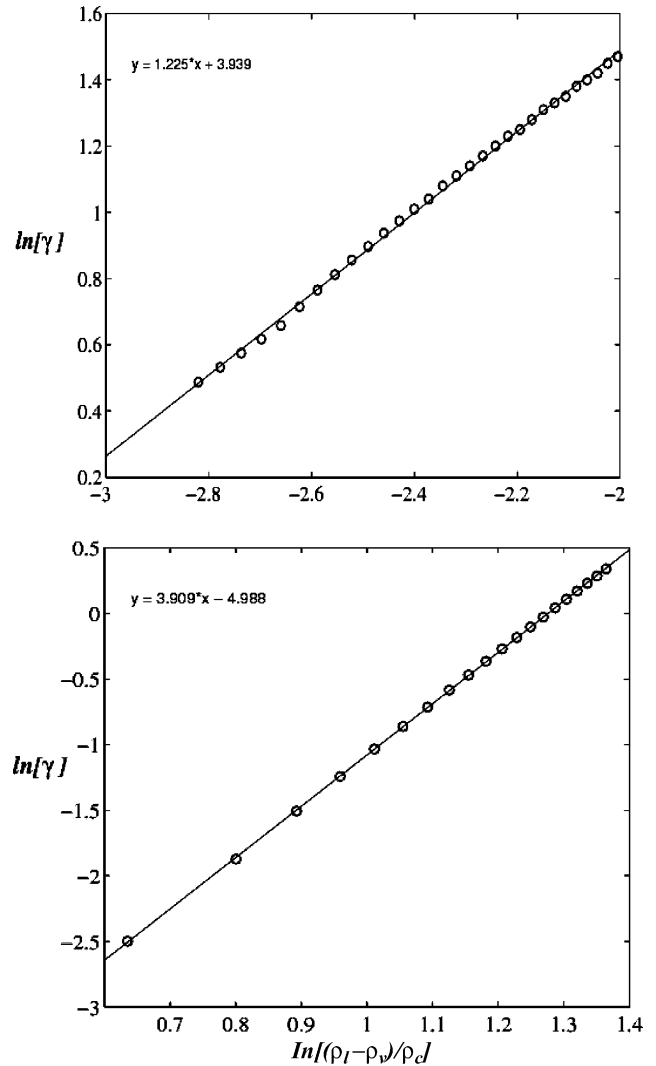

Fig. 4. Calculation of the critical exponents of the interfacial tension for perfluorobutane (a) temperature related coefficient and (b) density related coefficient. Symbols represent crossover soft-SAFT calculations and the solid line is the regression line.

of the critical point. This can be corroborated by calculating the critical exponent υ that describes the behaviour of the tension as approaching the critical point. The appropriate asymptotic relation for the interfacial tension with density is

$$\gamma = A \cdot \left(1 - \frac{T}{T_c}\right)^{2\upsilon} \tag{24}$$

$$\gamma = B \cdot |\rho_l - \rho_v|^{\frac{2\upsilon}{\beta}} \tag{25}$$

where, according to the literature (see for instance reference [61] and references therein) $2\upsilon \approx 1.26$ and $\beta \approx 0.324$. All calculations have been performed in the range of 0.5–5% below the critical point. For the series of *n*-perfluoroalkanes values in the range $2\upsilon \approx [1.20-1.26]$ and $\beta \approx [0.29-0.32]$ were obtained. These values are very close to the experimental ones showing the validity of our crossover approach. The slight underprediction of the critical exponents is due to an excessive flatness of the asymptotic curve near the critical point. As an example, calculations for perfluorobutane are shown in Fig. 4.

A final note is that the parameters used to model *n*-perfluoro-nonane were obtained from the correlations (18)–(22) without any further adjustment to experimental data. This result confirms the predictive potential of the model and gives confidence on
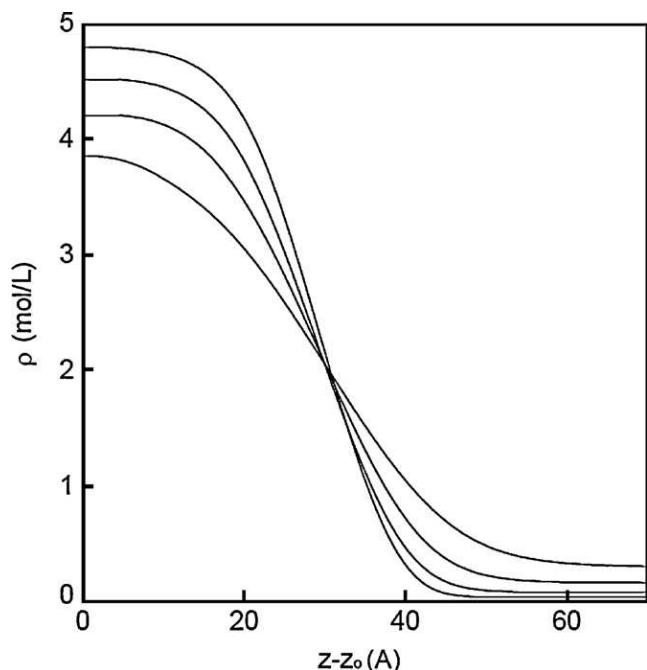
Fig. 5. Interfacial density profiles of perfluorohexane at four isotherms 325, 350, 375 and 400 K. The starting density corresponds to the liquid bulk density and the final point to the vapour value.

the optimized parameters. The approach presented here, with the crossover treatment considered, has some clear advantages, being the most important the fact that it allows the description of a given compound on an extended thermodynamic range with the same set of parameters and straightforwardly extend the study to mixtures once the physical trend of the parameters is assured.

The study of the interface is not only limited to the calculation of surface tension. The advantage of a theoretical approach is the possibility of studying the density profiles of a compound. Density profiles provide a valuable information about what is occurring in the interface and they cannot be easily measured. As an example, we have selected perfluorohexane at four different temperatures, ranging from 325 to 400 K, and plotted the corresponding equilibrium density profiles in Fig. 5. The extreme left-hand side of the graphic corresponds to the bulk liquid phase density while the extreme right-hand side is the bulk vapour density. The profiles are sharper at low temperatures, as the system is far away from the critical point and the density difference between liquid and vapour is large. However, as the temperature increases, the profiles become smoother and the width of the interface also becomes broader. Once the critical point is reached, there is no difference between liquid and vapour densities and the interface disappears.

The model was also applied to correlate the surface tension of perfluorobenzene and perfluorotoluene. As described in a previous work [3], a quadrupole moment was included when modelling both molecules because of the presence of the aromatic ring. We
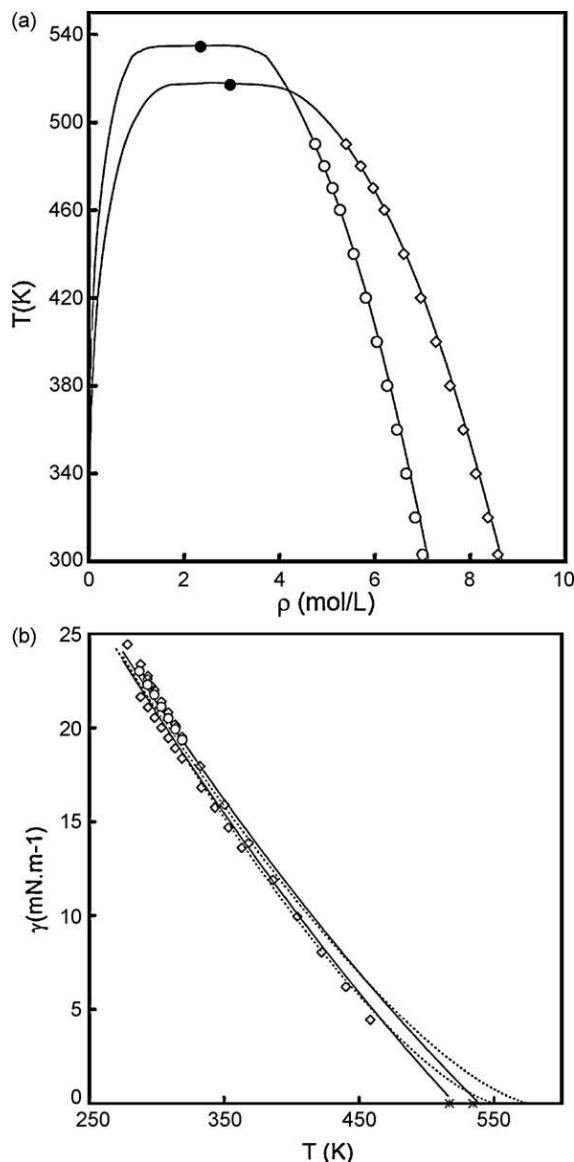

Fig. 6. (a) Vapour–liquid equilibrium of perfluorobenzene (triangles) and perfluorotoluene (diamonds) and (b) interfacial tension of the same compounds (ST expressed in mN m^{-1}). Symbols represent experimental data and full lines correspond to the crossover soft-SAFT combined with the DGT approach. The dashed line represents the results obtained with the original soft-SAFT model combined with DGT. The asterisk represents the critical temperature of the pure compounds.

provide in Table 3 the previous adjusted molecular parameters with the ones obtained in this work when the two extensions of the original soft-SAFT equations are combined (crossover and DGT). Fig. 6 depicts the surface tensions of both perfluorobenzene and perfluorotoluene obtained using an influence parameter equal to 2.8e^{-19} and 4.7e^{-19} (J m^5/mol^2), respectively. The dashed

Table 3
Molecular parameters adjusted for perfluorobenzene and perfluorotoluene with the original soft-SAFT and with crossover soft-SAFT.

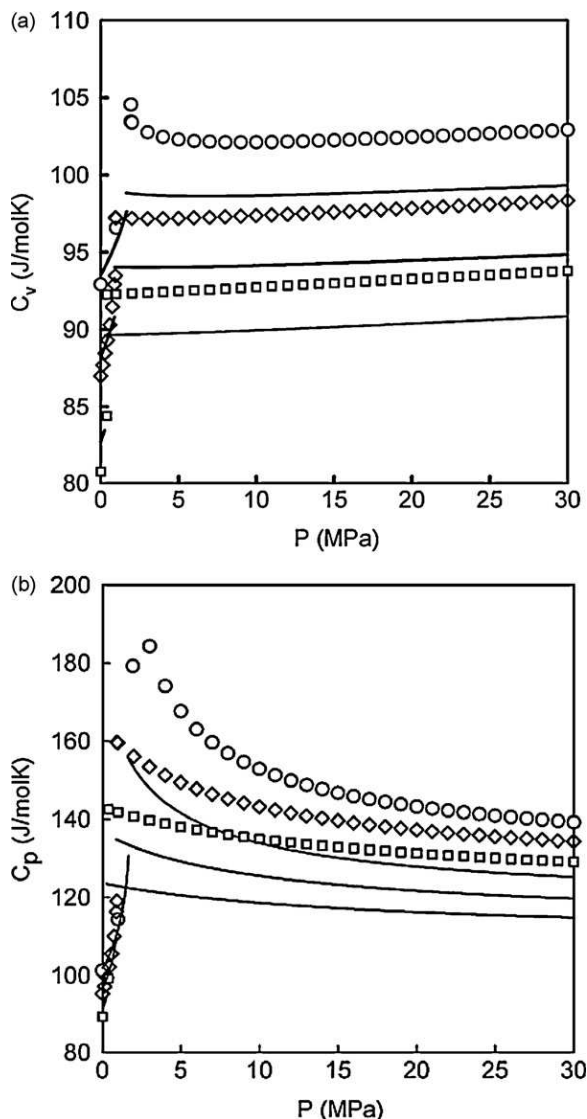| Molecular parameters	Perfluorobenzene		Perfluorotoluene	
	Crossover soft-SAFT	Original soft-SAFT	Crossover soft-SAFT	Original soft-SAFT
m	3.148	3.253	3.538	3.538
σ (Å)	3.655	3.602	3.770	3.764
ε/k_B (K)	257.0	245.5	255.0	253.0
Q (C m^2) [48]	5.00e^{-40}	5.00e^{-40}	5.00e^{-40}	5.00e^{-40}
ϕ	7.75	–	8.55	–
L/σ	1.35	–	1.44	–

Fig. 7. Gas and liquid subcritical heat capacity as a function of pressure for perfluoroethane at 225 K (squares). 250 K (diamonds) and 275 K (circles). (a) Isochoric heat capacity C_v and (b) isobaric heat capacity C_p. Symbols represent experimental data [58] and the solid lines are soft-SAFT predictions.

line in the figure represents the results obtained with the original soft-SAFT EoS, clearing showing a substantial over-prediction of the surface tension near the critical point when compared with the results obtained with the improved model used in this work. Results obtained with crossover soft-SAFT combined with DGT are represented by full lines. As observed in the figure, the performance of the extended equation is excellent.

The final part of the thermodynamic characterization performed here is completed by the evaluation of several second order thermodynamic derivative properties of common use and interest. This includes heat capacity, compressibility and speed of sound. Due to the lack of experimental data, we have restricted our study to light perfluoroalkanes for which more data is available, as a test of the model. Fig. 7 depicts the isochoric and isobaric heat capacity of perfluoroethane as a function of pressure at three subcritical isotherms, ranging from 225 to 275 K. Qualitative agreement is obtained for all the cases, although a slight underestimation is observed. This seems to indicate that the fluorine atom has a stronger contribution that is not completely taken into account. However, it is important to remark that the absolute average devi-

ation (AAD%) is only about 5% in both properties. Considering that these calculations are predictions without any additional adjustment, using the molecular parameters fitted to other properties at equilibrium, the transferability to estimate heat capacities is notable. Predictions for the speed of sound are depicted in Fig. 8. We show in Fig. 8a several predictions for perfluoroethane at the same temperatures used in Fig. 7. Quantitative agreement between the model and experimental data [58] is achieved in a large range of pressures. The better performance of the speed of sound compared to the heat capacities is due to the fact that the ratio between C_p and C_v is required in the calculation, being it very close to the real value, as both properties are similarly underestimated. The speed of sound in the gas phase for a very wide range of temperatures, from 215 till 475 K is presented in Fig. 8b. In this case, the soft-SAFT predictions are in excellent agreement with experimental data [62].

After these tests on the liquid and gas phases of a selected perfluoroalkane, we extended the calculations towards the supercritical phase, above the critical point. Two different perfluoroalkanes have been chosen (perfluorobutane and perfluoropentane) to check their properties at an isotherm over their critical points. Fig. 9 provides
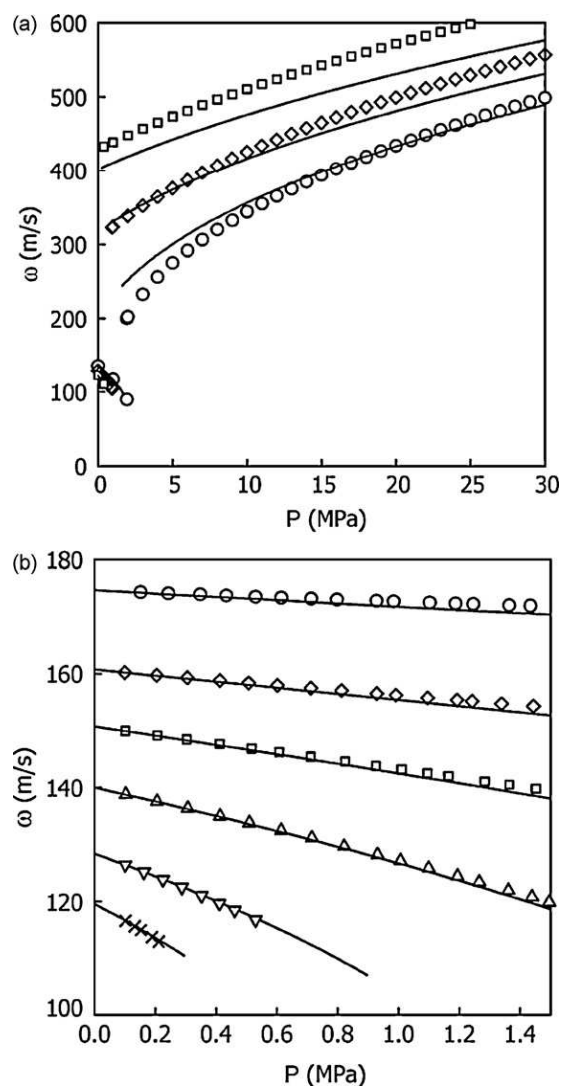

Fig. 8. Speed of sound as a function of pressure for perfluoroethane: (a) subcritical speed of sound at 225 K (squares). 250 K (diamonds) and 275 K (circles). (b) Speed of sound in the gas phase at 215 K (crosses). 250 K (triangles down). 300 K (triangles up). 350 K (squares). 400 K (diamonds) and 475 K (circles). Symbols represent experimental data taken from Ref. [58] in (a) and from Ref. [62] in (b). The solid lines correspond to soft-SAFT predictions.

predictions for residual heat capacities at 500 K as a function of the density. Fig. 9a is devoted to the residual isochoric heat capacity. Although qualitative agreement is still achieved, there is a considerable underestimation of the heat capacity value for both compounds. This is in accordance to the results obtained in a previous work for the n-alkanes family [63] although the fluorine atoms seem to slightly increment the difference. Note that the crossover term is not expected to correct this behaviour, as the temperature is well above the critical temperature, and hence the crossover term has not effect. In any case, it is remarkable the ability of the equation to capture the maximum and the minimum that C_v exhibits, as most equations are unable to capture them. Fig. 9b shows predictions for the isobaric heat capacity at the same temperature (500 K). Results are in very good agreement with experimental data [58] in the case of perfluorobutane, while an overestimation of the heat capacity around the critical density is visible for perfluoropentane. The isothermal compressibility for the same two compounds at the same chosen temperature of 500 K is presented in Fig. 10a. Predictions from soft-SAFT are in excellent agreement with experimental data [58] for the whole range of densities, which acts in favour of the transferability of the parameters and the robustness of the equa-

Fig. 10. Supercritical compressibility and sound velocity as a function of density for perfluorobutane (diamonds) and perfluoropentane (circles) at 500 K. (a) Isothermal compressibility and (b) speed of sound. Symbols and lines as in Fig. 9.

tion. Predictions for the speed of sound of the same compounds are presented in Fig. 10b. Again, excellent agreement is obtained when comparing to the experimental values. The correct prediction of the compressibility value is the key for an accurate prediction of the sound velocity.

4. Conclusions

The application of the crossover soft-SAFT EoS combined with DGT to real systems has proved to be a successful correlation/predictive method to accurately describe VLE data for linear and aromatic perfluoroalkanes. It was shown in this work that, within this approach, the use of a constant influence parameter and crossover parameters adjusted to density and vapour pressure data provide results equally accurate for phase and interfacial properties for pure systems in the whole thermodynamic range.

Correlations for the molecular parameters with the carbon numbers for the first eight members of the n-perfluoroalkane family have been provided here; this enables the equation with predictive power for higher members of the series, for which experimental data is not available, perfluoro-n-nonane was presented here as an example of this transferability.

The influence parameter for the n-perfluoroalkane series has shown to have a parabolic dependence of the carbon number of the chain and it can also be used as a predictive tool to calcu-
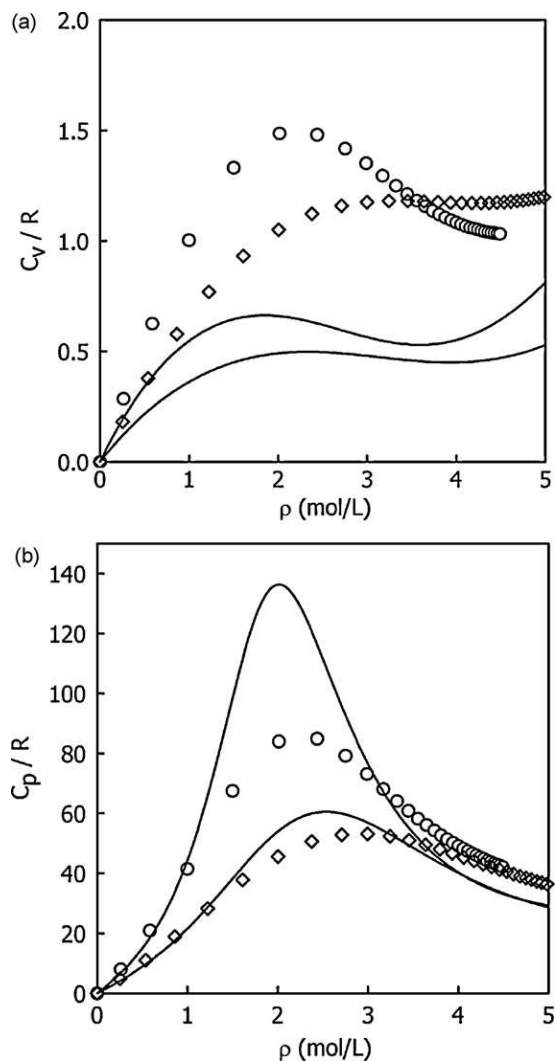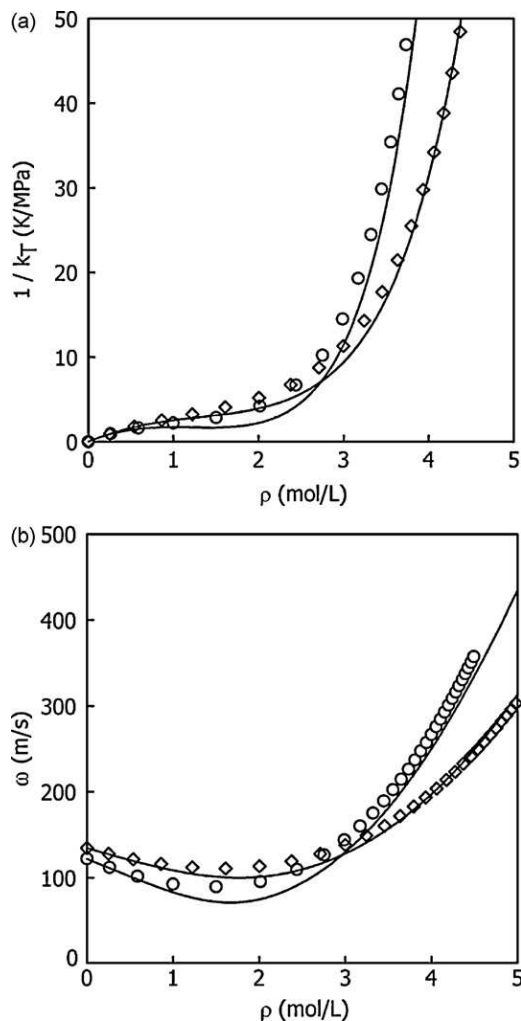

Fig. 9. Supercritical heat capacity as a function of density for perfluorobutane (diamonds) and perfluoropentane (circles) at 500 K. (a) Isochoric heat capacity C_v and (b) isobaric heat capacity C_p. Symbols represent experimental data [58] and the solid (perfluorobutane) and long-dashed (perfluoropentane) lines are soft-SAFT predictions.

late interfacial properties for other members of the series. The results presented in this work ensure that the proposed model can adequately be used for modelling surface tensions of non-polar compounds in a wide temperature range.

In addition, the same molecular parameters and model were used to describe second order derivative thermodynamic properties, in overall good agreement with experimental data. In summary, the extended soft-SAFT EoS, in which the density fluctuations in the near-critical region have been taken into account through a RG term, and in which the density gradient in the interface has been modelled through DGT is a powerful tool to describe a wide range of thermodynamic conditions with equal accuracy, including phase, interfacial and derivative properties. In order to achieve this successful modelling two ingredients are necessary: (1) to have an accurate EoS, with accurate physical terms, and (2) to use molecular parameters with intrinsic associated physical meaning and transferable.

List of symbols

a	Helmholtz free energy density of the bulk phases
c	influence parameter
m	number of LJ segments
P	equilibrium pressure
L	cut-off length
T	Temperature
CN	carbon number
N_A	Avogadro's number
k_B	Boltzmann constant

Greek symbols

σ	diameter of the LJ segment
ε	dispersive energy of the LJ segment
α	interaction volume with units of energy volume
w	range of the attractive potential
ϕ	average gradient of the wavelength function
γ	surface tension
μ	chemical potential
ρ	density
$\rho(r)$	molecular density profile
Ω^s	density fluctuations for the short-range attraction
Ω^l	density fluctuations for the long-range attraction
$\Delta\varpi$	excess grand free energy density

Superscripts

id	soft-SAFT ideal term
ref	soft-SAFT reference term
chain	soft-SAFT chain term
polar	soft-SAFT polar term
S	short-range attraction
L	long-range attraction

Subscripts

L	liquid phase
V	vapour phase

Acknowledgments

References

[1] H.C. Fielding, Organofluorine surfactants and textile chemicals, in: Organofluorine Chemicals and Their Industrial Applications, Ellis Horwood for the Society of Chemical Industry, Chichester, Great Britain, 1979, pp.214–234.
[2] K. Takai, T. Takagi, T. Baba, T. Kanamori, J. Fluorine Chem. 128 (2007) 10–15.
[3] A.M.A. Dias, H. Carrier, J.L. Daridon, J.C. Pàmies, L.F. Vega, J.A.P. Coutinho, I.M. Marrucho, Ind. Eng. Chem. Res. 45 (2006) 2341–2350.
[4] B. Ameduri, B. Boutevin, Well-Architectured Fluoropolymers: Synthesis, Properties and Applications, Elsevier Science, New York, 2004.
[5] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, Ind. Eng. Chem. Res. 29 (1990) 1709–1721.
[6] M.S. Wertheim, J. Stat. Phys. 35 (1984) 35–47.
[7] M.S. Wertheim, J. Stat. Phys. 42 (1986) 459–476.
[8] M.S. Wertheim, J. Stat. Phys. 42 (1986) 477–492.
[9] F.J. Blas, L.F. Vega, Mol. Phys. 92 (1997) 135–150.
[10] A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burguess, J. Chem. Phys. 106 (1997) 4168–4186.
[11] J. Gross, G. Sadowski, Ind. Eng. Chem. Res. 40 (2001) 1244–1260.
[12] E. Müller, K.E. Gubbins, Ind. Eng. Chem. Res. 40 (2001) 2193–2211.
[13] P. Morgado, C. McCabe, E.J.M. Filipe, Fluid Phase Equilib. 228 (2005) 389–393.
[14] R.P. Bonifacio, E.J.M. Filipe, C. McCabe, M.F.C. Gomes, A.A.H. Padua, Mol. Phys. 100 (2002) 2547–2553.
[15] C.M. Colina, A. Galindo, F.J. Blas, K.E. Gubbins, Fluid Phase Equilib. 222 (2004) 77–85.
[16] M.C. dos Ramos, Phase Equilibria of Complex Mixtures Involving Supercritical Carbon Dioxide, Water, Polymers and Surfactants Using the SAFT Equation of State, PhD thesis, Universidad de Huelva, 2006.
[17] A.M.A. Dias, J.C. Pàmies, J.A.P. Coutinho, I.M. Marrucho, L.F. Vega, J. Phys. Chem. B 108 (2004) 1450–1457.
[18] S. Aparicio, J. Supercrit. Fluids 46 (2008) 10–20.
[19] A.M.A. Dias, C.M.B. Goncalves, A.I. Caco, L.M.N.B.F. Santos, M.M. Pineiro, L.F. Vega, J.A.P. Coutinho, I.M. Marrucho, J. Chem. Eng. Data 50 (2005) 1328–1333.
[20] K.G. Wilson, Phys. Rev. B 4 (1971) 3174–3183.
[21] K.G. Wilson, Rev. Mod. Phys. 47 (1975) 773–840.
[22] T. Sakka, Y.H. Ogata, J. Fluorine Chem. 126 (2005) 371–375.
[23] M. Tsige, G.S. Grest, J. Phys. Chem. C 112 (2008) 5029–5035.
[24] D.B. Macleod, Trans. Faraday Soc. 19 (1923) 38–44.
[25] C.F. Weinaug, D.L. Katz, Ind. Eng. Chem. 35 (1943) 239–247.
[26] C. Miqueu, D. Broseta, J. Satherley, B. Mendiboure, J. Lachaise, A. Gracia, Fluid Phase Equilib. 172 (2000) 169–182.
[27] J.M. Haile, C.G. Gray, K.E. Gubbins, J. Chem. Phys. 64 (1976) 2569–2572.
[28] J. Winkelmann, Phys. Chem. Chem. Phys. 98 (1994) 1308–1316.
[29] F.J. Blas, E.M. del Rio, E. de Miguel, G. Jackson, Mol. Phys. 99 (2001) 1851–1865.
[30] J.F. Lu, D. Fu, J.C. Liu, Y.G. Li, Fluid Phase Equilib. 194 (2002) 755–769.
[31] S. Tripathi, W.G. Chapman, J. Chem. Phys. 119 (2003) 12611–12620.
[32] D. Duque, J.C. Pàmies, L.F. Vega, J. Chem. Phys. 121 (2004) 11395–11401.
[33] A.J. Queimada, C. Miqueu, I.M. Marrucho, G.M. Kontogeorgis, J.A.P. Coutinho, Fluid Phase Equilib. 228/229 (2005) 479–485.
[34] J.D. van der Waals, Zeit. Phys. Chem. 13 (1893) 657–725.
[35] J.S. Rowlinson, J. Stat. Phys. 20 (1979) 197–244.
[36] J.W. Cahn, J.E. Hilliard, J. Chem. Phys. 28 (1958) 258–267.
[37] J. Pàmies, Bulk and Interfacial Properties of Chain Fluids, a Molecular Modelling Approach, PhD thesis, University Rovira i Virgili, Tarragona, Spain, 2003.
[38] A. Mejia, J.C. Pàmies, D. Duque, L.F. Vega, J. Chem. Phys. 123 (2005) 034505.
[39] A. Mejia, L.F. Vega, J. Chem. Phys. 124 (2006) 244505.
[40] M.B. Oliveira, I.M. Marrucho, J.A.P. Coutinho, A.J. Queimada, Fluid Phase Equilib. 267 (2008) 83–91.
[41] Y. Jin, A. Boller, B. Wunderlich, B.V. Lebedev, Thermochim. Acta 234 (1994) 103–125.
[42] F. Llovell, J.C. Pàmies, L.F. Vega, J. Chem. Phys. 121 (2004) 10715–10724.
[43] D. Fu, J. Phys. Chem. B 110 (2006) 19575–19581.
[44] F.J. Blas, L.F. Vega, J. Chem. Phys. 115 (2001) 4355–4361.
[45] F.J. Blas, L.F. Vega, Ind. Eng. Chem. Res. 37 (1998) 660–674.
[46] J.C. Pàmies, L.F. Vega, Mol. Phys. 100 (2002) 2519–2524.
[47] L.F. Vega, F. Llovell, F.J. Blas, J. Phys. Chem. B 113 (2009) 7621–7630.
[48] J. Vrbancich, G.L.D. Ritchie, J. Chem. Soc. Faraday II 76 (1980) 648–655.
[49] G. Stell, J.C. Rasaiah, H. Narang, Mol. Phys. 27 (1974) 1393–1414.
[50] K.G. Wilson, M.E. Fischer, Phys. Rev. Lett. 28 (1972) 240–255.
[51] J.A. White, J. Chem. Phys. 112 (1992) 3236–3242.
[52] J.A. White, J. Chem. Phys. 112 (2000) 3236–3246.
[53] F. Llovell, L.F. Vega, J. Phys. Chem. B 110 (2006) 1350–1362.
[54] F. Llovell, C.J. Peters, L.F. Vega, Fluid Phase Equilib. 248 (2006) 115–122.
[55] A.M.A Dias, Thermodynamic Properties of Blood Substituting Liquid Mixtures, PhD thesis, University of Aveiro, Portugal, 2005.
[56] B. Smith, R. Srivastava, Thermodynamic Data for Pure Compounds, Elsevier, London, 1986.
[57] V. Vandana, D.J. Rosenthal, A.S. Teja, Fluid Phase Equilib. 99 (1994) 209–213.
[58] NIST Chemistry Webbook, http://webbook.nist.gov/chemistry.
[59] M.G. Freire, P.J. Carvalho, A.J. Queimada, I.M. Marrucho, J.A.P. Coutinho, J. Chem. Eng. Data 51 (2006) 1820–1824.
[60] R.N. Haszeldine, F. Smith, J. Chem. Soc. (1951) 603–608.
[61] E. de Miguel, N.G. Almarza, G. Jackson, J. Chem. Phys. 127 (2007) 034707.
[62] J.J. Hurly, Int. J. Thermophys. 20 (1999) 455–484.
[63] F. Llovell, L.F. Vega, J. Phys. Chem. B 110 (2006) 11427–11437.