INHOMOGENEOUS DENSITY THEORIES COUPLED INTO A MOLECULAR EQUATION OF STATE FOR THE DESCRIPTION OF THE FLUID-FLUID INTERFACE

Felix Llovell*, Oriol Vilaseca*, Lourdes F. Vega*

* MATGAS 2000 AIE, Campus de la UAB,
08193, Bellaterra, Barcelona, Spain

ABSTRACT
In this work, a short review of different approaches to estimate the surface tension, density profiles and other interfacial properties of pure fluids and mixtures is described. Particular attention is paid to two relevant methods usually coupled to molecular based equations of state from the SAFT family: the Density Functional Theory (DFT) and the Density Gradient Theory (DGT). The DFT approach is based on the construction of a free-energy functional by generally dividing the free-energy in two parts: a reference term that incorporates only the ideal and short-range interactions, and a perturbative term in which the long-range interactions are included. On the other hand, The DGT approach is based on the van der Waals theory for inhomogeneous fluids, as popularized by Cahn and Hilliard, where the Helmholtz free-energy density is expanded as a Taylor series in the density profile, which is truncated after the second term. Both treatments are physically well sounded and they are applicable to these type of EoSs, showing a very good performance to describe a wide variety of fluids, including hydrocarbons, amines, carbon dioxide, water and ionic liquids. Some examples will be shown here, highlighting the advantages and disadvantages of each methodology.

INTRODUCTION

The type and magnitude of the molecular interactions that occur at interfaces are responsible for many of the phenomena that are observed in nature. A detailed knowledge of the interfacial behaviour is required to deal with many industrial technological processes, especially those ones related to separation and extraction. However, the modelling of interfacial properties remains as a challenge due to its inhomogeneous nature. Only theories that explicitly consider property fluctuations are able to reproduce the physics behind the interface.

A quantitative evaluation of interfacial phenomena can be developed by starting from an accurate representation of the bulk homogeneous fluids. Among several possibilities, one of the most successful equations of state (EOSs) for fluid-phase equilibria is the statistical associating fluid theory (SAFT) [1], and its different versions. The general form of the SAFT expression for the Helmholtz free energy stems from the first-order perturbation theory for associating systems by Wertheim [2]-[4]. The total free energy comprises a sum of terms that contribute to the total energy of the systems, each with a rigorous statistical mechanical foundation.

A large body of literature has been devoted to the description and estimation of phase equilibrium properties of fluids following a variety of approaches. However, the application of theories of inhomogeneous systems is less common. One of the first successful approaches for the description of interfacial tensions in mixtures is the so-called parachor method, introduced by Macleod [5]. One can use this empirical approach to correlate the interfacial tension with the difference of the bulk coexisting densities. Despite its empirical basis, Fowler [6] showed that the relation can be derived as an explicit function of the intermolecular potential in the case of a stepwise density profile, which is a reasonable assumption far away from the critical point. Other popular approaches are based on the corresponding-states principle of Guggenheim [7], where empirical relations can be developed in terms of a specific reference fluid to provide an accurate representation of the surface tension [8]. Though useful in correlating data for the interfacial tension of fluid mixtures, these empirical relations offer little in way of predictive capability. This is the advantage of approaches developed from a more rigorous theoretical foundation such as the squared gradient theory (also referred to as density gradient theory (DGT)) and density functional theory (DFT).

The DGT methodology is rooted in the original theory for inhomogeneous fluids of van der Waals [9], which was rediscovered and popularized by Cahn and Hilliard. [10] In DGT, the local free energy density is expanded as a Taylor series about the density profile to second order, i.e., to the second derivative of the profile with respect to the distance from the interface (which in this case also corresponds to the square of the density gradient). The first term of the DGT essentially corresponds to the Helmholtz free-energy density of the uniform fluid evaluated at the local density. The square-gradient term can be expressed in terms of $c(r)$, the direct correlation function [11] because the form of $c(r)$ is generally unknown, it is often treated phenomenologically with the help of an adjustable parameter, the so-called "influence" parameter, which is estimated from real surface tension data.

By contrast to DGT, the DFT formalism in principle offers an entirely predictive approach with no adjustable parameters. DFT methods are based on the construction of a free-energy functional from which the thermodynamic properties of the inhomogeneous system can be calculated. Several authors have discussed the general approaches for the construction of free-energy functionals and the different approximations that are commonly employed. Though the functional form of the free energy in typical DFTs is mathematically more complex

(involving iterative variational techniques for their solution) than for a DGT treatment, they have become quite popular because of the enhanced predictive capability.

As a consequence, intermolecular parameters which have been estimated by optimization of experimental data for the bulk phases are sufficient to provide a predictive platform for the interfacial properties of the system within a DFT formalism without the need for additional surface tension data. The fundamental details of the DFT approach can be found in the seminal reviews by Evans [12] and Davis [13], including the various options for going from a general DFT formalism to an approximated theory that can be used to compute accurate results when applied to real fluids.

The purpose of this contribution is to show the capability of combining a physically sounding SAFT-type equation of state with the DGT and DFT methods for the estimation of the surface tension, density profiles and other interfacial properties of pure fluids and mixtures.

THEORY

DGT

The Density Gradient Theory (DGT) was originally proposed by van der Waals,[9] and rediscovered many years later by Cahn and Hilliard [10]. In the DGT approach, the Helmholtz free energy density is expanded in a Taylor series around a_0, the free energy density term of the homogeneous fluid at the local density, and truncated after the second order term.

$$A = \int \left[a_0(\rho) + \sum_i \sum_j \frac{1}{2} c_{ij} \nabla \rho_i \nabla \rho_j \right] d^3 r \tag{1}$$

where $a_0(\rho)$ is the Helmholtz free energy density of the homogeneous fluid at the local density ρ and ρ_i and ρ_j are the molar densities of components i and j; c_{ij} is the influence parameter, which is treated as an adjustable temperature independent parameter regressed from experimental data.

Eq. (1) is usually simplified by assuming a planar interface and neglecting the density dependence of c_{ij}. Hence, the surface tension γ is related to the square gradient expression following

$$\gamma = \sum_i \sum_j \int_{-\infty}^{\infty} c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} dz = 2 \int_{-\infty}^{\infty} \Delta\Omega(\rho_i, \rho_j) dz, \tag{2}$$

where $\Delta\Omega$ is, by definition, the grand thermodynamic potential: $\Delta\Omega(\rho_i, \rho_j) = a_o(\rho) - \sum_i \mu_{o,i} \rho_i + P_o$. μ_{0i} and P_0 correspond to the equilibrium chemical potential and pressure, respectively, and z is the direction perpendicular to the interface. The right hand expression of Eq. (2) had infinite limits in the integration. Poser and Sanchez [14] applied a transformation from local space to density space, allowing a way to evaluate density profiles. For the particular case of a binary mixture, the equation reads:

$$z = z_o + \int_{\rho_2(z_o)}^{\rho_2(z)} \sqrt{\frac{c'}{\Delta\Omega(\rho_1, \rho_2)}} d\rho_2 \tag{3}$$

where z_0 denotes an arbitrary chosen origin and c' is the result from the influence parameters of the pure components and the density profiles across the interface, and is described by,

$$c' = c_2 + 2c_{12} \left(\frac{d\rho_1}{d\rho_2} \right) + c_1 \left(\frac{d\rho_1}{d\rho_2} \right)^2 \tag{4}$$

The crossed parameter c_{12} is assumed to be given by the geometric mean combination rule, $c_{12} = \beta \sqrt{c_1 c_2}$. β is an adjustable parameter, either fitted to the mixture experimental surface tension data or kept equal to one for predictive purposes. For a fair comparison with DFT, β has been set to unity in all cases.

Using the above mentioned transformation, Poser and Sanchez [14] also derived an equation for the surface tension in binary mixtures that considers the change in the partial densities ρ_1 and ρ_2 within the interface,

$$\gamma = \sqrt{2} \int_{\rho_2(z_o)}^{\rho_2(z)} \sqrt{c' \Delta\Omega(\rho_1, \rho_2)} d\rho_2 \tag{5}$$

where the limits of integration are the bulk densities of component 2 in the coexisting phases. Further details concerning the computational performance of the grand thermodynamic potential for binary mixtures and how this can be coupled to a SAFT-type within framework can be found in literature [15].

DFT

The Density Functional Theory (DFT) formalism is based on a standard perturbative approach in which the Helmholtz free-energy functional is approximated as the sum of a reference functional and a perturbative contribution.

$$A[\{\rho_m(\mathbf{r})\}] = A^{\text{ref}}[\{\rho_m(\mathbf{r})\}] + A^{\text{att}}[\{\rho_m(\mathbf{r})\}] \tag{5}$$

The theory is based on the grand potential functional $\Omega[\rho_m(\mathbf{r})]$ of an inhomogeneous system. Assuming an open mixture at temperature T and chemical potential μ_i for each component in a volume V, and in the absence of external fields:

$$\Omega[\{\rho_m(\mathbf{r})\}] = A[\{\rho_m(\mathbf{r})\}] - \sum_{i=1}^{n} \mu_i \int d\mathbf{r} \, \rho_i(\mathbf{r}) \tag{6}$$

where $A[\{\rho_m(r)\}]$ is the intrinsic Helmholtz free energy functional. The minimum value of $\Omega[\{\rho_m(r)\}]$ is the equilibrium grand potential of the system and the corresponding equilibrium density profiles $\rho_{eq,i}(r)$ satisfy the condition

$$\left. \frac{\delta\Omega[\{\rho_m(\mathbf{r})\}]}{\delta\rho_i(\mathbf{r})} \right|_{eq} = \left. \frac{\delta A[\{\rho_m(\mathbf{r})\}]}{\delta\rho_i(\mathbf{r})} \right|_{eq} - \mu_i = 0 \tag{7}$$

The DFT approach tries to find an expression to relate the Helmholtz energy with the density of the system at the interface. From Eq. (5), the first term takes into account the short-range interactions between the segments that form the molecules. For a SAFT-type equation of state, they correspond to the ideal, hard-sphere, chain, and associative contributions, which are evaluated using the well-known local density approximation (LDA) [16].

$$A^\alpha[\{\rho_m(\mathbf{r})\}] = k_B T \int d\mathbf{r} \, f^\alpha(\{\rho_m(\mathbf{r})\}) \tag{8}$$

The second term accounts for the long-range attractive interactions among the molecules of the system (corresponding to the first-order perturbation terms of the free energy):

$$
\begin{aligned}
A^{\mathrm{att}}[\{\rho_m(\mathbf{r})\}] = & \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\int d\mathbf{r}\, m_i\rho_i(\mathbf{r})\int d\mathbf{r}'\, m_j\rho_j(\mathbf{r}') \\
& \times\ g_{ij}^{\mathrm{hs}}[\mathbf{r},\mathbf{r}';\{\rho_m(\mathbf{r}),\rho_l(\mathbf{r}')\}]\,\phi_{ij}^{\mathrm{att}}(|\mathbf{r}-\mathbf{r}'|).
\end{aligned}
\tag{9}
$$

At this point, two different approximations for the perturbative term can be applied: a full treatment in which the correlations between the chain segments are incorporated in an average manner through a set of approximations to estimate the pair distribution function of the inhomogeneous hard-sphere mixture fluid [17], and a mean-field approach where the effect of the pair distribution function is neglected.

The final expression using the full approach and applied to the case of the SAFT-VR equation of state reads:

$$
\begin{aligned}
A^{\mathrm{att}}[\{\rho_m(\mathbf{r})\}] = & \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\int d\mathbf{r}\, m_i\rho_i(\mathbf{r})\int d\mathbf{r}'\, m_j\rho_j(\mathbf{r}') \\
& \times\ g_0^{\mathrm{hs}}[\sigma_x;\overline{\xi_x^{\mathrm{eff}}}(\lambda_{ij};\{\rho_m(\mathbf{r}),\rho_l(\mathbf{r}')\})]\,\phi_{ij}^{\mathrm{att}}(|\mathbf{r}-\mathbf{r}'|)
\end{aligned}
\tag{10}
$$

The simplified mean-field expression is:

$$
A_{\mathrm{mf}}^{\mathrm{att}}[\{\rho_m(\mathbf{r})\}] = \frac{1}{2}\sum_{i=1}^{n}\sum_{i=1}^{n}\int d\mathbf{r}\, m_i\rho_i(\mathbf{r})\int d\mathbf{r}'\, m_j\rho_j(\mathbf{r}')\phi_{ij}^{\mathrm{att}}(|\mathbf{r}-\mathbf{r}'|)
\tag{11}
$$

The variation of the reference contribution with respect to densities $\rho_i(r)$ correspond to the local chemical potential which can be obtained from derivation of the Helmholtz free energy by the density. Once the equilibrium density profile is known, the surface tension is determined by using the thermodynamic relation

$$
\gamma = \frac{\Omega + pV}{\mathcal{A}}
\tag{12}
$$

A final point to remark is the discussion about the effect of capillary waves on the surface tensions. The standard DFT approach washes out capillary fluctuations. These fluctuations, which can be viewed as a superposition of sinusoidal surface waves (or two-dimensional normal modes, provided their amplitudes are small), would become increasingly important close to the critical point. These capillary-wave fluctuations are not taken into account explicitly here, based on the fact that a significant contribution to the thermodynamic properties of the interface away from the critical region is not expected. In fact, Henderson [18] has shown that the interfacial tension described by a capillary wave theory is equivalent to the thermodynamic interfacial tension (accessible, e.g., through a DFT treatment) in the case of long wavelength fluctuations. However, this is a point for discussion among different authors who consider the effect of capillary waves to be important and necessary in order to have a proper estimation of the surface tension [19].

INTERESTING EXAMPLES

In this section, we want to show the surface tension of different compounds calculated with the DGT and DFT treatments. We start first with the Density Gradient Theory, which has been used in conjunction with the soft-SAFT

equation of state. Soft-SAFT is a variant of the original SAFT developed in 1997 by Vega and Blas [20] and it is mainly characterised by using a Lennard-Jones (LJ) interaction potential among the monomers that form each molecule.

In Fig. 1, the surface tension of three common refrigerants (hydrofluorocarbons R134, R143 and R152) are modelled with the soft-SAFT equation of state + the DGT treatment. As it can be observed, excellent agreement with the experimental data is obtained in the whole range of temperatures corresponding to the vapour-liquid equilibrium line.
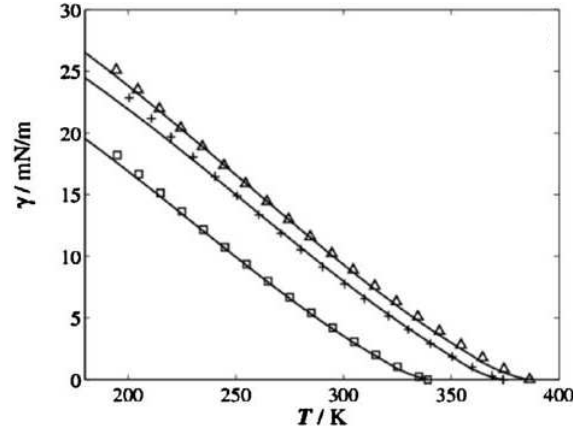

Fig. 1. Vapor–liquid interfacial tension for R125(Δ), R152a(+), R134a ($\square$). Lines are the theoretical calculations and the symbols represent the experimental data [21].

The density at each point of the interface is calculated using soft-SAFT, which establishes a reliable molecular model for each molecule. Hence, an accurate density estimation is also a key requirement for a good calculation of the surface tension. Additionally, it is important to remark that the influence parameter c_{ij} has been fitted to the surface tension data. This is the main disadvantage of the DGT approach, although in some cases, the influence parameter can be transferred from some compounds to others or related to the molecular weight within the same family of compounds [15]. An accurate estimation of the influence parameter is very important to have reliable predictions of mixtures. In Fig. 2, the surface tension of a mixture between two hydrofluorocarbons (R134 + R32) has been predicted from the information obtained for each pure compound [22]. No mixture data has been used. As it can be seen, the predicted results are in very good agreement with the experimental data.
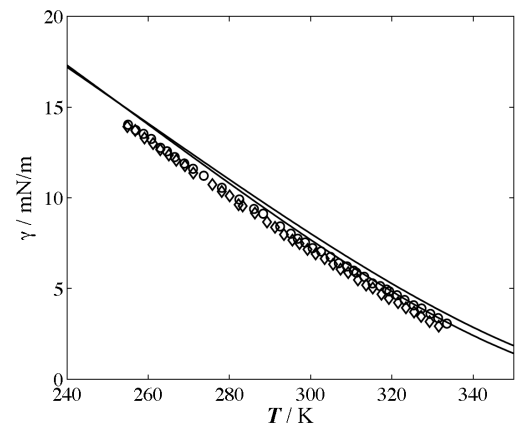

Fig. 2. Vapor–liquid interfacial tension of a R134 + R32 mixture at two different isopleths with a mass fraction of 0.4194 (Δ) and 0.6084 ($\circ$) of R32.

The DGT treatment is a very versatile treatment, not only limited to classical fluids but also applicable to novel fluids, such as ionic liquids. In Fig. 3, the surface tension of several ionic liquids from the $[C_nmim][Tf_2N]$ family have been calculated using the soft-SAFT + DGT treatment. The surface tension estimation of ionic liquids is particularly difficult, due to several reasons associated to their structure and thermophysical properties: Firstly, ionic liquids are characterized by a negligible vapour pressure. Secondly, as observed experimentally, the value of the interfacial tension decreases as the alkyl chain length of the cation increases, contrarily to the behaviour of other organic compounds. Finally, these compounds are exceptional in terms of interfacial phenomena, as they show an almost constant value when the alkyl chain length increases, as it happens for the $[C_nmim][Tf_2N]$ family beyond $[C_7mim][Tf_2N]$. All these particularities can be captured with DGT, and very good agreement is obtained between the experimental data and the theoretical calculations. Moreover, the fitted influence parameter can be correlated with the molecular weight (or number of carbons CN) following a parabolic function [23], allowing the prediction of other ionic liquids of the same family with a longer chain in the cation tail.
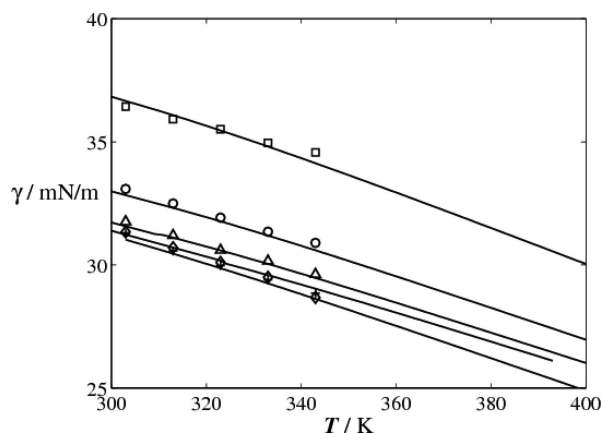

Fig. 3. Interfacial tensions for $[C_2mim][Tf_2N]$ (□), $[C_4mim][Tf_2N]$ (○), $[C_6mim][Tf_2N]$ (Δ), $[C_8mim][Tf_2N]$ (+), and $[C_{10}mim][Tf_2N]$ (◊).

This is the expression obtained by fitting the ionic liquid members of the $[C_n\text{-}mim][Tf_2N]$ family with the alkyl chain length ranging from C_2 to C_8.

$$10^{19} c_{Tf_2N} = 0.2233 \; CN^2 - 0.1872 \; CN + 15.275 \; [Jm^5mol^{-2}] \qquad (13)$$

This correlation allows obtaining the interfacial behaviour of heavier compounds of the series not included in the fitting procedure.

The surface tension is not the only property that can be evaluated through the use of DGT. Density profiles are a supporting tool that provide a lot of information on the mixture and cannot be obtained experimentally. For the case of mixtures, they allow explaining deviations from the ideal behaviour, due to the relative enrichment of one compound in the interface. In Fig. 4, an example of the density profile of a $[C_4mim][NTf_2] + [C_2mim][NTf_2]$ mixture. The dashed line corresponds to the $[C_4mim][NTf_2]$ density profile, who is adsorbed in the interface, reaching a maximum. However, this is not affecting the total density profile (solid line) of the mixture. As mentioned, this information can become crucial in order to understand the non-ideal behavior of some mixtures [24].
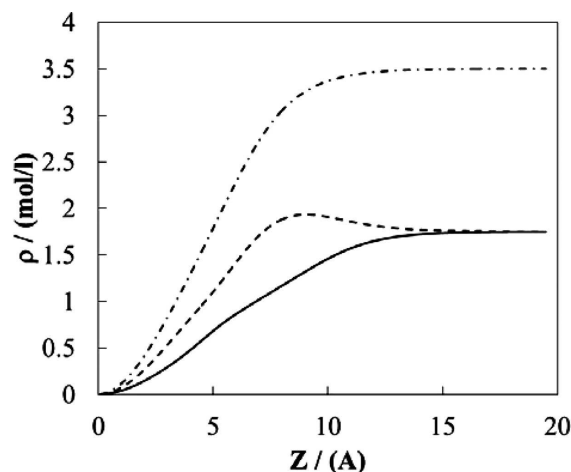

Fig. 4. Density profiles across the interface at 298.15 K for $[C_4mim][NTf_2] + [C_2mim][NTf_2]$.

Let us proceed to see some examples of the possibilities of the Density Functional Theory (DFT) methodology. As stated in the theory, this is a fully predictive approach, which can be particularly useful when experimental information is missing. The DFT theory has been coupled here with the SAFT-VR equation of state of Gil-Villegas and co-workers [25], another SAFT-type version that, in this case, uses a square-well potential to describe the interaction between the monomers of the system.

In Fig. 5 the interfacial tension of two amines is provided using SAFT-VR + DFT. The surface tension of monoethanolamine (MEA) is depicted in Fig. 4a and the one of 2-amino-1-propanol (AMP) is shown in Fig. 4b. In both cases, excellent agreement is achieved with the experimental data, although for the AMP case, only a limited range of data is available for comparison. As for the DGT case, the density at each point of the interface is taken from the SAFT-VR calculation, hence, a reliable estimation of this property is absolutely necessary for obtaining the right trends.
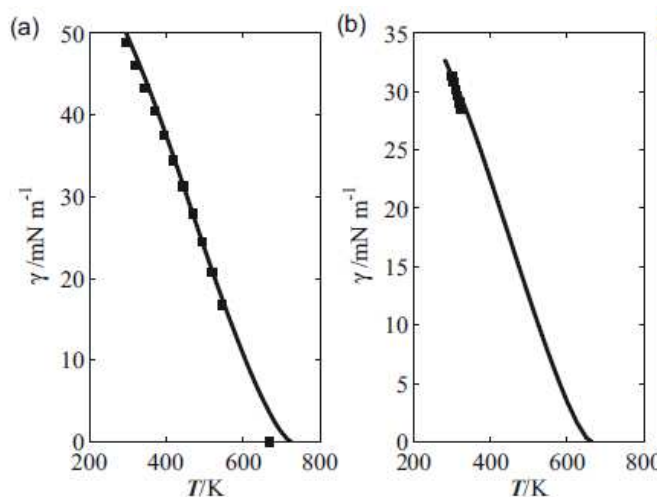

Fig. 5. Interfacial tensions for a) MEA b) AMP. More information is provided in reference [26].

The DFT treatment, as DGT, can also be applied to a wide variety of fluids and extended to mixtures. A very interesting field of application includes the carbon dioxide (CO_2) + hydrocarbon mixtures for enhanced oil recovery purposes. The CO_2 + n-decane mixture is particularly relevant because it is seen as a reasonable first approximation of a crude oil

mixture. In Fig. 6 an example of the surface tension of this mixture is shown. The SAFT-VR DFT (solid lines) is found to provide good predictions of the surface tension of the mixture over the whole range of pressures [27]. As for the mixtures of *n*-alkanes, the use of the mean-field approximation (dashed lines) is seen to lead to lower values of the vapour–liquid interfacial tension (in comparison with those corresponding to the version of the functional incorporating the correlations), especially at low pressures.
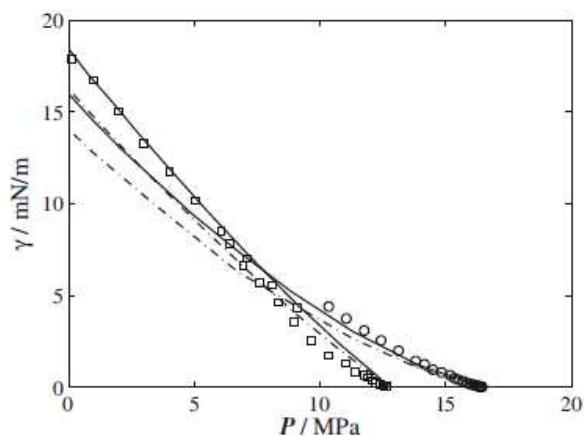

Fig. 6. Vapour-liquid interfacial tensions of a Carbon Dioxide + n-decane mixture at 344K (□) and 377K (○).

Another interesting ability of the DFT treatment is that it can be used to calculate either vapour-liquid (VL) or liquid-liquid (LL) interfacial tensions. In Fig. 7 the VL and LL interfacial tensions of a water + CO_2 mixture are modelled with SAFT-VR-DFT. Good agreement is found in a very wide range of temperatures and pressures, moving from one type of equilibrium to another. The methodology is able to capture the change from an equilibrium to another one using an only set of parameters and without mixture data [28].
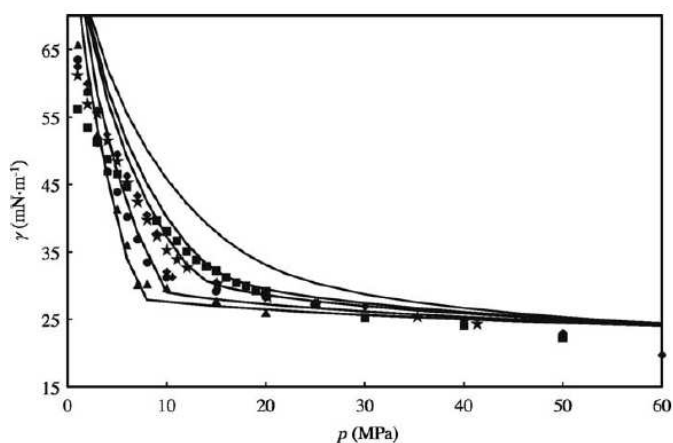

Fig. 7. Interfacial tension modelling and measurements of the (H_2O+CO_2) system as a function of pressure for different isotherms: (▲) at 297.9 K; (●) at 312.9 K; (♦) at 333.5 K; (x) at 343.3 K; (■) at 373.3 K.

CONCLUSIONS

A short review of different methodologies applied for the calculation of interfacial properties of fluid and fluid mixtures has been explored. In particular, the DGT and DFT treatments are highlighted based on their reliable physical background,

easiness of application and accuracy of results. These treatments have been coupled into SAFT-type equations of state to reproduce the surface tension of compounds of different molecular nature. Both approaches can accurately reproduce the surface tension of pure fluids and binary mixtures. The DGT approach requires the use of an additional parameter, the so-called influence parameter "c", although it keeps an elevated degree of predictability for mixtures, with excellent agreement in the calculation of the surface tension of complex ionic liquid mixtures. On the other hand, the DFT approach is fully predictive and it is accurate enough to estimate aqueous and CO_2 mixtures in a semiquantitative way, although it is computationally more demanding and, as a consequence, more difficult to extend to multicomponent systems. Therefore, there are still some open questions for both approaches, like the use of the β binary parameter on DGT and the inclusion of the effect of capillary waves on DFT. In any case, they both offer a reliable path for an accurate estimation of the interface of a wide variety of compounds.

ACKNOWLEDGEMENTS

NOMENCLATURE

Symbol	Quantity	SI Unit
A	Helmholtz free energy	J/mol
a_0	Helmholtz free energy density	J/dm³
γ	Surface tension	mN/m
c_{ij}	Influence parameter	J·m⁵/mol²
ρ	Density	mol/dm³
μ	Chemical Potential	J/mol
z	Distance from the interface	Å
β	Crossed influence parameter	Adim.
Ω	Grand Potential	J/mol
V	Volume	dm³
T	Temperature	K
P	Pressure	MPa
g_{ij}	Pair radial distribution function	Adim.
k_B	Boltzmann constant	J / K
m	Chain length SAFT parameter	Adim.

REFERENCES

[1] W. G. Chapman, K. E. Gubbins, G. Jackson, M. Radosz, New reference equation of state for associating liquids, *Ind. Eng. Chem. Res.*, vol. 29 pp.1709–1721, 1990.

[2] M. S. Wertheim, Fluids with Highly Directional Attractive Forces. 1. Statistical Thermodynamics. *J. Stat. Phys.* vol. 35, pp.19-34, 1984.

[3] M. S. Wertheim, Fluids with Highly Directional Attractive Forces. 2. Thermodynamic-Perturbation Theory and Integral-Equations. *J. Stat. Phys.* vol. 35, pp.35-47, 1984.

[4] M. S. Wertheim, Fluids with Highly Directional Attractive Forces. 3. Multiple Attraction Sites. *J. Stat. Phys.* vol. 42, pp. 459-476, 1986.

[5] D. B. Macleod, On a relation between surface tension and density. *Trans. Faraday Soc.,* vol. 19, pp. 38-41, 1923.

[6] R. H. Fowler, A Tentative Statistical Theory of Macleod's Equation for Surface Tension, and the Parachor, *Proc. R. Soc. London, Ser. A,* vol. 159, pp. 229-246, 1937.

[7] E. A. Guggenheim, The principle of corresponding states. *J. Chem. Phys.,* vol. 13, pp. 253-261, 1945.

[8] Y. X. Zuo and E. H. Stendby, Corresponding-states and parachor models for the calculation of interfacial tensions, *Can. J. Chem. Eng*., vol 75, 1130, 1997.

[9] J.D. van der Waals, Thermodynamische Theorie der Kapillarität unter voraussetzung stetiger, Dichteänderung, *Zeitschrift fur Physikalische Chemie-Leipzig*, vol. 13, pp. 657–725, 1894.

[10] J.W. Cahn, J.E. Hilliard, Free energy of a non-uniform system. I: interfacial energy, *Journal of Chemical Physics*, vol. 28, pp. 258–266, 1958.

[11] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity*, Clarendon, Oxford, 1982.

[12] R. Evans, "Density functionals in the theory of nonuniform fluids" *Fundamentals of Inhomogeneous Fluids*, Dekker, New York, 1992.

[13] H. T. Davis, *Statistical Mechanics of Phases, Interfaces and Thin Films*, VCH, Weinheim, 1996.

[14] C. I. Poser, I. C. Sanchez, Interfacial tension theory of low and high molecular weight liquid mixtures, *Macromolecules*, vol. 14, pp. 361–370, 1981.

[15] O. Vilaseca, L.F. Vega, Direct calculation of interfacial properties of fluids close to the critical region by amolecular-based equation of state, *Fluid Phase Equilibria*, vol 306, pp. 4-14, 2011.

[16] D.E. Sullivan, Statistical mechanics of a nonuniform fluid with long-range attractions, Phys. Rev. A, vol. 25 pp. 1669–1682, 1982.

[17] F. Llovell, A. Galindo, F.J. Blas, G. Jackson, Classical density functional theory for the prediction of the surface tension and interfacial properties of fluids mixtures of chain molecules based on the statistical associating fluid theory for potentials of variable range, *J. Chem. Phys.* 133, 024704, 2010.

[18] J. R. Henderson, *Statistical Mechanics of Spherical Interfaces in Fluid Interfacial Phenomena*, Wiley, New York, 1986.

[19] J. Gross, A density functional theory for vapor–liquid interfaces using the PCP-SAFT equation of state, J. *Chem. Phys.* 131, 204705, 2009.

[20] F.J. Blas, L.F. Vega, Thermodynamic behaviour of homonuclear and heteronuclear Lennard-Jones chains with association sites from simulation and theory, *Mol. Phys*. vol. 92, pp. 135–150, 1997.

[21] NIST Chemistry Webbook; http://webbook.nist.gov/chemistry.

[22] O. Vilaseca, F. Llovell, J. Yustos, R. M. Marcos, L. F. Vega. Phase equilibria, surface tensions and heat capacities of hydrofluorocarbons and their mixtures including the critical region. *J. Supercrit. Fluids,* 55 pp. 755–768, 2010.

[23] F. Llovell, E. Valente, O. Vilaseca, L. F. Vega, Modeling Complex Associating Mixtures with [$C_n$mim][Tf_2N] Ionic Liquids: Predictions from the Soft-SAFT Equation*J. Phys. Chem. B* vol. 115, pp. 4387–4398, 2011.

[24] M. B. Oliveira, M. Domínguez-Pérez, M. G. Freire, F. Llovell, O. Cabeza, J. A. Lopes-da-Silva, L. F. Vega, J. A. P. Coutinho. Surface Tension of Binary Mixtures of 1− Alkyl – 3 - methylimidazolium Bis(trifluoromethylsulfonyl)-imide Ionic Liquids: Experimental Measurements and Soft-SAFT Modeling, *J. Phys. Chem. B*, 116, pp. 12133−12141, 2012.

[25] A. Gil-Villegas, A. Galindo, P.J. Whitehead, S.J. Mills, G. Jackson, A.N. Burgess, Statistical associating fluid theory for chain molecules with attractive potentials of variable range, *J. Chem. Phys.,* vol. 106, pp. 4168–4186, 1998.

[26] N. Mac Dowell, N. MacDowell, F. Llovell, C.S. Adjiman, G. Jackson, A. Galindo, Modelling the fluid phase behaviour of carbon dioxide in aqueous solutions of monoethanolamine using transferable parameters with the SAFT-VR approach, *Ind. Eng. Chem. Res.,* vol. 49, pp. 1883–1899, 2010.

[27] F. Llovell, N. Mac Dowell, F. J. Blas, A. Galindo, G. Jackson, Application of the SAFT-VR density functional theory to the prediction of the interfacial properties of mixtures of relevance to reservoir engineering, *Fluid Phase Equilib*. vol 336, pp. 137-150, 2012.

[28] A. Georgiadis, F. Llovell, A. Bismarck, F.J. Blas, A. Galindo, G. C. Maitland, J. P. M. Trusler, G. Jackson, Interfacial tension measurements and modelling of (carbon dioxide + n-alkane) and (carbon dioxide + water) binary mixtures at elevated pressures and temperatures, *J. Supercrit. Fluids* vol. 55, pp. 743–754, 2010.