Interfacial Tensions of Industrial Fluids from a Molecular-Based Square Gradient Theory

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This work reports a procedure for predicting the interfacial tension (IFT) of pure fluids. It is based on scaling arguments applied to the influence parameter of the van der Waals theory of inhomogeneous fluids. The molecular model stems from the application of the square gradient theory to the SAFT-VR Mie equation of state. The theory is validated against computer simulation results for homonuclear pearl-necklace linear chains made up to six Mie ($\lambda = 6$) beads with repulsive exponents spanning from $\lambda = 8$ to 44 by combining the theory with a corresponding states correlation to determine the intermolecular potential parameters. We provide a predictive tool to determine IFTs for a wide range of molecules including hydrocarbons, fluorocarbons, polar molecules, among others. The proposed methodology is tested against comparable existing correlations in the literature, proving to be vastly superior, exhibiting an average absolute deviation of 2.2%. © 2016 American Institute of Chemical Engineers AIChE J. 00: 000–000, 2016

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Introduction

Interfacial tension (IFT) is arguably the key thermophysical property that governs the behavior of inhomogeneous fluids. Its relevance is rooted in the fact that the magnitude of the IFT and its relationship to other state variables (i.e., temperature, pressure, composition) controls several interfacial phenomena such as wetting transitions, interfaces at the vicinity of critical states, nucleation of new phases, etc. The physical understanding and modeling of IFT also provides a route to link tensions to the Helmholtz energy in the limit of an infinitesimal perturbation in the interfacial area. Empirically, IFT can be related to some characteristic dimensions of the system, such as the liquid height in a capillary tube (e.g., capillary rise tensiometer) or the silhouette of a pendant or ellipsoid drop (e.g., pendant drop and spinning drop tensiometers, respectively). For further discussions related to tensiometers and the experimental techniques the reader is redirected to Refs. 3 and 7. From a molecular simulation perspective, inhomogeneous fluids can be simulated in the canonical ensemble by using both Molecular Dynamics (MD) and Monte Carlo schemes. In both schemes, the IFT can be computed from the mechanical and/or the thermodynamic route. In the mechanical route or IK method, the IFT is computed from the integration of the difference between the normal and tangential pressure (Hulshof’s integral), which are described by the diagonal components of the Irving and Kirkwood tensor. In the thermodynamic route or Test Area method, the IFT is computed from the change in the Helmholtz energy in the limit of an infinitesimal perturbation in the interfacial area. Empirically, IFT can be related to the difference between the liquid and vapor densities through a phenomenological relationship known as the Parachor. Such an approach is useful from a practical standpoint, but its
lack of rigour precludes any meaningful extrapolation. From a more fundamental viewpoint, the calculation of the IFT can be based on corresponding states principles and statistical mechanics perturbation methods, where the Square Gradient Theory (SGT) stands out as one of the most widely used. From a formal perspective, classical density functional theory also provides a route to determine density profiles and IFT in simple scenarios, but it us yet to be fully developed for non-spherical fluids. In SGT, the Helmholtz energy density of the interfaceal fluid is described by the sum of two contributions. The first part takes into account the Helmholtz energy density for the homogeneous fluid at a local-density, while the second part represents the inhomogeneous contribution of Helmholtz energy by a product of square local-density gradients and some characteristic parameters. These latter parameters have been historically called influence parameters since their values govern the stability and characteristic length scales of the interfaces. The popularity of SGT can be attributed to its relative simplicity and to the unique proposition of using the same equation of state to model simultaneously the homogeneous (e.g., phase equilibria) and inhomogeneous (interfacial properties) behavior of fluids in a good agreement with experimental data. Additionally, SGT provides other interfacial properties such as density or concentration profiles along the interfacial zone, interface thickness, excess adsorption, surface enthalpy, and surface entropy, etc. The physical reliability of SGT has been verified by several authors for pure fluids and multicomponent fluid mixtures in different phase equilibria scenarios, such as vapor–liquid, liquid–liquid, vapor–liquid–liquid, and four phases. All these calculations have been carried out by using a myriad of equations of state (EoS) to model the homogeneous part of the interfacial Helmholtz energy. A representative but not exhaustive list of the most common used EoS are cubic van der Waals-type EoS, cubic plus association EoS, non-cubic EoS, technical EoS, and molecular based EoS.

Despite the success of SGT for describing interfacial properties of pure fluids and fluid mixtures, this theory depends crucially on the independent determination of the influence parameter. Theoretically, the influence parameter can be computed from its molecular definition (i.e., integration of the direct correlation function of the homogeneous fluid), but the available theories for the two-body direct correlation function between two species in homogeneous fluids are not completely developed, as the results still exhibit poor performance when compared to experimental or MD results. To circumvent this problem, Carey proposed to invert the problem and back-calculate the influence parameter using experimental data of IFT and SGT to later correlate the results to the EoS parameters. This semi-empirical approach has been broadly used for pure fluids and nowadays quite refined correlations are available. For instance, Zu and Stenby have used for pure fluids and nowadays quite refined correlations are available. For instance, Zu and Stenby have used the Peng-Robinson EoS and its volume translated version in SGT to correlate the influence parameter as a function of temperature and theacentric factor. These correlations have shown a remarkably good agreement between SGT estimations and experimental data. The same procedure has been also used starting from molecular based EoS, such as statistical associating fluid theory (SAFT) EoS and its variants, where both experimental data and MD simulations have been used to correlate the influence parameter (see for instance Refs. 48,53,71, and 78). Mixtures add another dimension of complexity, whereas the corresponding binary (cross) influence parameter must then be determined, usually in an empirical fashion through simple geometric mixing rules or by fitting to binary experimental data. This approach seems to work for most simple cases and is trivially extendable to multicomponent mixtures.

In summary, while SGT is a powerful theory for describing the IFT of pure fluids and fluid mixtures its main limitation for it to be used as a predictive theory is the lack of generality and limited transferability of the influence parameters. The main goal of this work is to develop a flexible, transferable and universal set of relations for the influence parameter for pure fluids. A rather long-standing affort has been made to produce a molecular-based equation of state that can faithfully represent in a quantitative fashion the macroscopic thermodynamic properties of fluids with variable range potentials. The latest version of these theories, the SAFT-VR-Mie equation, which will be discussed later, has been successfully employed both as a tool for fitting, correlating, and subsequent prediction of fluid phase equilibria in a wide range of scenarios (e.g., vapor–liquid equilibria, water-octanol partition coefficients, liquid–liquid equilibria, etc.) for a collection of industrially relevant fluids including, but not limited to polar fluids, refrigerants, crude oils, polymers, etc. However, possibly, the most interesting feature of these equations is the direct and quantitative link to the underlying potential, such that information gathered by experiments can be incorporated into intermolecular potentials of interest here. The aim of this work is to garner experience from the molecular simulation of vapor–liquid interfaces to directly feed into this framework and to build a robust and transferable model capable of predicting the properties of an interfacial system from a minimal amount of commonly available experimental information, such as critical constants (see Refs. 65–67 and 81–87 for a complete discussion).

This article is organized as follows: we summarize the main working expressions of the SGT and the SAFT-VR Mie EoS in Section “Theory”. In Section “Computational Methods” we briefly consider the Molecular simulation methodology used in this work. The main results obtained from the corresponding states correlations for IFT and applications for selected fluids are discussed in Section “Results and Discussion”. Finally, the main conclusions are summarized in Section “Concluding Remarks”.

Theory

The SGT for fluid interfaces

The SGT for fluid interfaces was proposed by van der Waals in the latter part of the XIX century, with the original paper published in 1894 after he confirmed the reliability of this theory by describing the observed experimental data of pure ether near to the critical state measured by de Vries in 1893. In the original work, van der Waals proposed for the first time a smooth density variation through the interface region rather than the infinitely sharp variation proposed by Laplace. For a complete historical description of the origin and motivations involved in the development of SGT and also its similarities to the work of Rayleigh and Fuchs on capillarity, the reader is redirected to the books by Kipnes et al., Levelt Sengers, and Rowlinson, and Rowlinson and Widom. The SGT was rediscovered and extended for mixtures by Cahn and Hilliard 60 years later. In the middle of 1970s, the SGT was remastered simultaneously and independently by Bongiorno and Davis and Yang et al. by using statistical mechanics arguments. However, its popularity rises at the end of 1970s, when Carey gave a boost to SGT by applying it to the Peng-Robinson EoS and reported interfacial properties for
both pure fluids and fluid mixtures. Since Carey’s seminal work, multiple authors have used SGT to describe interfacial properties for pure fluids and multicomponent mixtures in biphasic, triphasic, and multi-phase equilibrium. In fact, according to our records there are over 150 scientific papers related to SGT available in the open literature and this theory has been used as base for several PhD thesis (see for example, Refs. 76 and 94–98). As SGT has been broadly discussed in the references above, this section only condenses the main working expressions for modeling the interfacial behavior for the case of pure fluids in vapor–liquid equilibrium. The reader is directed Refs. 99 and 100 and the corresponding PhD thesis for a complete deduction of SGT.

In the SGT, the interfacial density of a pure fluid, \( \rho(z) \), varies continuously from the bulk density of a vapor \( (\rho(z \to -\infty) = \rho^V) \) to the bulk density of a liquid \( (\rho(z \to +\infty) = \rho^L) \). To describe this continuous evolution, van der Waals proposed to express the Helmholtz energy \( (A) \) of an interfacial or inhomogeneous fluid as a second order Taylor expansion about the homogenous Helmholtz energy density, \( a_0 \), at the local density \( \rho \). For the case of pure fluids characterized by flat interfaces between adjacent phases, the Taylor expansion may be performed along the interface width by considering a normal \( z \)-coordinate (perpendicular to the plane of the interface) as follows:

\[
A = \int_{-\infty}^{+\infty} \left[ a_0(\rho(z)) + \frac{1}{2} \left( \frac{d\rho(z)}{dz} \right)^2 \right] dz
\]  

(1)

where \( S \) corresponds to the interfacial area and \( c \) denotes the influence parameter. In this expression, the first term within the integral refers to the homogeneous fluid contribution and the second term corresponds to the inhomogeneous part expressed as gradient term multiplied by the influence parameter \( (c) \). The minimization of Eq. 1 for a closed system leads to the following second order differential equation of \( \rho(z) \):

\[
\frac{d}{dz} \left( \frac{c}{2} \left( \frac{d\rho(z)}{dz} \right)^2 \right) = \frac{d\Omega(\rho)}{d\rho}
\]  

(2)

in Eq. 2, \( \Omega \) represents the grand thermodynamic potential, which is defined as \( \Omega(\rho) = a_0(\rho) - \rho(\partial a_0/\partial \rho) \rho^0 \), where the superscript denotes that the term is evaluated at phase equilibrium conditions, and \( a_0 \) is the molar Helmholtz energy.

Considering the boundary conditions for a planar interface in vapor–liquid equilibrium (i.e., \( \rho(z \to +\infty) = \rho^L, \rho(z \to -\infty) = \rho^V \) and \( d\rho/dz(z \to \pm \infty) = 0 \)), the integration of Eq. 2 yields the interfacial density profile:

\[
z - z_0 = \int_{\rho_L^0}^{\rho(z)} \frac{c}{2(\Omega - \Omega^0)} d\rho
\]  

(3)

where \( z_0 \) is an arbitrary spatial coordinate for the bulk density \( \rho_0 \). \( \Omega^0 \) denotes the grand thermodynamic potential at equilibrium where \( \Omega^0 = \Omega^0(\rho^0) = \Omega^L(\rho^L) = -P^0_1 \) and \( P^0 \) is the bulk equilibrium pressure (or vapor pressure).

Within the SGT (cf. Equation 1), the IFT, \( \gamma \), between vapor–liquid phases can be computed from the following expression:

\[
\gamma = \left( \frac{\partial A}{\partial S} \right)_{\text{NTV}} = \int_{-\infty}^{+\infty} c \left( \frac{d\rho}{dz} \right)^2 dz
\]  

(4)

Alternatively, the IFT of pure fluids can be also calculated by using the following integral expression, which is obtained by combining Eqs. 3 and 4:

\[
\gamma = \int_{\rho_0^0}^{\rho^0} \sqrt{2c(\Omega + P^0)} d\rho
\]  

(5)

Inspection of Eqs. 3–5 reveals that the calculation of \( \rho(z) \) and \( \gamma \) depend on the EoS model and crucially, on the undetermined parameter \( c \).

The SAFT EoS

As is obvious from above, one of the key inputs of SGT is the EoS model. The EoS model not only provides a model for \( a_0 \) but also a framework to calculate the phase equilibrium and the corresponding bulk phase densities. Following Carey’s seminal work describing the procedure to link modern EoS to SGT, several EoSs have subsequently been used in SGT, being the Peng–Robinson EoS\(^77\) and SAFT EoS the most popular choices. In this context, the main advantage of cubic EoSs is their mathematical simplicity and the parametrization of their parameters in terms of critical coordinates and acentric factor. However, cubic EoSs display well documented limitations for simultaneous fitting both liquid densities, vapor pressures, and critical points. This limitation can be circumvented by using more sophisticated molecular EoS models such as the SAFT EoS (see McCabe and Galindo\(^101\) for a recent review on this EoS).

In this work, we select the most updated version of SAFT, the SAFT–VR–Mie EoS,\(^79\) which represents a significant advance in SAFT models.\(^102\) The main improvement of this version vs. older encarnations is the expression up to third order in the residual Helmholtz energy of the monomer term and the flexibility brought about by being based on the Mie potential,\(^103\) \( u_{\text{Mie}} \), which can be represented by

\[
\gamma_{\text{Mie}}(r_{ij}) = C_\varepsilon \left[ \frac{\sigma_{r_{ij}}}{\sigma_{r_{ij}}} - \left( \frac{\sigma_{r_{ij}}}{\lambda_{ij}} \right)^{\frac{2}{\varepsilon}} \right]
\]  

(6)

In Eq. 6, \( \lambda_\varepsilon \) and \( \lambda_{ij} \) are the repulsion and attraction parameters of the intermolecular potential, respectively, \( r_{ij} \) is the center-to-center distance of the interacting segments, \( \varepsilon \) is the energy scale corresponding to the potential well depth, \( \sigma \) is the length scale, corresponding loosely with an effective segment diameter, and \( C \) is a constant defined as:

\[
C = \frac{\lambda_\varepsilon}{\lambda_{ij} - \lambda_\varepsilon} \left( \frac{\lambda_{ij}}{\lambda_\varepsilon} \right)^{\frac{2}{\varepsilon}}
\]  

(7)

The Mie potential reverts to the well-known Lennard-Jones model\(^104\) if the repulsive and attractive exponents are taken as 12 and 6, respectively. The expression of the Helmholtz energy density of SAFT–VR Mie EoS for a non-associating chain fluid is given by\(^79\)

\[
a_0 = (a_{\text{IDEAL}} + a_{\text{MONO}} + a_{\text{CHAIN}}) \rho N_m \frac{N_m}{\beta}
\]  

(8)

where \( a_0 = A_0(N/k_BT) \) and \( A_0 \) is the total Helmholtz energy, \( N \) is the total number of molecules, \( N_m \) is the Avogadro constant, \( T \) is the temperature, \( k_B \) is the Boltzmann constant, \( \beta = 1/(k_BT) \), and \( \rho \) is the molar density of the fluid. \( a_{\text{MONO}} \) represents the monomer (unbounded) contribution for a chain composed of \( m \) tangential segments, \( a_{\text{CHAIN}} \) accounts for the formation of chain molecules and \( a_{\text{IDEAL}} \) is the ideal gas contribution. For a complete overview of this model the reader is referred to Ref. 79.

Coarse-graining of fluid potential using SAFT

In this work, the pure fluids are modeled as freely jointed tangential non-associating spheres (pearl-necklace model)
characterized by five parameters: \( m, \lambda_r, \lambda_a, \epsilon, \) and \( \sigma \), which can be found from several routes. One could be tempted to fit these parameters to the properties of a lower resolution model, for example, a fully atomistic classic molecular model of the Optimized Potentials for Liquid Simulations family. As the models proposed here are of lower fidelity some degrees of freedom would have to be factored out during this procedure which would result in a coarse grained (CG) model that is usually state dependent and unreliable. An alternative approach is to use the equation of state to fit macroscopic experimental thermophysical properties that derive from the Helmholtz energy, such as pressures and densities along the vapor–liquid saturation curve. This approach provides a pathway for obtaining robust parameters that describe the average pairwise interactions. An implicit assumption is that the equation of state describes precisely the underlying Hamiltonian, which is the case in the version of SAFT employed herein. This top–down CG parametrization is discussed in detail by Müller and Jackson. Talking this approach further, Mejía et al. expressed the SAFT-VR Mie EoS in a corresponding state form finding explicit links between a small number of well defined properties (critical temperature, acentric factor, and liquid density) and the force field parameters. This latter procedure is followed herein. The number of beads, \( m \), that describe a molecular model is determined beforehand by observation of the molecule geometry. The underlying model requires the bead to be tangent to each other and in a linear configuration (pearl-necklace model). Ramrattan et al. have shown that there is a conformality relationship between the exponents of the Mie potential; an infinite number of exponent pair \((\lambda_a, \lambda_r)\) will provide essentially the same fluid phase behavior. Following this, we chose to fix the attractive potential \( \lambda_a = 6 \) leaving the repulsive exponent \( \lambda_r = \lambda \) as the lone parameter that defines the range of the intermolecular potential.

Once the EoS parameters have been fixed, Eq. 8 is used to predict the vapor–liquid phase equilibrium according to the conditions of isothermal phase equilibrium for bulk phases: 

\[
\Omega(p) \ominus \Omega(p^c) = -p^c
\]  

(9)

\[
\left( \frac{\partial \Omega}{\partial \rho} \right)_{p^c, c} = \left( \frac{\partial \rho_a}{\partial \rho} \right)_{p^c, c} - \left( \frac{\partial \sigma_a}{\partial \rho} \right)_{p^c, c}
\]

(10)

\[
\left( \frac{\partial^2 \Omega}{\partial \rho^2} \right)_{p^c, c} = \left( \frac{\partial^2 \sigma_a}{\partial \rho^2} \right)_{p^c, c} > 0
\]

(11)

Equation 9 corresponds to the mechanical equilibrium condition \((p^c = p^0)\), Eq. 10 expresses the chemical potential constraint \((\partial \rho_a / \partial \rho)_{T, c} \equiv \mu, \mu^0 = \mu^l = \mu^g\), and Eq. 11 is a differential stability condition for interfaces, comparable to the Gibbs energy stability constraint of a single phase.

The influence parameter

In the original van der Waals theory, the influence parameter, \( c \), is defined as a constant, but modern versions of this theory reflect that this parameter should be a function of the direct correlation function of the homogeneous fluid. According to Bongiorno et al. and Yang et al., the rigorous definition of \( c \) is given by the following integral expression:

\[
c = \frac{k_B N_m^2}{6} \int \frac{\rho(r)}{V} \, dr
\]

(12)

where \( c^0(r; \rho) \) is the direct correlation function of homogeneous fluid and \( r \) is a spatial coordinate. Since \( c^0(r; \rho) \) is intracatable from an analytic viewpoint, some models have been developed to estimate the influence parameters from other measurable or computable quantities. According to Rowlinson and Widom, one of the most successful approximations for \( c^0 \) is to consider \( c^0(r; \rho) \approx c^0(r; T) \) where \( c^0(r; T) \) can be described by the Percus–Yevick approximation:

\[
c^0(r; T) = g(r)[1 - \exp(-u(r)/k_BT)]
\]

(13)

where \( g(r) \) is the radial distribution function of a fluid in the homogeneous state and \( u(r) \) is the intermolecular potential, respectively. In a mean field approximation, a locally uniform fluid distribution can be assumed, hence, \( g(r) \approx 1 \). Linearizing Equation 13, a mean-spherical approximation for the direct correlation function of homogeneous fluid can be obtained:

\[
c^0(r, T) \approx -u(r)/k_BT
\]

(14)

which if replaced in Eq. 12, and considering an isotropic fluid becomes

\[
c = -\frac{4\pi N_m^2}{6} \int_0^\infty r^4 u(r) dr
\]

(15)

Equation 15 represents the simplest approximate model for \( c \) and it acquires a final form once the intermolecular potential is defined. For the case of the Mie potential (cf. Eqs. 6 and 15) simplifies to:

\[
c = -\frac{2\pi N_m^2 C^c_{\sigma^5}}{3} \left[ \left( \frac{1}{\lambda_a-5} \right) - \left( \frac{1}{\lambda_a-5} \right) \right]
\]

(16)

From Eq. 16 it follows that \( c \) can be treated as a constant once the intermolecular potential exponents \((\lambda_a, \lambda_r)\) and fluid parameters \((\epsilon, \sigma)\) have been defined. Some particular cases of Eq. 16 have been used to predict the interfacial behavior of pure fluids and fluid mixtures. For example, \( \lambda_a = 12 \) and \( \lambda_a = 6 \) (i.e., the Lennard-Jones potential) has been used by Carey, to predict the \( c \) value and relate it to the Peng–Robinson EoS constant (i.e., \( a \) and \( b \)), whereas Tardón et al. used it to predict the interfacial behavior in asymmetric Lennard-Jones mixtures that display molar isopycnicity inversion. The reported results of concentration profiles show a qualitative agreement between theory and molecular simulations. Other examples include the use of \( \lambda_a = -\infty \) and \( \lambda = 6 \) (i.e., the Sutherland potential). This potential has been used by Poser to describe the interfacial properties of low molecular weight fluids and some polymers and Mejía and Segura used it to explore qualitatively the multiphase interfacial behavior of Type IV and Shield region. While a constant \( c \) value (cf. Eq. 16) can be used for describing qualitatively the interfacial properties for pure fluids and fluid mixtures, some previous works based on molecular simulations and SGT have demonstrated that the \( c \) values are a function of the shape factor (elongation, chain length, etc.) for nonspherical molecular fluids and are seen to vary with temperature. Specifically, Duque et al. have shown that as the molecular chain length increases the \( c \) values increases whereas Baidavok et al. and Galliero et al. reported values of \( c \) as a function of temperature for the case of spherical fluids. In addition, the values calculated from Eq. 16 for the case of monomer Lennard-Jones pure fluids display some overpredictions when they are compared to the values obtained from molecular simulation results. As an illustrative example, Eq. 16 predicts \( c \approx 7.181 N_m^2 \sigma^5 \) for a Lennard-Jones pure fluid which is 1.6 times the value reported by Duque et al.
In summary, the mean-spherical approximation for the direct correlation function of homogeneous fluid provides a route to obtain an analytical expression for $c$. This expression can be used for qualitative description of interfacial properties from SGT, but requires refinement if it is to be used as a predictive tool. In this work, the refinement of the theory is carried out by exploiting the direct link between EoS and the underlying intermolecular potential. Specifically, molecular simulations of the chain fluids composed of Mie beads are compared to the theory seeking a quantitative agreement. These resulting equations are the base for a molecular thermodynamic framework to correlate the IFT of industrial-relevant fluids.

**Computational Methods**

To provide a high fidelity data set for molecular fluids, we have carried out MD simulations of pure fluid interfacial properties, using the direct coexistence technique in inhomogeneous simulation boxes. We employ here canonical simulations where $N$ molecules at a fixed temperature $T$ are placed in a an elongated simulation cell of constant volume $V$. Following the methodology proposed by Martínez-Veracoechea and Müller, all simulations are started from a high temperature homogeneous monophasic system that is quenched abruptly to the simulation temperature until equilibration is reached through diffusive mass transport. In this work, chain molecules are treated as freely-jointed tangent Mie spheres, that is, bond distances are kept constant at a value of $\sigma$ and no further intra-molecular interactions are considered. All the sites have the same mass, and interact with each other through an effective pairwise Mie $\kappa r^{-6}$ intermolecular potential (c.f. Eq. 6).

MD simulations are performed on systems containing from 6500 to 12,600 Mie beads at conditions where the vapor–liquid interface is present. The simulation cell is a parallelepiped with periodic boundary conditions in all three directions. Specifically, $L_x$ and $L_y$ are parallel to the interfacial surface, while $L_z$ direction is normal to the interface. These values are chosen to ensure a cell large enough to accommodate liquid and gas regions with enough molecules to ensure a representative bulk phase. To guarantee this, $L_z$ is set to be 5–7 times larger. In all cases, the two interfaces spontaneously appear in the $x$–$y$ plane. To reduce the potential truncation and system size effects involved in the phase equilibrium and interfacial properties calculations, the cut-off radius ($r_c$) has been taken equal to a relatively large value of $10\sigma$. It has been shown that a cut-off above six

![Figure 1. Relationship between reduced tensions calculated from MD (ordinate) and the results from SGT (c.f. Eq. 20).](image-url)

The slope of the curve is proportional to $\sqrt{G/(m_s)}$. (a) Mie (8-6), (b) Mie (10-6), (c) Mie (12-6), (d) Mie (20-6) molecular chains fluid. Mie $\lambda - 6$ chains formed from $m_s = 1$ (circle), $m_s = 2$ (squares), $m_s = 3$ (diamonds), $m_s = 4$ (inverted triangles), $m_s = 5$ (triangles), $m_s = 6$ (right triangles) segments.
segment diameters provides a reliable description for the pressure and interfacial properties of the Lennard-Jones fluid and we expect that to translate to Mie fluids.

A modified version of the DL_POLY simulation package (which includes a specific routine to perform pressure components profile calculations) has been used, considering a Verlet-leapfrog algorithm with a time step of 0.003 in reduced units of \( \frac{e}{\sqrt{M}} \), where \( M \) denotes the particle or atom mass, and a Nose-Hoover thermostat with a time constant equal to 1.0 in reduced units of \( \frac{e}{\sqrt{M}} \). After the initial temperature quenching, the systems are equilibrated for \( 1 \times 10^5 \) time steps. After this equilibration stage, a production run is performed for at least another \( 4 \times 10^5 \) time steps.

To characterize the bulk phase and interfacial behavior, density profiles are calculated by dividing the system in 400 slabs along the \( z \) direction. The molecular density profiles, \( \rho_i(z) \), are obtained by assigning the position of each bead, \( z_i \), to the corresponding slab, and constructing the molecular density from mass balance considerations. Additionally, these profiles are displaced so that the center of mass of the liquid slab lies at the center of the simulation cell, this displacement helps to avoid smearing of the profiles due to fluctuations of the center of mass location. To estimate errors on the variables computed, the sub-block average method has been applied. In that approach, the production period is divided into \( n \) independent blocks. The statistical error is then deduced from the standard deviation of the average divided by \( n^{-1/2} \). The equilibrium pressure and IFT are obtained using the Irving-Kirkwood method, where the profiles of the pressure tensor diagonal elements are calculated employing the virial expression:

\[
P_{kk} = k_BT \rho(z) + \frac{1}{2} \sum_i \sum_{j>i} \frac{1}{|z_i-z_j|} \left( f_{ij}(r_{ij}) \right)_k
\]

where \( P_{kk} \) is the pressure tensor elements, the subscript \( kk \) represents the spacial coordinate, either \( x \), \( y \), or \( z \), \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( S \) is the interfacial area, \( N \) is the number of molecules, \( f_{ij} \) is the force on molecule \( i \) due to molecule \( j \), and \( r_{ij} \) represents the distance between molecules \( i \) and \( j \). \( f_{ij} \) contributions have been equally distributed among the slabs corresponding to each molecule and all the slabs between them. The term \( k_BT \rho(z) \) in Eq. 17 takes into account the kinetic contribution, which is proportional to the ideal gas pressure. The term inside the \( \langle \cdots \rangle \) brackets corresponds to the configurational part which is evaluated as ensemble averages and not at instantaneous values. From the pressure elements of Eq. 17, the vapor pressure can be determined, corresponding to the \( P_{zz} \) element, while the IFT, \( \gamma \), can be calculated as:

\[
\gamma = \frac{k_BT}{2} \left( \frac{P_{xx} + P_{yy} - P_{zz}}{2} \right)
\]
In this expression, the additional factor 1/2 comes from having two interfaces in the system. The specific details related to the technical implementation of the previous expressions and their evaluations have been discussed extensively in the literature (see Refs. 8, 49, and 120 for further details). This method, based on the mechanical definition of the pressure tensor, has been selected in this case among the diverse alternatives available, as for instance the so-called Test-Area method,11 that produces equivalent results for this type of systems, as demonstrated by Galliero et al.53

Results and Discussion

New expression for the influence parameter

The direct correspondence of SAFT-VR-Mie Eos with the results obtained from an exact solution, obtained via molecular simulations, of the macroscopic behavior of the underlying intermolecular potential suggests the possibility of obtaining the influence parameter directly by forcing the SGT model to reproduce exactly IFT data, as proposed originally by Carey.22,76 However, instead of employing data of real fluids. To consistently match the SGT to the IFT data, we use the same fluid model in MD and SGT. The advantage of this combination is that the fluid is described by the same five parameters: $m_s$, $\lambda_a$, $\lambda_r$, $\sigma$, and $\epsilon$ in both approaches. As explained previously, the attractive exponent can be fixed ($\lambda_a = 6$) leaving the repulsive exponent $\lambda_r = \lambda$ as the lone parameter that defines the range of the intermolecular potential, without any loss of generality.106,107

To combine the MD results of IFT (Eq. 18) to SGT (Eq. 5), we postulate that $c$ is a constant for each particular fluid (i.e., $c = 3(m_s, \sigma, \epsilon, \lambda, 6)$). If so, the influence parameter can be regressed from the integral (Eq. 5). It proves valuable to express the IFT from MD (Eq. 18) and SGT (Eq. 5) in reduced variables:

$$\gamma_{MD} = \frac{1}{2} \int_{-\infty}^{+\infty} \left[ P_{zz}(z) - \frac{P_{xx}(z) + P_{yy}(z)}{2} \right] dz \quad (18)$$

$$\gamma_{SGT} = \frac{1}{m_s} \sqrt{\frac{2c}{\epsilon \sigma^3}} \int_{0}^{e} \sqrt{(\Omega^2 + P^{\sigma})} d\rho^* \quad (20)$$

Of course, both equations, Eqs. 19 and 20, must provide the same numerical results as we compare the exact results from MD to those predicted from the theory. The integral on the right hand side of Eq. 20 can be evaluated without recourse to
specifying a particular value of the influence parameter, hence a plot of the tension calculated through MD \((c_{MD}/C3)\) as a function of the \(\phi_q/C3; L_q/C3; V_{\sqrt{\phi U}}/C31; P/C3; \theta(q)/C3; p_{\phi q}/C3\) provides a means of evaluating the prefactor of Eq. 20, namely \(1/m_s\sqrt{c/e}\). Since \(m_s, e, \) and \(a\) are specified \(a\ priori\), the procedure provides an explicit value of the influence parameter.

Figure 1 shows the results from MD vs. SGT (i.e., \(c_{MD}/C3; \phi_q/C3; L_q/C3; V_{\sqrt{\phi U}}/C31; P/C3; \theta(q)/C3; p_{\phi q}/C3\)) for pure fluids with different molecular chain length (i.e., \(m_s = 1\) to \(m_s = 6\)) and some selected values of \(k\) (Figure 1a: \(k = 8\); Figure 1b: \(k = 10\); Figure 1c: \(k = 12\); Figure 1d: \(k = 20\)). Simulation and theory results span a wide range of temperatures and chain lengths. Figure 1 evidences a remarkable linear dependence between the ordinate and the abscissa for each Mie \(k = 6\) fluid, up to a chain length value \(m_s = 6\). The slope of these curves corresponds to the term: \(1/m_s\sqrt{c/e}\). In other words, the straight lines in Figure 1 can be used to regress a temperature-independent influence parameter. This behavior clearly evidences a quasi-perfect universal behavior, which had already been predicted using scaling laws and was suggested from a corresponding states viewpoint. Particularly, Blas and co-workers have presented results\(^{121-124}\) studying the interfacial properties for the Lennard-Jones fluids (for both flexible and rigid chains) showing a similar agreement. Galliero\(^{114}\) also reported similar behavior by using a corresponding states approach for the case of short flexible Lennard-Jones chains, composed of up to five segments.

In the Supporting Information we summarize the numerical values of the slopes for Mie \(k = 6\) fluids as a function of \(k\). (see Table S. I). The challenge is to be able to generalize these results. Recently, Ramrattan et al.,\(^{107}\) pointed out that the behavior of Mie fluids is governed by the value of the integrated cohesion energy captured by the so-called the van der Waals constant, \(\alpha\), defined as\(^{125}\):

\[
\alpha = \frac{1}{k} \int_0^\infty u(r)r^2dr = C\left(\frac{1}{\lambda^3 - 3} - \frac{1}{\lambda^3 - 3}\right)
\]

From the results presented in Table S. I (provided in the Supporting Information), it is possible to observe that \((1/m_s)\sqrt{c/e}\) decreases with \(\alpha\), for a extended range of repulsive exponents. Indeed, from this analysis the term \((1/m_s)\sqrt{c/e}\)
can be correlated linearly with the van der Waals constant, \( \alpha \), and thus, we propose the following generalized function for the influence parameter of Mie \( \lambda - 6 \) chains fluids:

\[
\sqrt{\frac{c}{N^2 \omega \sigma^3}} = m_0 (0.12008 + 2.21979 \alpha)
\]  

(23)

Equation 23 is a general expression for the calculation of the influence parameter, valid for \( m_0 = 1-6 \) and \( \lambda = 8-38 \).

It is interesting to point out the differences between the estimation of influence parameters presented here to the results published using previous versions of SAFT-VR Mie coupled with SGT. In this work, we obtain a temperature-independent influence parameter for very soft potentials such as for instance the Mie (8-6) fluid, even when chain length increases (c.f. Figure 1a). For the same soft potential, Galliero et al.\(^{53} \) have obtained a different behavior using a previous SAFT-VR Mie model. In fact, they reported a strong temperature dependent influence parameter, especially when the fluid is approaching the critical region. Presumably this thermal dependence of the influence parameter is an artifact product of the inability of previous SAFT models to represent accurately the critical and near-critical region.\(^{128} \) The success of the current version of the SAFT theory relies on the extraordinary ability of the third-order expansion term proposed by Laftie et al.\(^{79} \) to produce a satisfactory description of VLE near the critical region.

**Interfacial properties for molecular fluids**

The correlation proposed above is validated by comparing the results obtained from the SGT + SAFT-VR Mie EoS to MD simulation results for the same molecular models (i.e., Mie chains of variable repulsive exponent value and number of segments). Specifically, we test the accuracy of Eq. 23 for use within the theory for predicting interfacial properties, such as interfacial density, \( \rho^*_i = \rho_i \sigma^3 \), profile along the interfacial region, \( \xi^* = \xi / \sigma \) and IFT, \( \gamma^* = \gamma / \sigma^2 \). Figure 2 shows the \( \rho^*_i - \xi^* \) profiles for the case of molecular chain fluids \( (m_i = 2, 3, 4, \) and 5) interacting by a Mie (10-6) potential. As expected, as the temperature increases, the interfacial region becomes wider, however, the take-home message from these figures is the very good agreement between MD and SGT with the influence parameter calculated from Eq. 23. In addition to the interfacial profiles in Figure 3 we display the IFT as a function of \( T^* \) for molecular chain fluids \( (m_i = 1-6) \) interacting through a Mie \( (\lambda, 6) \) potential with \( \lambda = 8, 10, 12, \) and 20. From Figure 3 it is possible to observe that at fixed Mie \( (\lambda, 6) \) and \( m_i \), the IFT decreases as the temperature increases, showing a characteristic hyperbolic tangent curve near to the critical state. From these figures, it evident how for a fixed value of the Mie \( (\lambda, 6) \) potential, the IFT increases with \( m_i \). Again the key issue evident in Figure 3 is the excellent quantitative agreement between both approaches (MD and SGT), over a wide range of repulsive exponents, molecular chain lengths, and temperature, including a satisfactory description near the critical region. The average absolute deviation of the results displayed in Figure 3 are 2.8% for Mie (8, 6), 1.67% for Mie (10, 6), 1.28% for Mie (12, 6) and 2.31% for Mie (20, 6).

As a comparison, Figure 3c includes the \( \gamma^* - T^* \) results for the case of Lennard-Jones chain fluid Mie (12-6) reported by Duque et al.\(^{48} \) The results reported here display a better agreement to MD results than those reported by Duque et al.,\(^{48} \) particularly for the longer chains.

**Corresponding states correlations for IFT**

An essential part of the seminal work of van der Waals is the idea that the properties of fluids could be scaled with respect to those of the critical point, providing a means of reporting a universal behavior referred to as the corresponding states principle. For the case of IFT, \( \gamma \), van der Waals\(^{16} \) used the critical pressure \( (P_c) \) and critical temperature \( (T_c) \) of the fluid to form the dimensionless group \( \gamma / P_c^{3/2} T_c^{1/2} \) and he proposed to correlate it with \( (1 - T/T_c) \). Based on the van der Waals ideas, some authors have used the corresponding state principia to propose IFT correlations. According to Poling et al.,\(^{13} \) the most popular correlations, based on the corresponding state principia, are the Brock and Bird\(^{129} \) and Pitzer,\(^{130} \) Zuo and Stenby,\(^{131} \) and Sastri and Rao.\(^{132} \)

Specifically, Brock and Bird\(^{129} \) have correlated \( \gamma \) as a function of \( P_c, T_c \) and the normal boiling temperature \( (T_b) \) for nonpolar fluids:

\[
\frac{\gamma}{P_c^{3/2} T_c^{1/2}} = (0.132 \xi - 0.279) (1 - T/T_c)^{11/9}
\]  

(24)

In Eq. 24 \( T_c \) is the reduced temperature \( (T_c = T/T_c) \) and \( \xi \) is the Riedel \(^{133} \) parameter at the critical point. This parameter has been correlated to \( P_c \) and \( T_c \) by Miller\(^{134} \):

\[
\xi = 0.9076 \left[ 1 + \frac{T_{br} \ln (P_c/1.01325)}{1 - T_{br}} \right]
\]  

(25)

In the last expression, \( T_{br} \) denotes the reduced normal boiling temperature \( (T_{br} = T/T_c) \). In Eqs. 24 and 25, the temperature is in Kelvin and the pressure is in bars.

A second popular correlation has been proposed by Curl and Pitzer\(^{130} \):

\[
\frac{\gamma}{P_c^{3/2} T_c^{1/2}} = \frac{1.86 + 1.18 \omega}{19.05} \left[ \frac{3.75 + 0.91 \omega}{0.291 + 0.08 \omega} \right]^{2/3} (1 - T/T_c)^{11/9}
\]  

(26)

as an extension of the scaling proposed initially by Guggenheim.\(^{14} \) In the Pitzer expression, \( \omega \) is theacentric factor, which is related to the deviation between the vapor pressure of a given fluid and that of a noble gas. A further correlation for \( \gamma \) has been proposed by Zuo and Stenby.\(^{131} \) In this work, the authors interpolate between two well-defined reference fluids. The final expression for \( \gamma \) is given by the following expressions:

\[
\gamma_i = \ln \left( 1 + \frac{\gamma}{P_c^{3/2} T_c^{1/2}} \right)
\]  

(27)

\[
\gamma = \gamma^{(a)} + \frac{\omega - \omega^{(a)}}{\omega^{(b)} - \omega^{(a)}} \left( \gamma_i^{(b)} - \gamma_i^{(a)} \right)
\]  

(28)

the superscripts \((a)\) and \((b)\) denote the reference fluids. Zuo and Stenby recommend to use methane \( \gamma^{(a)} = 40.520 \) \((1 - T/T_c)^{1.287}\) and \( n \)-octane \( \gamma^{(b)} = 52.095 \( (1 - T/T_c)^{1.2158}\).

According to Poling et al.,\(^{13} \) the methods described previously are satisfactory for nonpolar liquids. For other chemical families, such as alcohol- and acids, Poling et al.,\(^{13} \) recommend the use of Sastri and Rao correlation\(^{132} \):

\[
\gamma = KP_c^{3/2} T_c^{1/2} \left[ \frac{1 - T/T_c}{1 - T_{br}} \right]^m
\]  

(29)

In Eq. 29 \( K, x, y, z, m \) are constants unique for each chemical family. For example, for alcohols: \( K = 2.28, x = 0.25, y = 0.175, z = 0, m = 0.8 \). For acids: \( K = 0.125, x = 0.50, y = -1.5, z = 1.85, m = 11/9 \). For other families: \( K = 0.158, x = 0.25, y = 0.5,z = 0, m = 0.8 \).
Some application examples of the previous expression can be found in Poling et al.\textsuperscript{13}

In addition to the previous correlations, Miqueu et al.,\textsuperscript{135} have proposed the following expression:

\[
y = k_B T_c \frac{N_{av}}{V_c} \left( 4.35 + 4.14 \alpha \right)^{1/26} \left( 1 + 0.19 r^{0.5} + 0.25 t \right)
\]

In Eq. 30, \(V_c\) is the critical volume of the fluid and \(t = 1 - T/T_c\). This correlation has been successfully applied for petroleum fluids (i.e., light gases, saturated hydrocarbons, aromatics) and polar compounds (i.e., refrigerants).

**Interfacial properties for industrial fluids**

In this section, we test the proposed correlation for the case of industrial fluids. It is important to note that the approach used here is able to only calculate the variation of the IFT to the temperature but also to calculate the interfacial density profiles. As an example, we retake the model for hexane discussed in detail in Ref. 106. Hexane is modeled in a coarse-grained fashion as a dimer, \(m_s = 2\), and following the M & M procedure described in Ref. 106, an exponent of \(\lambda = 19.26\) is obtained. Use of Eq. 22 prescribes a value of \(\alpha = 0.669\). Further use of the correlations in Ref. 106 yield \(\epsilon/k_B = 376.35\) K and \(\sigma = 4.508\) Å. With these data Eq. 23 produces a value of \(c = 36.182 \times 10^{-20}\) J m\(^2\) mol\(^{-1}\). The predicted results for phase equilibria, density profiles, and surface tension are shown in Figures 4a–d. Specifically, Figures 4a,b show the phase equilibrium in \(\rho - T\) and \(T - P\) projections, respectively. In these figures we have included SAFT-VR Mie predictions, MD results employing the same potential (\(\lambda = 19.26\), \(\epsilon/k_B = 376.35\) K, and \(\sigma = 4.508\) Å) and recommended experimental data from DEHEMA\textsuperscript{136} and Figures 4c,d display the interfacial properties calculated from SAFT-VR Mie + SGT and the proposed expression for the influence parameter (see Eq. 23) and MD simulations carried out by using the same Mie parameters than the theory. From Figure 4c, it is seen that these profiles display the expected behavior, (i.e., they decrease monotonically across the interface following a hyperbolic tangent shape, that spans from the liquid to the vapor bulk phase). Noticeably there is a very good agreement between theory and simulations over a broad temperature range. Figure 4d represents the IFT behavior as a function of temperature. From the latter figures, it is evident that there is a remarkable quantitative agreement to the MD results as well as to experimental tensiometry results all the way from low temperatures to the critical temperature. In the Supporting Information, we include a workbook written in Mathematica code that performs all calculations described above for \(n\)-hexane.

To evaluate the performance of SAFT-VR Mie + SGT and the new expression for the influence parameter (see Eq. 23), \(m = 11/9\). Some application examples of the previous expression can be found in Poling et al.\textsuperscript{13}

In Eq. 30, \(V_c\) is the critical volume of the fluid and \(t = 1 - T/T_c\). This correlation has been successfully applied for petroleum fluids (i.e., light gases, saturated hydrocarbons, aromatics) and polar compounds (i.e., refrigerants).

**Table 1. Force Field Parameters for some Coarse Grained Mie \(\lambda\) – 6 Fluids**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>(m_s)</th>
<th>(\epsilon/k_B) (K)</th>
<th>(\sigma) (Å)</th>
<th>(\lambda)</th>
<th>(\alpha)</th>
<th>(c) (J m(^{-2}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH(_4))</td>
<td>1</td>
<td>170.75</td>
<td>3.752</td>
<td>16.39</td>
<td>0.729</td>
<td>1.921</td>
</tr>
<tr>
<td>Propane (C(_2)H(_6))</td>
<td>1</td>
<td>426.08</td>
<td>4.929</td>
<td>34.29</td>
<td>0.518</td>
<td>10.387</td>
</tr>
<tr>
<td>Sulfur Hexafluoride (SF(_6))</td>
<td>1</td>
<td>389.10</td>
<td>4.898</td>
<td>43.97</td>
<td>0.490</td>
<td>8.015</td>
</tr>
<tr>
<td>Tetrafluoromethane (CF(_4))</td>
<td>1</td>
<td>269.37</td>
<td>4.381</td>
<td>38.34</td>
<td>0.510</td>
<td>3.415</td>
</tr>
<tr>
<td>Nitrogen (N(_2))</td>
<td>1</td>
<td>122.85</td>
<td>3.753</td>
<td>20.02</td>
<td>0.656</td>
<td>1.140</td>
</tr>
<tr>
<td>Hexane (C(_6)H(_14))</td>
<td>2</td>
<td>376.35</td>
<td>4.508</td>
<td>19.26</td>
<td>0.669</td>
<td>36.182</td>
</tr>
<tr>
<td>Heptane (C(_7)H(_16))</td>
<td>2</td>
<td>436.13</td>
<td>4.766</td>
<td>23.81</td>
<td>0.606</td>
<td>46.227</td>
</tr>
<tr>
<td>Naphthalene (C(_8)H(_8))</td>
<td>2</td>
<td>557.75</td>
<td>4.623</td>
<td>19.50</td>
<td>0.665</td>
<td>60.132</td>
</tr>
<tr>
<td>p-Xylene (C(_8)H(_10))</td>
<td>2</td>
<td>475.76</td>
<td>4.524</td>
<td>21.17</td>
<td>0.639</td>
<td>42.889</td>
</tr>
<tr>
<td>HFC-1234yf (C(_3)F(_8))</td>
<td>2</td>
<td>265.53</td>
<td>4.074</td>
<td>18.22</td>
<td>0.688</td>
<td>16.215</td>
</tr>
<tr>
<td>Butanal (C(_4)H(_8)O)</td>
<td>3</td>
<td>382.23</td>
<td>3.998</td>
<td>17.69</td>
<td>0.699</td>
<td>21.864</td>
</tr>
<tr>
<td>Decane (C(_10)H(_22))</td>
<td>3</td>
<td>415.19</td>
<td>4.585</td>
<td>20.92</td>
<td>0.643</td>
<td>90.785</td>
</tr>
<tr>
<td>HFC (C(_4)H(_8)O)</td>
<td>4</td>
<td>279.42</td>
<td>4.068</td>
<td>17.36</td>
<td>0.706</td>
<td>39.963</td>
</tr>
<tr>
<td>Tetradecane (C(_14)H(_30))</td>
<td>4</td>
<td>438.11</td>
<td>4.619</td>
<td>22.22</td>
<td>0.625</td>
<td>167.920</td>
</tr>
<tr>
<td>Eicosane (C(_20)H(_42))</td>
<td>6</td>
<td>453.10</td>
<td>4.487</td>
<td>24.70</td>
<td>0.597</td>
<td>310.718</td>
</tr>
</tbody>
</table>

\(x = 0.50, \ y = -1.50, \ z = 1.85, \ m = 11/9\).

Figure 5. Comparison between calculated (lines) with the SAFT-VR Mie + SGT and Eq. 23 for the influence parameters and experimental\textsuperscript{136} (symbols) interfacial tensions as a function of temperature for various components.

Information about the SAFT-VR Mie parameters that were used in the calculations and the experimental data can be found in Table 2.
we selected some test fluids (e.g., hydrocarbons, N₂, refrigerants, etc.), and applied a two-step predictive approach. First, the fluids are idealized as chains of CG tangential spheres interacting with each other through a Mie (1 - 1) potential, whose parameters (m_e, ε, σ, λ) are obtained via the corresponding state principles described by Mejía et al.¹⁰⁶ Basically, in this step once the number of beads in the chain is defined (n), by examining the overall molecular geometry (i.e., its length to breadth ratio), the value of ε is calculated from the acentric factor of the fluid (Ω), expressing the relationship between the range of the potential and the vapor pressure of the fluid. In an analogous fashion, the energy parameter (ε) is obtained from the critical temperature of the fluid (T_c), and the value of σ is calculated from the liquid density evaluated at 0.7 of T_c. Once the Mie (1 - 6) parameters have been identified, the van der Waals constant, a, can be computed from Eq. 22 and the influence parameter is obtained from Eq. 23. A second final step is to calculate the phase equilibrium from Eqs. 9 - 11 and the corresponding IFT from Eq. 5.

Table 1 summarizes the Mie (1 - 6) parameters for an unabridged selection of fluids, taken from Ref. 106, and Figures 5a,b displays the variation of the IFT with temperature for these selected fluids. These figures include also the experimental tensiometry data reported by The DECHEMA data base.¹³⁶ Figure 5a displays the very good agreement with experimental data obtained from the theory. In fact, the overall Average Absolute Deviation (% AAD) of the calculated IFTs is 2.8% in the case of hydrocarbons (see Figure 5a), and 3.7% for the other fluids selected (see Figure 5b).

To evaluate the performance of the proposed methodology to other correlations, Table 2 includes the Average Absolute Deviation for the IFT (% AAD) obtained from this work (i.e., from Eqs. 5 and 23) and those calculated from correlations based on the corresponding state principles. Specifically, Table 2 summarizes the % AAD obtained from the correlations developed by Brock and Bird,¹²⁹ Curl and Pitzer,¹³⁰ Zuo and Stenby,¹³¹ Sastri and Rao,¹³² and Miqueu et al.¹³⁵ It is seen that the proposed method is not only more accurate than other available correlations, but it is also broader in terms of applicability range.

Concluding Remarks

Several correlations exist which, based on semi-empirical corresponding states principles or otherwise, allow the calculation of IFT of industrially relevant fluids. However, their application is typically restricted to the chemical family used to fix the constants involved. In this work we combine a molecular thermodynamic theory and molecular simulations to obtain faithful description of the tensiometry of molecular models of fluids and a mapping of it to experimental data. Specifically, this work combines a theoretical approach based on the SAFT-VR Mie EoS with the SGT approach based on the SAFT-VR Mie EoS and MD. This approach is based on the description of the interfacial properties for short flexible chains composed of 2, 3, 4, 5, and 6 freely-jointed tangent spheres through a Mie (1 - 6) (λ = 8, 10, 12, 20) potential. From the MD results, a simple, flexible and accurate expression for the correlation of the influence parameter in SGT is obtained. This expression provides a route to calculate the influence parameters for pure chain fluids by only using the molecular characteristics of the model fluid (m_e, ε, σ, λ). By combining this approach with previous mappings of the Mie potential to pure fluids (Ref. 106) one can effectively predict the bulk and interfacial properties of pure fluids from the knowledge of only three widely available properties: the critical temperature, the acentric factor, and a liquid density. A key aspect of the methodology is the internal consistency of the molecular model, that is, both the theory and the simulations are based on the same set of unique force field descriptors. The correlation for the influence parameter can be used for describing the interfacial properties of molecular CG fluids with an absolute deviation lower than 2.02%.

Uniquely, the procedure could also be inverted: given the desired IFT of a fluid, a set of Mie parameters can be specifically found by a simple analytical approach without the need of performing simulations. From these parameters, a search in databases (e.g. www.bottledsaft.org) could provide a route to reverse-engineer the identify of the desired fluid. This is particularly useful in developing top–down coarse-grain potentials.
for simulations of surfactants and interfacial fluids. This extension is not pursued here but will be the subject of future work.

The proposed molecular model is both robust and transferable, producing both a set of molecular parameters amenable to be used in molecular simulation and a fully consistent theory for predicting the interfacial properties of Mie fluids. It is applicable in as much as a homonuclear non-associating chain remains a good model of the pure fluid; that is, if is not expected to work for strongly associating fluids (e.g., water and small alcohols). However, where applicable, the predictions show a remarkable accuracy when compared to traditional corresponding state principia correlations. In addition, the proposed approach not only gives an excellent model to predict the IFT over a wide temperature range, even very close to the critical region, but also provides a route to obtain microscopic information of the interfacial region, such as interfacial density profiles.

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Literature Cited


