

New Model for the Correlation of the Surface Tension Based on Friction Theory

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A new correlation method for the surface tension of fluids is proposed, which is based on friction theory applied to the interface of a two-phase system. The substance properties enter the model by a regular equation of state. Here we derive the method and test it with the Lennard-Jones 12-6 fluid as the reference system using molecular dynamics simulations of the vapor–liquid interface in combination with a new Lennard-Jones 12-6 equation of state. Further correlations of experimental surface tension data based on the Peng–Robinson and the PC-SAFT equations of state are presented. As a result, we find that the method allows an accurate correlation of the surface tension of pure fluids.

1. Introduction

Surface tension is an important property of pure fluids and their mixtures for many technical applications, for example, ink jet printing or oil recovery where the surface tension is a key property for the flow through porous media. There are several different approaches for the correlation of the surface tension. Some methods are purely empirical such as the Weinaug and Katz¹ model, which is widely used in the oil industry. Other approaches have a more theoretical background and may be based on statistical mechanics concepts such as the van der Waals–Cahn–Hilliard theory,^{2–4} the density functional theory,^{5,6} the gradient theory,^{7,8} or the hard sphere fluid scaled particle theory.⁹ Furthermore, it is possible to calculate the surface tension from molecular simulation of an interface based on the interactions between the atoms and molecules only.^{10,11} However, statistical mechanics approaches as well as molecular simulations are either limited to specific systems or require a too large numerical effort for routine applications. On the other hand the empirical methods cannot be reliably used for extrapolation or for the calculation of the surface tension of mixtures. In industrial applications, it is desirable to have an easily applicable method giving accurate results but based on models of a mathematical simple nature. Therefore there is a need for physically based correlation models, which are easy to handle, that can be used for extrapolations and require little computing effort.

2. The Friction Model

2.1. Basic Concepts. The starting point of the model is the mechanical definition of the surface tension by Irving and Kirkwood¹²

$$\gamma = \int_{-\infty}^{\infty} (p_N - p_T) dz \quad (1)$$

where p_N is the normal pressure and p_T the tangential pressure at an interface between a liquid and a vapor in equilibrium. Thus, for a two-dimensional symmetric interface the stress tensor \mathbf{T} acting throughout the interface can be defined as

$$\mathbf{T} = \begin{pmatrix} \sigma_1 & 0 \\ 0 & \sigma_2 \end{pmatrix} \quad (2)$$

Here $\sigma_1 = -p_N$ and $\sigma_2 = -p_T$ are the principal stress tensor components. In an arbitrary direction however a shear component τ is present that follows from a rotation of the frame of reference away from the principal directions that are given by the tangential and normal directions to the interface. The components of the stress tensor in an arbitrary direction can be represented graphically by a Mohr circle with the radius R (Figure 1) that also gives a relation between the principal stresses and the shear component of the stress tensor. One obtains for the maximum shear stress

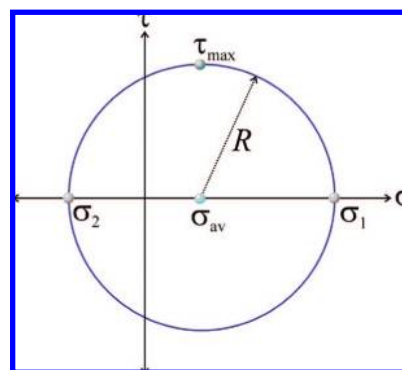


Figure 1. Mohr circle for a two-dimensional system.

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$$\tau_{\max} = \frac{\sigma_1 - \sigma_2}{2} = R \quad (3)$$

Replacing the σ_i by the pressure components gives

$$\tau = \frac{p_T - p_N}{2} \quad (4)$$

where hereafter the shear stress τ will always denote the maximum shear stress.

Thus, by substituting eq 4 in eq 1 an equation relating the shear stress to the surface tension is obtained

$$\gamma = -2 \int_{-\infty}^{\infty} \tau \, dz \quad (5)$$

2.2. Friction Model. The Amontons–Coulomb friction law establishes the relation between the shear stress τ and the normal stress σ through a Taylor series expansion of the form

$$\tau = \sum_{i=0}^n \mu_i \sigma^i \quad (6)$$

If σ is identified as the normal stress exerted by the weight of a body onto a surface, setting $n = 1$ (first order truncation) and $\mu_0 = 0$ (levitation condition, i.e., no friction under no weight) eq 6 results in the classical first order Amontons–Coulomb friction law. In the case of the related friction theory work for viscosity, similar concepts have been applied by taking advantage of the van der Waals attractive and repulsive contributions to the pressure that are derived from an equation of state (EoS).^{13,14} In this work, we closely follow the same EoS-based approach for the modeling of surface tension.

Thus, we first assume that an appropriate EoS showing a stable interfacial van der Waals loop between the coexisting liquid and the vapor phases is available, that is, the subcritical isotherms of the EoS show a single loop confined within the phase boundaries. Consequently, the calculation of densities from the EoS at an equilibrium pressure gives three roots: the orthobaric liquid and vapor densities and an unstable root between them. The van der Waals EoS and related cubic EoS are examples of models delivering such stable van der Waals interfacial loops. In contrast, most of the highly accurate reference EoS cannot be used for interfacial properties due to the unphysical behavior they normally show in the nonstable region, particularly at low temperatures. Figure 2 illustrates this problem by comparing the full isotherms of CO₂ for temperatures of T_c , $0.9 T_c$ and $0.8 T_c$ for the highly accurate Span and Wagner (SW) reference EoS¹⁵ and the Peng and Robinson (PR) EoS.¹⁶ Clearly, in spite of its high accuracy for the calculation of stable phase properties, the SW EoS cannot be applied to interfacial properties or any other property involving metastable or unstable states.

Mechanical equilibrium requires that the stress normal to the interface (p_N) be constant through the interface and equals the equilibrium pressure. Then, the friction model proposed in this work is simply based on the normal stress σ resulting from the difference between the local thermodynamic pressure p along all points within the van der Waals loop and the equilibrium vapor pressure p_N

$$\sigma = p - p_N \quad (7)$$

Substituting again eq 7 in eq 6, truncating the series at the first order, and imposing the condition of zero shear at zero normal stress gives the following Amontons–Coulomb friction model for the interfacial shear

$$\tau = \kappa(p - p_N) \quad (8)$$

where κ is a friction constant. The model clearly satisfies the condition of zero shear outside the interfacial region where the stress tensor must become isotropic ($p = p_N = p_T$ outside the interfacial region). The model could also, in principle, include higher order terms as in the related viscosity work for improved high-pressure performance; in the case of surface tension however a first order model appears to suffice.

By applying the chain rule to eq 5 it is possible to write the limits of integration in terms of the bulk densities

$$\gamma = -2 \int_{\rho_{\text{liq}}}^{\rho_{\text{vap}}} \tau \left(\frac{dz}{d\rho} \right) d\rho \quad (9)$$

where $z(\rho)$ is the interfacial density profile. Next, one can replace the shear stress τ by the friction model (eq 8) and apply the mean-value theorem to solve the integral

$$\gamma = 2\kappa \left(p_m - p_N \right) \frac{dz}{d\rho} \Big|_{\rho_m} (\rho_{\text{liq}} - \rho_{\text{vap}}) \quad (10)$$

Here $p_m = p(\rho_m)$ and $(dz/d\rho)|_{\rho_m}$ are the thermodynamic pressure and density profile gradient evaluated at the mean-point density ρ_m with $\rho_{\text{vap}} < \rho_m < \rho_{\text{liq}}$.

Finally, the friction model for the interfacial tension is completed by the addition of a secondary model for the interfacial density profile, namely

$$\rho(z) = \frac{1}{2}(\rho_{\text{liq}} + \rho_{\text{vap}}) - \frac{1}{2}(\rho_{\text{liq}} - \rho_{\text{vap}}) \tanh\left(\frac{2z}{d}\right) \quad (11)$$

This hyperbolic tangent based model has been widely used in literature.^{17,18} Here, z is the coordinate perpendicular to a vapor–liquid interface centered at the origin and d the interfacial thickness. This hyperbolic tangent model appears to be reasonably accurate for the modeling of molecular

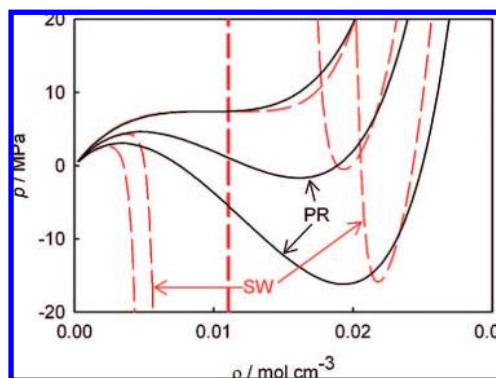


Figure 2. Plot of the van der Waals loops for CO₂ at $T/T_c = 1.0, 0.9,$ and 0.8 . Dashed (red) curves: Span-Wagner¹⁵ reference CO₂ EoS. Solid (black) curves: CO₂ using the Peng–Robinson¹⁶ EoS.

simulation results in addition to having a mathematically simple derivative

$$\left(\frac{dz}{d\rho}\right) = \frac{d(\rho_{\text{liq}} - \rho_{\text{vap}})}{4(\rho - \rho_{\text{liq}})(\rho - \rho_{\text{vap}})} \quad (12)$$

leading to

$$\gamma = \frac{\kappa d(p_m - p_N)(\rho_{\text{liq}} - \rho_{\text{vap}})^2}{2(\rho_m - \rho_{\text{liq}})(\rho_m - \rho_{\text{vap}})} \quad (13)$$

Equation 13 is therefore introduced as the fundamental friction model for interfacial tension. Clearly, the model still depends on the interfacial thickness d , which, according to the mean field theory, should diverge with $(T_c - T)^{-0.5}$. However, this part of the model will be discussed later for specific examples.

3. Model Fluids

3.1. The Lennard-Jones 12-6 Fluid. The Lennard-Jones 12-6 fluid is one of the best-studied theoretical reference fluids and therefore a good reference case for testing and developing the friction model proposed in this work. It is necessary, of course, to have an appropriate EoS for the Lennard-Jones fluid. Most existing Lennard-Jones (LJ) EoS are based on the virial expansion or on the BWR EoS.¹⁹ Such EoS cannot be guaranteed to have single van der Waals loops and hence cannot be used here.

The LJ EoS used in this work is the one previously proposed by Quiñones-Cisneros, Piñeiro, and Deiters²⁰ (QPD LJ EoS). It consists of three parts, a repulsive p_r part, an attractive p_a part, and a dispersive part

$$p = p_r + p_a + p_{\text{dis}} \quad (14)$$

In reduced variables ($T^* = (k_B/\epsilon)T$, $p^* = (\sigma^3/\epsilon)p$ and $\rho^* = \sigma^3\rho$, where k_B is the Boltzmann constant, σ is the particle diameter, and ϵ is the depth of the LJ potential) the QPD LJ EoS formulation is given by

$$p_r^* = \frac{T^*\rho^* + (\alpha_0 + \alpha_1\Delta T^{*-0.5} + \alpha_2\Delta T^{*0.5})\rho^{*2} + (\alpha_3 + \alpha_4\Delta T^{*-0.5} + \alpha_5\Delta T^{*0.5})\rho^{*4}}{1 - b\rho^*} \quad (15)$$

$$p_a^* = -(\beta_2\rho^{*2} + \beta_4\rho^{*4}) \quad (16)$$

and

$$p_{\text{dis}}^* = (e_0 + e_1\Delta T^{*-1} + e_2\Delta T^{*-2})\rho^{*1.9} \exp[(\mu_0 + \mu_1\Delta T^* + \mu_2\Delta T^{*2})\rho^{*3}] \quad (17)$$

with

$$\Delta T^{*n} = T^{*n} - 1.35^n \text{ and } b = 0.548207 \quad (18)$$

The QPD LJ EoS is mainly based on the extensive analysis of the simulation data of Meier²¹ and Johnson et al.²² The values

TABLE 1: Parameters of the Lennard-Jones EoS (Equation 14)

| i | α_i | β_i | e_i | μ_i |
|-----|------------|-----------|----------|-----------|
| 0 | 14.3497 | | 2.65673 | 6.14597 |
| 1 | -1.62136 | | 6.85164 | 4.75496 |
| 2 | 5.61570 | 23.1076 | -2.87586 | -0.386968 |
| 3 | 2.65199 | | | |
| 4 | 0.932491 | 7.00775 | | |
| 5 | 0.00752666 | | | |

for the QPD LJ EoS parameters are reported in Table 1. The overall model performance is basically that of a reference EoS; the overall absolute average deviation (AAD) is better than 0.9% for a T^* range from 0.7 to 6 and ρ^* up to 1.0 (p^* exceeding 50 in some cases). For the liquid state, the most recent calculation results of Meier are reproduced with an AAD of 0.12% and the data of Johnson with 0.52%. The highest model uncertainty is encountered in the low-density low-temperature vapor phase with deviations of around 2%. The critical point of the QPD LJ EoS is at $\rho_c^* = 0.323622$, $T_c^* = 1.3321$ and $p_c^* = 0.13873$.

In order to test the proposed friction model for surface tension, MD simulations were performed for the Lennard-Jones 12-6 fluid.²³ The simulations yield the surface tension, which is a macroscopic property, as well as the interfacial thickness, which is a parameter in the surface tension model.

A first step in testing the friction model follows from substituting eq 4 into eq 8, resulting in the following model for the tangential pressure component p_T

$$p_T = 2\kappa(p - p_N) + p_N \quad (19)$$

where the friction constant κ can be considered an adjustable parameter, possibly temperature dependent. It can be determined, for example, by fitting against simulation data of the tangential pressure component p_T using the vapor pressure for p_N and an equation of state for p . Figure 3 shows the result of such correlation considering κ constant and using the QPD LJ EoS.

Despite the simplicity of the model, the agreement between the simulations results and eq 19 is remarkable. At low temperatures the model tends to deviate from the simulated data. However, it should be pointed out that few metastable data, no unstable data, and certainly none of the simulation data used in this work went into the original correlation of the QPD LJ EoS parameters. In fact, the shape of the van der Waals loop in the QPD LJ EoS is largely qualitative. The only data having a

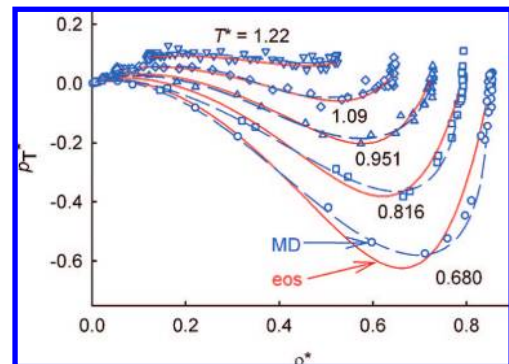


Figure 3. Plot of the tangential pressure versus density across the interface at different temperatures. Symbols and dashed (blue) curves: data obtained from MD simulation together with the correlation of these data.²³ Solid (red) curves: friction model results, eq 19, using a constant fitted value of $\kappa = 0.261422$ and the QPD LJ EoS.

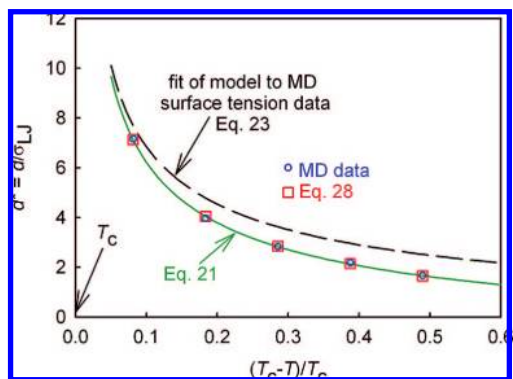


Figure 4. Interfacial thickness of the LJ 12-6 vapor–liquid interface. Symbols, data obtained from MD simulations;²³ solid curve (green), correlation of the MD data by eq 20; dashed curve (purple), resulting d^* after a correlation of the friction model (eqs 13 and 20) directly with the MD surface tension data.

weight in shaping the loop are the equilibrium data, which require the canceling of the areas related to the Maxwell construction. The accuracy of this property tends to deteriorate at low temperatures. As such, the deviations shown in Figure 3 may originate from the fact that the equation of state can only provide an interpolation into the nonstable region. Consequently, the analysis provided here can also help to improve the performance of some EoS into the metastable or even the unstable region possibly resulting in the development of accurate EoS also applicable to interfacial properties, a major limitation of current reference EoS. Furthermore eq 19 provides an alternative expression for the approach given in eq 4 of Imre et al.²³

Coming back now to eq 13 it is recalled that the friction model still depends on the interfacial thickness d and that, according to the mean field theory,²⁴ d should diverge with $(T_c - T)^{-0.5}$. Thus, a basic model for d is given by

$$d = d_0 + d_1 \left(1 - \frac{T}{T_c}\right)^{-0.5} \quad (20)$$

Figure 4 shows MD simulation data of the interface thickness plotted versus the temperature. The data correlated with eq 20 represent the simulation data very well. The resulting parameters for this fit are

$$d^* = \frac{d}{\sigma} = -2.09367 + 2.62900 \left(1 - \frac{T}{T_c}\right)^{-0.5} \quad (21)$$

Next, substituting eq 12 into eq 9 yields

$$\gamma = \frac{1}{2} \kappa d \int_{\rho_{\text{vap}}}^{\rho_{\text{liq}}} \frac{(p - p_N)(\rho_{\text{liq}} - \rho_{\text{vap}})}{(\rho - \rho_{\text{liq}})(\rho - \rho_{\text{vap}})} d\rho \quad (22)$$

an integral that now can be solved yielding the surface tension. The results of these calculations are indicated in Figure 5 as direct results. Clearly, although the trend appears to be correct a systematic deviation is observed at low temperatures. The source for these deviations can be explained from the decoupling observed in the low temperature isotherms shown in Figure 3. As previously explained, the QPD LJ EoS had been developed independent from this work, and its van der Waals loops are essentially interpolations into the metastable and unstable

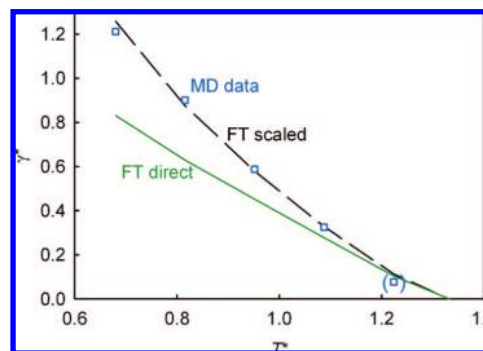


Figure 5. Surface tension results for the LJ 12-6 fluid. Symbols data obtained from MD simulations;²³ solid curve (green): direct surface tension friction model predictions directly using the MD data as estimation for the interfacial thickness; dashed curve (purple): surface tension friction model predictions after regressing the parameters for the interfacial thickness model against the surface tension data.

regions. Such deviations are more pronounced in the liquid metastable region of the low temperature isotherms, a region that has the highest specific weight in the total value of the integral defined in eq 22.

An alternative approach to circumvent possible shortcomings of an EoS and certainly valid for real fluids can be a direct fit of the parameters in eq 20 against the final interfacial data by means of eq 22. Such a procedure results in the scaled model for the interface thickness also shown in Figure 4 that corresponds to

$$d^* = -1.05267 + 2.49755 \left(1 - \frac{T}{T_c}\right)^{-0.5} \quad (23)$$

Using this model an excellent agreement is finally achieved in the reproduction of the surface tension results for the LJ 12-6 fluid, as also depicted in Figure 5.

Finally, before leaving this section, a simplified model for the surface tension of the LJ 12-6 fluid is presented. As a first step, it is pointed out that by coinciding eq 22 and eq 13 the mean-point density ρ_m can be calculated. Furthermore, since ρ_m should necessarily be between ρ_{vap} and ρ_{liq} the following relation can be proposed

$$\rho_m = \frac{\rho_{\text{liq}} + \rho_{\text{vap}}}{2} + \varphi \frac{\rho_{\text{liq}} - \rho_{\text{vap}}}{2} \quad (24)$$

This leads to an algebraic simplification of eq 13 resulting in

$$\gamma = \frac{2d\kappa(p_N - p_m)}{1 - \varphi^2} \quad (25)$$

Dividing eqs 22 and 13 by $(d\kappa)$ shows that the value of the resulting integral does not depend on any surface tension data. Therefore one can solve the integral for various temperatures and attempt a general correlation for the ϕ parameter of eq 24. Such results are depicted in Figure 6 with the final correlation given by

$$\varphi = 0.3792 \left(1 - \frac{T}{T_c}\right)^{1.5} - 1.0268 \left(1 - \frac{T}{T_c}\right) + 0.8269 \left(1 - \frac{T}{T_c}\right)^{0.5} \quad (26)$$

Therefore, eq 25 in conjunction with the QPD LJ EoS as well as the correlations given in eqs 23 and 26 along with

$$\kappa = 0.261422 \quad (27)$$

result in a highly accurate model for the calculation of the surface tension of the LJ 12-6 fluid. Consistent with the uncertainty of the simulations, the model AAD is below 1%.

3.2. The Peng–Robinson Fluid. In this section, the model is summarized and applied to some selected systems of industrial interest. For this the PR EoS has been selected, which is a simple EoS widely used in numerous industrial applications where surface tension is a key property, such as enhanced oil recovery. Exactly the same model as proposed for the LJ fluid can now be used for “real” fluids that can be described with the PR EoS. However, when one considers industrial applications one should also consider possible limitations to be found in more complex situations such as mixtures (work currently in progress). In the case of mixtures there are more degrees of freedom and, as a consequence, the critical points are not invariant. Hence, models for thermophysical properties that explicitly refer to critical properties of mixtures may pose potential problems. For the description of the interface thickness it would be preferable to use an alternative model that depends on local properties only instead of the critical constants. Such alternative model is given by

$$d = d_0 b(\rho_{\text{liq}} - \rho_{\text{vap}}) + \frac{d_1}{b(\rho_{\text{liq}} - \rho_{\text{vap}})} \quad (28)$$

Equation 28 is a two-parameters, d_0 and d_1 , model where b is the van der Waals covolume of the PR EoS introduced here for scaling purposes only. Clearly, eq 28 is consistent with mean field theory since in the vicinity of the critical point we have

$$d \propto \frac{1}{(\rho_{\text{liq}} - \rho_{\text{vap}})} \propto \left(1 - \frac{T}{T_c}\right)^{-0.5} \quad (29)$$

Figure 4 also shows the results of using eq 28 instead of eq 20 for the modeling of the LJ interface thickness showing no

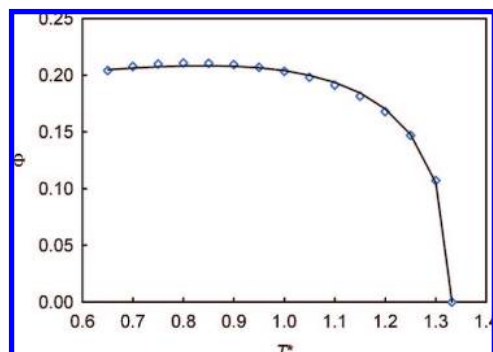


Figure 6. Model for the midvalue point corresponding to the QPD LJ EoS.²⁰

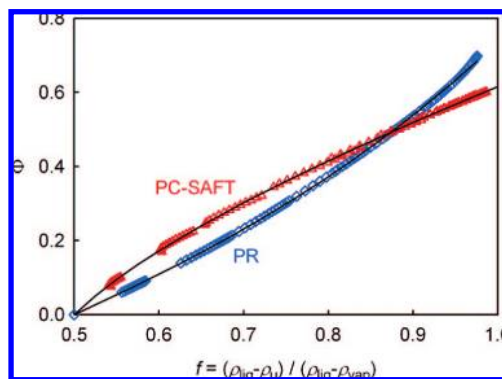


Figure 7. Calculated data for the mean value Φ parameter for the PR EoS¹⁶ and the PC-SAFT EoS,²⁵ along with their corresponding empirical correlations eqs 32 and 36, respectively.

difference when using either one of the models. Thus, substitution of eq 28 into eq 13 leads to

$$\gamma = \kappa_s \frac{(p_N - p_m)(\rho_{\text{liq}} - \rho_{\text{vap}})^2}{2(\rho_{\text{liq}} - \rho_m)(\rho_m - \rho_{\text{vap}})} \left(D_0 b(\rho_{\text{liq}} - \rho_{\text{vap}}) + \frac{1}{b(\rho_{\text{liq}} - \rho_{\text{vap}})} \right) \quad (30)$$

which is a two parameter model ($\kappa_s = \kappa d_1$ and $D_0 = d_0/d_1$). This model exhibits basically the same performance as the one proposed for the LJ fluid. Only, the interface thickness model has been replaced for an equivalent model depending only on local properties namely the equilibrium density difference.

For convenience one can rewrite the expression for the mean density ρ_m . In the light of the ongoing applied work of extending the PR model to mixtures, it has been found of convenience to represent the mean value density as

$$\rho_m = \rho_u + \Phi(\rho_{\text{liq}} - \rho_{\text{vap}}) \quad (31)$$

where ρ_u is the unstable third middle root provided by the PR EoS van der Waals loop at the equilibrium pressure. Equation 31 is very similar to eq 24; in fact, in the vicinity of the critical point both expressions eq 24 and eq 31 are equivalent by symmetry, since $\rho_u \rightarrow ((\rho_{\text{liq}} + \rho_{\text{vap}})/2)$.

With the expression given in eq 31, the friction model cannot be reduced to such a compact expression as the one reported in eq 25, except in the vicinity of the critical point. On the other hand, eq 31 has the advantage that Φ collapses onto a universal curve function of $(\rho_{\text{liq}} - \rho_u)/(\rho_{\text{liq}} - \rho_{\text{vap}})$ when the interfacial integral is evaluated for an extended range of PR parameters. This property is depicted in Figure 7 where several points corresponding to reduced temperatures $T_r = T/T_c$ ranging from 0.4 to 1.0 and acentric factor ω between 0 and 1.5 are reported as a function of the related densities ratio. It should be pointed out that the PR EoS has a constant critical compressibility factor and therefore, in terms of properly reduced quantities, the shape of the PR EoS orthobaric curves and all related coexistence properties will only depend on the acentric factor ω and on T_r . Consequently, it is also feasible to propose an empirical equation for Φ in order to take advantage of the mean value theorem and to avoid carrying out the interfacial integration each time. In the case of the PR EoS the following empirical equation results in a good approximation:

$$\Phi = 1.06078 \left(\frac{\rho_{\text{liq}} - \rho_u}{\rho_{\text{liq}} - \rho_{\text{vap}}} - 0.5 \right) + 1.24125 \left(\frac{\rho_{\text{liq}} - \rho_u}{\rho_{\text{liq}} - \rho_{\text{vap}}} - 0.5 \right)^{2.6} \quad (32)$$

Equation 32 is also depicted in Figure 7.

In summary this approach gives a PR friction model for the surface tension depending on two parameters, κ_s and D_0 . As far as current results show, the model can reproduce the surface tension of basically all cases that can be described with the PR EoS with a high level of accuracy.

The PR friction model for surface tension has been applied to the homologous normal alkane series, from methane to eicosane, and CO₂ with high accuracy. The required model parameters and results are reported in Table 2 while some selected examples are also shown in Figure 8. An interesting observation is that the value of κ_s , which has unit of length, is about the size of the molecule.

3.3. Generalized Application. In the previous section, the approach has been presented based on a cubic type EoS. The main result to be underlined is that the approach is actually linking molecular simulations results to a stable interfacial van der Waals loop. In the development of advanced EoS multiple property correlations are necessary and the approach allows the incorporation of interfacial tension as one such property. This is particularly of value considering that the accuracy of a property such as the vapor pressure significantly deteriorates at low temperatures while interfacial tension is a property that becomes more reliable as the temperature is lowered. Thus, to illustrate an application of the approach to a more complex model we have also calculated some interfacial tension friction parameters for the perturbed-chain SAFT (PC-SAFT) EoS.²⁵

Following the arguments given for the PR EoS, in the case of the PC-SAFT EoS, the model given in eq 28 may also be applied by simply using the following definition for the reducing covolume parameter b

$$b_{\text{PC-SAFT}} = N_A \sigma^3 \quad (33)$$

where N_A is Avogadro's number.

In general, provided a model for the interfacial profile is given, it is possible to substitute eq 8 into eq 9 and solve the integral

$$\gamma = -2\kappa \int_{\rho_{\text{liq}}}^{\rho_{\text{vap}}} (p - p_N) \left(\frac{dz}{d\rho} \right) d\rho \quad (34)$$

Then, using again the hyperbolic tangent interfacial model gradient for the interfacial profile, eq 12, and eq 28, the following relation is readily obtained

$$\gamma = -\frac{\kappa_s}{2} \left(D_0 b (\rho_{\text{liq}} - \rho_{\text{vap}})^2 + \frac{1}{b} \right) \int_{\rho_{\text{liq}}}^{\rho_{\text{vap}}} \left(\frac{p - p_N}{(\rho - \rho_{\text{liq}})(\rho - \rho_{\text{vap}})} \right) d\rho \quad (35)$$

Equation 35 is a similar model to eq 30, except that the mean value theorem has not been used in this case.

In the case of the PC-SAFT EoS the interfacial integral has also been calculated and the Φ parameter in eq 31 also has been evaluated for a broad range of the EoS main parameters: depth of pair potential divided by the Boltzman's constant (ϵ/k) between 100 and 400 K, segment diameter (σ) between 3 and 4.5 Å, and number of segments (m) up to 15. Remarkably, similarly to the PR EoS case, the PC-SAFT mean value Φ parameter appears to also closely follow a common curve strongly dependent on local properties as also shown in Figure 7. Thus, though some scattering is observed, an effective empirical equation for the PC-SAFT Φ parameter solution can also be regressed

TABLE 2: PR parameters for the normal alkanes homologous series and model CO₂^a

| | reference | T_c (K) | p_c (bar) | ω | $^a \kappa_s$ (Å) | D_0 | AAD (%) |
|-----------------|------------------------------------|-----------|-------------|----------|-------------------|------------|---------|
| C1 | Jasper ²⁷ | 190.555 | 45.95 | 0.01045 | 3.50801 | -0.639826 | 0.50 |
| C2 | Jasper ²⁷ | 305.43 | 48.7976 | 0.09781 | 4.566552 | -0.812823 | 0.08 |
| C3 | Baidakov and Sulla, ^{28b} | 369.82 | 42.4953 | 0.15416 | 5.155039 | -0.809245 | 0.03 |
| C4 | Jasper ²⁷ | 425.16 | 37.9661 | 0.20096 | 5.497227 | -0.8163017 | 0.36 |
| C5 | Somayajulu, ^{29b} | 469.7 | 33.6902 | 0.25143 | 6.00507 | -0.8216718 | 0.01 |
| C6 | Jasper ²⁷ | 507.3 | 30.1236 | 0.30075 | 6.428685 | -0.8258605 | 0.06 |
| C7 | Jasper ²⁷ | 540.1 | 27.3575 | 0.35022 | 6.502604 | -0.807672 | 0.17 |
| C8 | Jasper ²⁷ | 568.76 | 24.8649 | 0.39822 | 6.625552 | -0.7905889 | 0.34 |
| C9 | Jasper ²⁷ | 594.56 | 22.879 | 0.44517 | 6.78347 | -0.7832515 | 0.31 |
| C10 | Jasper ²⁷ | 617.5 | 21.0349 | 0.49052 | 6.962928 | -0.7766049 | 0.28 |
| C11 | Jasper ²⁷ | 638.73 | 19.6569 | 0.53631 | 7.112911 | -0.7750768 | 0.25 |
| C12 | Jasper ²⁷ | 658.2 | 18.2383 | 0.57508 | 7.358251 | -0.7731008 | 0.22 |
| C13 | Jasper ²⁷ | 675.8 | 17.2251 | 0.62264 | 7.447704 | -0.7708549 | 0.20 |
| C14 | Jasper ²⁷ | 691.8 | 16.2118 | 0.66735 | 7.502791 | -0.76345 | 0.22 |
| C15 | Jasper ²⁷ | 706.8 | 15.1986 | 0.70694 | 7.717191 | -0.7607576 | 0.17 |
| C16 | Jasper ²⁷ | 720.6 | 14.1854 | 0.74397 | 7.881665 | -0.7536226 | 0.19 |
| C17 | Jasper ²⁷ | 736 | 13.4 | 0.77 | 7.995885 | -0.7449851 | 0.17 |
| C18 | Jasper ²⁷ | 745.2 | 12.1589 | 0.79278 | 8.708481 | -0.7456833 | 0.16 |
| C19 | Jasper ²⁷ | 755 | 11.6 | 0.827 | 8.987896 | -0.7497366 | 0.20 |
| C20 | Jasper ²⁷ | 768 | 10.7 | 0.907 | 9.137266 | -0.7465196 | 0.20 |
| CO ₂ | Rathjen and Straub, ^{30b} | 304.21 | 73.8243 | 0.225 | 4.032523 | -0.7905615 | 0.19 |

^a κ_s has units of length. For application purposes however, if the numerical value reported here (in Å) is simply divided by 100 and the pressures (p_N and p_m) given in bar, this will result in units of (mN m⁻¹) for γ . ^b Data calculated with REFPROP v.8³¹

$$\Phi_{\text{PC-SAFT}} = -0.652177 \left(\frac{\rho_{\text{liq}} - \rho_{\text{u}}}{\rho_{\text{liq}} - \rho_{\text{vap}}} - 0.5 \right)^{0.5} + 1.68915 \left(\frac{\rho_{\text{liq}} - \rho_{\text{u}}}{\rho_{\text{liq}} - \rho_{\text{vap}}} - 0.5 \right)^{0.65} \quad (36)$$

Substitution of eqs 33 and 36 into eqs 30 and 31 results in a model based on the friction theory and the PC-SAFT EoS. The correlation results for the PC-SAFT surface tension model parameters and deviations are reported in Table 3 for the same fluids as in Table 2, along with the corresponding PC-SAFT EoS parameters recommended by Gross and Sadowski.²⁵ As shown in Table 3, the results obtained with the PC-SAFT friction interfacial model are also highly accurate.

4. Conclusions

In this work a new model for the surface tension of fluids is presented. The approach is based on the friction theory and derived from the liquid–vapor interfacial physics (interfacial density profile) and bulk properties (equilibrium and surface tension) of the Lennard-Jones 12-6 fluid. The method requires the use of an equation of state showing a stable van der Waals loop. For the Lennard-Jones 12-6 fluid analysis, the MD results for the interface of Imre et al.²³ in conjunction with the QPD LJ EoS²⁰ were used. The model closely reproduces the MD surface tension results of the Lennard-Jones 12-6 fluid.

The friction approach for surface tension has also been applied to some selected fluids of industrial interest (normal alkanes from methane to eicosane and carbon dioxide) in conjunction with the PR EoS and the PC-SAFT EoS. This resulted in simple, accurate, and easy to apply surface tension models. Future work, already in progress, will focus on the extension of the approach to mixtures so that the friction theory modeling of surface tension may become complementary to the already well-developed friction theory modeling of viscosity. The focus of this work is the relation between molecular simulation and equation of state results in the case of pure fluids as an initial step. This initial extension of the friction theory to the modeling of interfacial properties is a major step toward the development of a more comprehensive interfacial friction model for the description of the rheological properties of complex fluids such as emulsions.

An important result of the approach follows from the correlation of the surface tension with an EoS that must necessarily show a stable van der Waals loop. This, in combination with molecular simulation results, may also lead to an alternative methodology for the development of highly accurate EoS. Many of the reference type of EoS, such as the model cited in this work for carbon dioxide,¹⁵ develop a pathological behavior within the two-phase region, resulting in serious limitations of their applicability. To circumvent many current problems, it would be desirable to have models of reference quality that may also show stable van der Waals loops. By means of molecular simulation, it is currently possible to derive reasonable estimations for the interfacial profile of many fluids of interest (such as CO₂²⁶). Thus, the simulated interface model along with the friction surface tension model could be included in the experimental data that are used for the development of reference type EoS. This would not only add another thermophysical property to reference models, but also achieve a physically reasonable behavior in the two-phase region. This in turn would bring about many further positive effects, such as more stable corresponding states approaches for the extension of the reference models to mixtures, which at present are

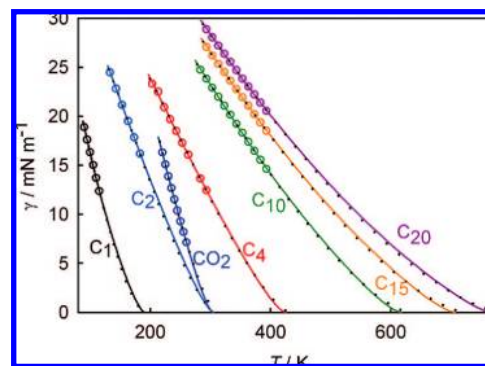


Figure 8. Correlation of the surface tension of n-alkanes and carbon dioxide. The symbols are experimental reference data (see Table 2), the curves and the dots are correlations with eq 30 using the PR EoS,¹⁶ and the PC-SAFT EoS,²⁵ respectively.

TABLE 3: PC-SAFT Model Parameters for the Normal Alkanes Homologous Series and CO₂^c

| | <i>m</i> | σ (Å) | ϵ/k (K) | ^a κ_s (Å) | <i>D</i> ₀ | AAD (%) |
|-----------------|----------|--------------|------------------|-----------------------------|-----------------------|---------|
| C1 | 1 | 3.7039 | 150.03 | 2.26897 | -0.06674 | 0.35 |
| C2 | 1.6069 | 3.5206 | 191.42 | 1.83525 | -1.42514 | 0.07 |
| C3 | 2.002 | 3.6184 | 208.11 | 1.65018 | -2.45056 | 0.19 |
| C4 | 2.3316 | 3.7086 | 222.88 | 1.42403 | -3.37014 | 0.33 |
| C5 | 2.6896 | 3.7729 | 231.2 | 1.31382 | -4.78459 | 0.01 |
| C6 | 3.0576 | 3.7983 | 236.77 | 1.13646 | -6.07278 | 0.03 |
| C7 | 3.4831 | 3.8049 | 238.4 | 0.96504 | -7.47654 | 0.11 |
| C8 | 3.8176 | 3.8373 | 242.78 | 0.84117 | -8.20020 | 0.26 |
| C9 | 4.2079 | 3.8448 | 244.51 | 0.74587 | -9.53569 | 0.25 |
| C10 | 4.6627 | 3.8384 | 243.87 | 0.66919 | -11.54880 | 0.23 |
| C11 | 4.9082 | 3.8893 | 248.82 | 0.62846 | -12.23029 | 0.22 |
| C12 | 5.306 | 3.8959 | 249.21 | 0.58497 | -14.35476 | 0.21 |
| C13 | 5.6877 | 3.9143 | 249.78 | 0.55289 | -16.47954 | 0.20 |
| C14 | 5.9002 | 3.9396 | 254.21 | 0.51102 | -16.46263 | 0.24 |
| C15 | 6.2855 | 3.9531 | 254.14 | 0.48764 | -18.75263 | 0.19 |
| C16 | 6.6485 | 3.9552 | 254.7 | 0.45341 | -20.33204 | 0.20 |
| C17 | 6.9809 | 3.9675 | 255.65 | 0.43147 | -21.98526 | 0.18 |
| C18 | 7.3271 | 3.9668 | 256.2 | 0.40851 | -23.97449 | 0.17 |
| C19 | 7.7175 | 3.9721 | 256 | 0.39364 | -27.24173 | 0.20 |
| C20 | 7.9849 | 3.9869 | 257.75 | 0.37716 | -28.55048 | 0.19 |
| CO ₂ | 2.0729 | 2.7852 | 169.21 | 1.17507 | -1.78905 | 0.22 |

^c The reference data are the same as in Table 2 and similar comments on κ_s also apply.

seriously hampered by the bad performance of EoS in the two-phase region.

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