A collocation method for surface tension calculations with the density gradient theory

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ABSTRACT

Surface tension calculations are important in many industrial applications and over a wide range of temperatures, pressures and compositions. Empirical parachor methods are not suitable over a wide condition range and the combined use of density gradient theory with equations of state has been proposed in literature. Often, many millions of calculations are required in the gradient theory methods, which is computationally very intensive. In this work, we have developed an algorithm to calculate surface tensions an order of magnitude faster than the existing methods, with no loss of accuracy. The new method can be used with any equation of state, and gives much improved performance. In this work, the new method for solving the gradient density theory equations is combined with cubic equations of state and the Cubic-Plus-Association model. Applications for both binary and multicomponent mixtures and for both hydrocarbon and associating systems are shown. For most systems, the predictions obtained are in good agreement with experimental data. However, cases have been identified where further investigation is needed.

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1. Introduction

Surface tension calculations are needed in many industrial applications, such as distillation column design and reservoir modeling.

Interfacial tensions for aqueous and other complex systems can present non-trivial behavior. For example, the interfacial tension of the methane − water system goes through a minimum with increasing pressure along the higher temperature (373 & 473 K) isotherms [34]. This minimum with increasing pressure has been exhibited in other experimental investigations for the interfacial tension of hydrocarbon − water systems [14].

There are many methods to model surface and interfacial tensions, which range from the simple empirical correlations to those based on statistical thermodynamics. The simpler methods, such as the Parachor method [31,35], suffer in their accuracy to model for example hydrocarbon + water systems and are rarely used

successfully at high pressures and for complex systems. One of the first efforts to combine thermodynamic models in the prediction of surface tensions was by Ref. [30] where they used UNIFAC, where the molar surface area of the components was used as fitting parameter. Promising results were presented for several mixtures in this short publication but there has not been any follow up of this work.

The techniques which are derived from statistical thermodynamics and the theory of inhomogeneous fluids are considered to be theoretically more sound, accurate and robust calculation methods. There are two main theories − the van der Waals [37] gradient theory and the Ebner et al., [7] perturbation theory. There have been shown to be equivalent ([6]), and thus in this work we focus on the van der Waals gradient theory.

The gradient theory of fluid interfaces is one of the most widely used frameworks for interfacial tension calculations, providing a way of relating an equation of state to interfacial properties.

Surface tensions occur at the interface between e.g. a vapor phase and a liquid phase. Density gradient theory says we can calculate the magnitude of the surface tension by integrating the gradients of the component densities.

The gradient theory of fluid interfaces originated, as mentioned, from the work of van der Waals [37]; but only after Cahn and

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Hilliard [4] it found widespread use. The Cahn and Hilliard [4] theory describes the thermodynamic properties of a system where an interface exists between two fluid phases. In contrast to systems of pure components, in binary mixtures the density and composition change across the interface. The calculations with the density gradient theory can be computationally very intensive and the reasons will be explained in Sections 2 and 3 where the gradient theory and the existing solution methods are presented and discussed.

Partially due to these computational problems, the use of the density gradient theory, combined with equations of state, for estimating interfacial tensions of pure component and mixture systems is rather limited.

Table 1 summarizes several recent investigations on using thermodynamic models especially association equations of state like CPA and SAFT for calculating surface and interfacial tensions in combination with the density gradient theory.

As can be seen in Table 1, Carey [5]; and Miqueu [20] used the PR EoS for interfacial tension calculations of several binary and ternary mixtures, and Cornelisse [6] used PR and the associated perturbed anisotropic chain theory (APACT) for surface and interfacial tension calculations of pure fluids and mixtures (varying from non-polar hydrocarbons to very polar and associating mixtures). Kahl and Enders [16] used PR, Sanchez − Lacombe (SL) and SAFT EoS for surface tension calculations of water and hydrocarbons, and Kahl and Enders [15] used PR and SAFT for interfacial tension calculations of alcohol − hydrocarbons. Many more applications of the SAFT equation of state with the gradient theory have been presented by the group of Enders, as shown in Table 1. In some of these studies e.g. Ref. [16] it is shown that details in the fluid model (e.g. type of the association scheme used in SAFT) may have significant influence on the results for the surface tension.

Finally Refs. [25,26,32,11] used CPA for surface tensions of water, alcohols, hydrocarbons, biodiesel (and other mixtures) and Mejia et al., [19] used PR with modified Huron−Vidal mixing rules for interfacial tensions of various mixtures.

In several of the above investigations satisfactory correlation results are presented, especially for pure compounds and for binary mixtures. In all cases an adjustable parameter, called influence parameter (see Section 2) is fitted to experimental pure compound surface tension data and it is often considered to be temperature dependent.

The few studies for binary mixtures show promising results but only very few investigations have been reported for multicomponent systems. Moreover, problems have been reported for some complex mixtures e.g. water-heavy alcohol interfacial tensions [9]. In most studies, for mixtures, no correction to the cross influence parameter is used (i.e. $\beta_{ij} = 0$ in Eq. (5) below). As exception to this norm, in some of the studies by Enders and co-workers (e.g. Ref. [15]), this correction parameter to the cross influence parameter has been used for some complex mixtures and it is shown, as might have been expected, to improve the results e.g. for alcohol-alkane interfacial tensions.

The computational aspects are only on occasion discussed in most literature studies. However, such aspects are very important, because, as discussed in the next section, in order to compute interfacial tension with the gradient theory, the density profiles in the interface should first be determined. The numerical effort in resolving the density profiles has been described in the works of Carey [5], Cornelisse [6], Miqueu [20] and more recently by Ref. [18]. The significant computational effort that is needed has led some researchers (e.g. Refs. [39−41]) to propose linear versions of the gradient theory (number density assumed to be distributed linearly between the co-existing equilibrium bulk phases through a planar interface), which eliminate the need to solve the set of time consuming density profile equations that are inherent with the gradient theory approach. Such linear methods have serious problems and require many, often temperature dependent adjustable parameters, and will not be considered further in this work.

The rather limited discussion of computational aspects of the density gradient theory (especially over the recent years) is unfortunate as the required calculations are computationally very intensive. In many existing methods [20−22] the integration of the gradients of the component densities is done by choosing a reference density and discretizing it into 500 points. We will propose a new more efficient method in this work. In our method, we calculate the density path from the liquid phase to the vapor phase. Doing so allows us to make a coarse map of the density path (using only 8 steps). The path is then refined where necessary using successive bisection. Cubic spline interpolation is used to

Table 1

Applications of the Density Gradient Theory in combination with thermodynamic models for calculating surface and interfacial tensions. When SAFT is mentioned, different versions of SAFT are used e.g. original SAFT, PC-SAFT, soft SAFT and polar versions of PC-SAFT.

Equation of state	Application	Reference
APACT, PR	Many fluids	[6]
PR	Many fluids	[5]
		[20]
SAFT, PR	Water, hydrocarbons	[16]
Sanchez-Lacombe	Alcohol-hydrocarbons	[15]
	Water-alcohols	[9]
	Water-glycolethers	[10]
	DMF + alkanes	[33]
	CO_2+water	[24]
	Alcohols	[12]
	Alkanes, alcohols, CO_2 and related mixtures	[27]
QCHB	Water, Alcohol, non-polars, polymers, etc. Alcohol-hydrocarbons	[28]
CPA	Water, alcohols	[32]
CPA	Biodiesel	[11]
CPA	Alkanes, alcohols, fluoroalkanes Alcohols + alkanes Alcohols + alcohols Alkanes + alkanes	[25] [26];
SRK + linear gradient theory	Water-methane interfacial tension	[34]
Cubic EoS	Wide range of non-polar fluids esp. refrigerants	[18]