



# Modeling properties of the one-dimensional vapor-liquid interface: Application of classical density functional and density gradient theory

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## ABSTRACT

This study compares surface tensions as calculated from the classical density functional theory (DFT) and from density gradient theory (DGT) to experimental data. This comparison is inevitably not on equal ground, because the DFT is purely predictive for interfacial properties, both for pure substances and for mixtures, whereas DGT requires an adjustable influence parameter for each pure component (adjusted to surface tension data) and possibly a further adjustable parameter for each binary pair. In that sense, our comparison takes the perspective of a user who, because experimental data is available, finds it acceptable to correlate interfacial properties with adjustable parameters but who can alternatively decide for applying the DFT method. The perturbed-chain polar statistical associating fluid theory (PCP-SAFT) is used to determine phase equilibrium properties as well as the local Helmholtz energy density for DGT. For DFT, a Helmholtz energy functional consistent with PCP-SAFT is applied. DGT correlations and DFT predictions of surface tension for pure components as well as results for mixtures agree very well and exhibit excellent agreement to reference data for non-associating non-polar and polar molecules. Only for pure associating compounds, the adjustable parameter of DGT leads to significant improvements over DFT results. For mixtures, depending on the system, results can be better for either method. In the case of alkane-alcohol mixtures, DGT with the geometric combining rule for the cross-wise influence parameter leads to non-physically steep gradients in the density profiles. Adjusting a binary correction parameter for the influence parameter to experimental mixture surface tension data helps to alleviate this problem. However, the practical utility of this binary correction parameter to improve mixture surface tension results is very limited. We conclude that DFT is for most applications a preferable approach.

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## 1. Introduction

Properties of vapor-liquid interfaces play an important role in many industrial applications. Density functional theory (DFT) and density gradient theory (DGT) are two approaches commonly applied to calculate these interfacial properties.

The framework of density functional theory was first developed to study the inhomogeneous electron gas by Hohenberg and Kohn [1] and Mermin [2] and was later applied to classical systems by Ebner et al. [3,4]. The fundamentals of density gradient theory date back to the work of Van der Waals [5]. Later, Cahn and Hilliard [6] provided a rigorous derivation and extension of the DGT. For a detailed description of the historical development of both theories

we refer to the book of Henderson [7].

Applied to a classical, inhomogeneous system of  $N$  components at given values of temperature  $T$ , volume  $V$  and chemical potentials  $\mu_i$  ( $i = 1, \dots, N$ ), both approaches aim to find the equilibrium species density profiles  $\rho_i(\mathbf{r})$  that minimize the grand potential  $\Omega = A - \int \sum_i \mu_i \rho_i d\mathbf{r}$  of the system. The fundamental difference between DFT and DGT as they are applied in this work is the approximate expression for the Helmholtz energy  $A[\rho(\mathbf{r})]$  of an inhomogeneous system. In DGT, an approximation of  $A[\rho(\mathbf{r})] = \int a[\rho(\mathbf{r})] d\mathbf{r}$  is obtained by an expansion of the local Helmholtz energy density  $a[\rho(\mathbf{r})]$  about the local density approximation  $a_0(\mathbf{r}) = a(\rho(\mathbf{r}))$  truncated after the square density gradient term. The prefactor of this gradient term is the so called influence parameter  $c_{ii}$ , which is a component specific property. Theoretical approaches [8–10] and several correlations [11–15] exist to determine  $c_{ii}$ . In most cases however, the value of  $c_{ii}$  is adjusted to

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experimental surface tension data. The appeal of DGT is its ease of implementation: besides the value of  $c_{ij}$  only an equation of state to evaluate  $a_0$  is required. For an extensive list of previous studies using various equations of state to evaluate  $a_0$ , we refer to a previous study [16].

DFT, on the other hand, does not require any additional parameters beyond those of the equation of state to calculate interfacial properties.  $A$  is treated as a functional of the spatially varying density profile. Common approximations are derived from perturbation theory for the Helmholtz energy by decomposing the intermolecular potential into a predominantly repulsive part (defining the reference fluid) and an attractive part of the intermolecular potential. Furthermore, the unknown correlation function of the inhomogeneous fluid is approximated by its value for the homogeneous fluid evaluated at averaged densities. As shown by Evans [10], DFT can be seen as a generalization of the DGT approach of Van der Waals. For an overview of current applications of DFT, we refer to the following review articles [17–20].

The chemical potentials as well as the densities of the coexisting vapor and liquid phases enter the DFT and DGT calculations. Therefore, the first step when DFT or DGT are applied to the one-dimensional vapor-liquid interface, is the calculation of these phase equilibrium properties. This has to be done using the same model that is applied to calculate  $a_0$  in DGT and the model has to be consistent with the Helmholtz energy functional employed in the DFT approach.

In this work, we compare results for the surface tension of pure components and of mixtures obtained from DFT and DGT for non-polar and non-associating compounds, polar molecules and associating components. The PCP-SAFT equation of state [21–24] is applied to determine the bulk properties at phase equilibrium and to evaluate the local Helmholtz energy density  $a_0$  in DGT. PCP-SAFT has proven to yield accurate results of thermodynamic properties for a wide range of systems. A Helmholtz energy functional consistent with PCP-SAFT has been developed by Gross [25], Klink and Gross [26] and Sauer and Gross [27]. This DFT approach is used here with the modification that associative interactions are treated in a non-local description using the Helmholtz energy functional of Bymaster and Chapman [28], which is a modification of the work of Segura et al. [29]. For mixtures, two algorithms to solve the DGT equations are applied: the path function approach of Liang et al. [30] which requires the geometrical combining rule for the influence parameter ( $c_{ij} = \sqrt{c_{ii}c_{jj}}$ ) and the stabilized algorithm of Qiao and Sun [31] that allows to use a binary correction parameter  $\beta_{ij}$  ( $c_{ij} = \sqrt{c_{ii}c_{jj}}(1 - \beta_{ij})$ ). Limitations of the practical utility of  $\beta_{ij}$  are discussed. Like in most DGT-studies, we treat the pure component influence parameters  $c_{ii}$  as temperature-independent and follow the study of Amézquita et al. [32] in applying the constant  $c_{ii}$  values unchanged to components which are supercritical at mixture conditions. Both, the DFT or DGT approach, give the same bulk phase properties, which allows us to attribute differences in the interfacial properties to the DFT or DGT approach, respectively.

## 2. Theoretical background of DGT and DFT

In this section, we summarize the basic equations of DFT and DGT for a one-dimensional system with a vapor-liquid interface. For further details on the underlying molecular model of PCP-SAFT, we refer to the original literature [21–24]. Detailed descriptions of DGT can be found in Refs. [6,33,34] and more information on the DFT approach applied in this work is available in previous studies [25–27,35].

The goal of both approaches is to determine the equilibrium density profiles  $\rho_i(\mathbf{r})$  across the interface which minimize the value

of the grand potential  $\Omega$  of a system of  $N$  components at given values of temperature  $T$ , chemical potentials  $\mu_i$  and volume  $V$ .

In the absence of an external field,  $\Omega$  is given by

$$\Omega[\{\rho_k\}] = A[\{\rho_k\}] - \sum_i^N \int \mu_i \rho_i(\mathbf{r}) d\mathbf{r} \quad (1)$$

where the dependencies of  $A$  and  $\Omega$  on  $T$ ,  $\mu_i$  and  $V$  are dropped for brevity and the curly brackets denote the dependency on all species-densities.

Eq. (1) is the starting point for both DGT and DFT. The main difference between the two approaches is the route to describe the intrinsic Helmholtz energy of the system  $A[\{\rho_k\}]$ , which is a functional of all species-densities  $\rho_i(\mathbf{r})$  (as denoted by the square brackets). In our DFT approach,  $A[\{\rho_k\}]$  is modeled as a sum of contributions according to the PCP-SAFT model

$$A[\{\rho_k\}] = A^{ig}[\{\rho_k\}] + A^{hs}[\{\rho_k\}] + A^{chain}[\{\rho_k\}] + A^{disp}[\{\rho_k\}] + A^{assoc}[\{\rho_k\}] + A^{polar}[\{\rho_k\}] \quad (2)$$

where the individual contributions to the Helmholtz energy are for the ideal gas, hard sphere interactions, chain formation, dispersion, association (i.e. hydrogen bonding) and polar (dipolar or quadrupolar) interactions. In this work, we use the functionals developed by Rosenfeld [36] in the modified form of Roth et al. [37] and Yu and Wu [38] for  $A^{hs}[\{\rho_k\}]$ , Tripathi and Chapman [39] with the adaptations of ref. [25] and [26] for  $A^{chain}[\{\rho_k\}]$ . Furthermore, for  $A^{disp}[\{\rho_k\}]$  and for  $A^{polar}[\{\rho_k\}]$  we adopt functionals of Sauer and Gross [27], respectively and for  $A^{assoc}[\{\rho_k\}]$  we use functionals proposed by Bymaster and Chapman [28]. The final form of these functionals is presented in Refs. [27] and [35].

In equilibrium, where  $\Omega[\{\rho_k\}]$  reaches its minimum value with respect to density profiles  $\rho_i(\mathbf{r})$ , the functional derivatives with respect to all species-density profiles  $\rho_i(\mathbf{r})$  vanish

$$\frac{\delta\Omega[\{\rho_k\}]}{\delta\rho_i(\mathbf{r})} = \frac{\delta A[\{\rho_k\}]}{\delta\rho_i(\mathbf{r})} - \mu_i = 0 \quad \forall i \quad (3)$$

Eq. (3) can be discretized on a one-dimensional grid. As described in a previous study [35], a matrix-free inexact Newton method is applied to solve the resulting system of nonlinear equations.

In the DGT approach,  $A[\{\rho_k\}]$  is not decomposed into a sum of functionals as for DFT. Instead, the Helmholtz energy density of the inhomogeneous fluid is expanded about the local density approximation  $a_0(\{\rho_k\})$  truncated after the square density gradient term

$$A[\{\rho_k\}] = \int a_0(\{\rho_k\}) + \frac{1}{2} \sum_i^N \sum_j^N c_{ij} \nabla\rho_i \nabla\rho_j d\mathbf{r} \quad (4)$$

with the local density gradient  $\nabla\rho_i$  and the influence parameter  $c_{ij}$ . In this work, we evaluate interfacial properties for the case, where the influence parameter is determined from a geometric combining rule, as  $c_{ij} = \sqrt{c_{ii}c_{jj}}$ , but also for the case, where  $c_{ij}$  is an adjustable parameter. It is convenient therefore to cast the influence parameter in the form

$$c_{ij} = \sqrt{c_{ii}c_{jj}}(1 - \beta_{ij}) \quad (5)$$

where parameter  $\beta_{ij}$  is zero for the geometric combining rule and non-zero for an adjusted value of  $c_{ij}$ . The local Helmholtz energy density evaluated at the local density value is then split according

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