### A New Dispersion Contribution Based on the PCP-SAFT Equation of State in the Framework of Classical Density Functional Theory

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Le doute n'est pas un état bien agréable, mais l'assurance est un état ridicule.

Doubt is not a pleasant condition, but certainty is an absurd one.

VOLTAIRE

# Contents

1	Introduction		19	
	1.1	PCP-S	SAFT Equation of State	20
	1.2	Classi	cal Density Functional Theory	21
	1.3	Helmh	noltz Energy Functionals based on SAFT Equations of State	22
		1.3.1	Hard-Sphere Contribution	22
		1.3.2	Chain Contribution	23
		1.3.3	Dispersion Contribution	24
	1.4	Scope	and Outline of this thesis $\ldots \ldots \ldots$	31
	Bibl	iograph	ly	33
<b>2</b>	Cla	ssical	Density Functional Theory for Liquid-Fluid Interfaces and	
	Cor	nfined	Systems: A Functional for the Perturbed-Chain Polar Sta-	
	$\mathbf{tist}$	ical As	sociating Fluid Theory Equation of State	<b>41</b>
	2.1	Introd	uction	41
	2.2	Classi	cal Density Functional Theory	45
		2.2.1	Application: Interfacial Tensions	46
		2.2.2	Application: Confined Systems	47
	2.3	Helmh	noltz Energy Functional	48
		2.3.1	The Hard-Sphere Contribution	49
		2.3.2	The Chain Contribution	49
		2.3.3	The Contribution from Dispersive Attractions	50
		2.3.4	The Associative Attraction	53
		2.3.5	The Multipolar Attraction	54
	2.4	Result	s and Discussion	54
		2.4.1	Liquid Film on Solid Wall	55
		2.4.2	Confined Systems	57
		2.4.3	Interfacial Tensions	61
	2.5	Conclu	usion	66
	App	endix A	A: Functional Derivatives	66
	App	endix I	B: Comparison with Shen et al.	68

	App	endix (	C: Derivation of the Weighted Density Formalism	69
	App	endix I	D: Chain Contribution	74
	Bibl	liograph	ру	76
3	Pre twe	diction en Cla	n of Adsorption Isotherms and Selectivities: Comparison be- assical Density Functional Theory Based on the PC-SAFT	
	Ear	ation	of State and Ideal Adsorbed Solution Theory	85
	3.1	Introd	luction	85
	3.2	Metho	ods	87
		3.2.1	Classical Density Functional Theory	89
		3.2.2	Molecular Simulation	90
		3.2.3	Solid-Fluid Interactions	92
		3.2.4	Ideal Adsorbed Solution Theory	94
	3.3	Result	ts and Discussion	95
		3.3.1	Argon, Krypton and their Mixture	96
		3.3.2	Methane, <i>n</i> -Butane and their Mixture	100
	3.4	Concl	usion	106
	Bibliography		107	
4 Prediction of Contact Angles and Density Profiles of Sessile Droplets Using Classical Density Functional Theory Based on the PCP-SAFT Equation of State				
		of State	117	
	4.1	Introd	luction	117
	4.2	Simula	ation Details	121
4.3 Classical Density Functional Theory		cal Density Functional Theory	123	
		4.3.1	Helmholtz Energy Functional	123
		4.3.2	DFT Implementation	123
	4.4	Deter	mination of Contact Angles from MC and DFT	125
	4.5	Exper	imental Method	126
	4.6	Result	ts and Discussion	127
		4.6.1	Cutoff Radii in MC Simulations	127
		4.6.2	Comparison between DFT and MC	129
		4.6.3	Size Dependence of Contact Angles for Sessile Droplets	13/
		4.6.4	Comparison between DFT and Experimental Data	TOT
			1	134 $138$
	4.7	Concl	usion	138 140
	4.7 Bibl	Concl	usion	134 138 140 141

$\mathbf{A}$	Appendices	
Α	Supporting Information to Chapter 2	153
в	Supporting Information to Chapter 3	157
С	Supporting Information to Chapter 4	161

## List of symbols

## Latin letters

ã	reduced Helmholtz energy
A	Helmholtz energy
A	surface area
A, B	Association site
$c_0, c_1, c_2, c_3$	torsional potential parameter TAMie force field
$C_1$	compressibility expression PC-SAFT
d	temperature-dependent segment diameter
e	unit vector
f	Helmholtz energy density
F	Helmholtz energy functional
g	radial distribution function or pair correlation function
$\hat{g}$	generalized Fourier transformed function
h	total correlation function
Н	wall distance
i	imaginary number
$I_1, I_2$	power series PC-SAFT
$J_{\nu}$	Bessel function of the first kind and order $\nu$
k	Boltzmann's constant
$k_{\Theta}$	bond angle parameter TAMie force field
$k_{ij},  l_{ij}$	binary parameters
K	abbreviation
L	characteristic length
m	segment number
$ar{m}$	mean segment number
n	weighted density of the FMT contribution
n	Mie repulsion exponent
N	number of particles
$N_c$	number of components
$N_i$	number segments in molecule $i$
$N_{A_i}$	number of association sites of type $A$ in molecule $i$
p	pressure
Q	quadrupole moment
r	radial coordinate in cylindrical coordinate system
$r_0$	bond length TAMie force field
$r_c$	cutoff radius
$\hat{r}$	distance

r	three-dimensional spatial coordinate vector
R	radius
$R_0$	radius of a critical nucleus
S	selectivity
S	supersaturation
T	temperature
$T_c$	critical temperature
V	volume
$V^{\rm ext}$	external potential
w	weighting function
x	cartesian coordinate
x	mole fraction
$\bar{x}$	mole fraction calculated from weighted densities
y	cartesian coordinate
y	mole fraction
y	cavity correlation function
z	cartesian coordinate

#### Greek letters

$\beta$	inverse temperature
$\gamma$	interfacial tension
δ	Dirac delta function
$\Delta$	distance parameter of the Steele potential
$\Delta^{A_i B_i}$	association strength
ε	depth of pair potential
$\varepsilon^{A_i B_i}$	association energy
$\eta$	packing fraction
$\theta$	contact angle
Θ	Heaviside step function
$\Theta_0$	bond angle parameter TAMie force field
$\kappa^{A_iB_i}$	effective association volume
$\lambda$	perturbation parameter
$\lambda$	weighted density of the chain contribution
Λ	de Broglie wavelength
$\mu$	chemical potential
$\mu$	dipole moment
$ ilde{\mu}$	reference chemical potential

ξ	prefactor to the solid-fluid interaction
ξ	FMT factor calculated from vector weighted densities
$\pi$	circular number
$\pi$	spreading pressure of an adsorbed phase
П	macrostate probability distribution
ρ	particle number density
$\hat{ ho}$	mean density
$\bar{ ho}$	weighted density
$ ho^{(2)}$	two-particle density
$\sigma$	temperature-independent segment diameter
$\phi$	pair potential
arphi	polar coordinate in cylindrical coordinate system
$\Phi$	reduced Helmholtz energy density
$\chi^{A_i}$	fraction of non-bonded association sites of type ${\cal A}$ on molecule $i$
$\psi$	model parameter
$\psi_{ m A}$	individualization parameter TAMie force field
Ω	grand potential

#### Miscellaneous

Ŧ	Fourier transform
$\mathscr{H}_{ u}$	Hankel transform of order $\nu$

## Subscripts

1, 2	order term of the perturbation series
1, 2, 3	indices for spatial coordinates
i, j, k	indices for components
ab	generic index for $\{lv, sl, sv\}$
Ar	argon
av	average
$CH_3$	methyl bead
CO	carbon monoxide
EoS	equation of state
f	fluid
iso	isodensity line
Kr	krypton
1	lower
lv	liquid-vapor

LJ	Lennard-Jones
max	maximum displacement
Me	methane
S	solid phase
sl	solid-liquid
SV	solid-vapor
SW	square well
u	upper
THF	tetrahydrofuran
TMMC	Transition Matrix Monte Carlos
WDA1, WDA2	variants of the dispersion contribution
x, y, z, r	coordinates
α	index of FMT weighted densities or weighting functions
$\alpha_i,  \beta_i$	indices of segments in molecule $i$
$\lambda$	perturbation parameter

## Superscripts

*	index for spatial coordinates
*	dimensionless quantity
0	pure component
(0)	initial
assoc	association
b, bulk	bulk phase
$\mathrm{CH}_2$	methylene bead
$CH_3$	methyl bead
chain, CHAIN	hard-chain
DFT	Density Functional Theory
disp	dispersion
disp,1, disp,2	variants of the dispersion contribution
eff	effective
ex	excess
FMT	Fundamental Measure Theory
hc	hard-chain
hs	hard-sphere
id, ID	ideal gas
dew	dew point
end	background function at the end of the $r$ domain

L	liquid
liq	liquid
LJ	Lennard-Jones
lr	long-ranged
macro	macroscopic
MC	Monte Carlo
mp	multipolar
PT	perturbation part
pt	phase transition
P1, P2	indices for phases
pore	pore system
ref	reference fluid
res, RES	residual
sat	saturation
seg	segment
sr	short-ranged
SW	square well
TAMie	Transferable Anisotropic Mie force field
target	target fluid
V	vapor

## Kurzzusammenfassung

Prädiktive und genaue Methoden zur Beschreibung von Stoffeigenschaften inhomogener Systeme, wie Adsorptionsisothermen oder Grenzflächenspannungen, sind wertvoll für viele ingenieurwissenschaftliche Anwendungen. Die klassische Dichtefunktionaltheorie bietet einen vielversprechenden theoretischen Rahmen für die Entwicklung einer solchen Methode, benötigt jedoch ein geeignetes Modell für das Helmholtzenergie-Funktional. In dieser Dissertation wird ein neues Helmholtzenergie-Funktional präsentiert, welches, angewandt auf homogene Systeme, zur PCP-SAFT Zustandsgleichung übergeht. Es werden zwei Modellvarianten eines Dispersionsbeitrags eines Helmholtzenergie-Funktionals basierend auf der weighted-density-Näherung vorgestellt und verglichen. Die relativ einfache mathematische Form beider Varianten ermöglicht eine schnelle und effiziente Lösung der Modellgleichungen. Mithilfe von experimentellen Daten und Ergebnissen aus Monte Carlo Simulationen wird die bessere der beiden Varianten identifiziert. Die überlegene Variante wird systematisch mithilfe von Untersuchungen von fluid-fluid und fluid-fest Grenzflächen sowie Drei-Phasen-Kontaktwinkeln auf ihre Vorhersagefähigkeit hin analysiert und bewertet. Für diese Bewertung werden drei verschiedene Systemtypen berücksichtigt: eindeutig definierte, idealisierte Systeme, realistischere Systeme und reale, durch experimentelle Daten charakterisierte, Systeme. Das entwickelte Modell liefert für alle drei Systemtypen genaue Ergebnisse. Eine gute Übereinstimmung mit Referenzdaten wurde für verschiedene thermodynamische Größen gefunden: Adsorptionsisothermen und -selektivitäten, Grenzflächenspannungen und Kontaktwinkel von Tropfen in Kontakt mit einer Feststoffoberfläche.

#### Summary

Predictive and accurate approaches for properties of inhomogeneous systems such as adsorption isotherms or interfacial tensions are valuable for many engineering applications. Classical Density Functional Theory is a promising framework for the development of such an approach, but requires a sophisticated model for the Helmholtz energy functional. This work proposes a new Helmholtz energy functional that simplifies to the PCP-SAFT equation of state when homogeneous conditions are regarded. Two variants of a dispersion contribution to the Helmholtz energy functional based on the weighted density approximation are presented and compared. The relatively simple mathematical formulation of both variants enables fast and efficient solving of the equations. Experimental data and results obtained from Monte Carlo simulations are used to determine the superior variant. The proposed model is systematically assessed for its predictive capabilities for fluid-fluid and solid-fluid interfaces as well as for three phase contact angles. For the assessment, systems of three different levels were taken into account: clearly defined but rather artificial systems, more realistic systems and real systems characterized by experimental data. The developed model provides accurate results for all three levels. Good agreement with reference data was found for several thermodynamic properties such as interfacial tensions, adsorption isotherms, adsorption selectivities, and contact angles of sessile droplets.

## Journal publications

This thesis led to the following publications:

- Chapter 2: Sauer, E.; Gross, J. Classical Density Functional Theory for Liquid– Fluid Interfaces and Confined Systems: A Functional for the Perturbed-Chain Polar Statistical Associating Fluid Theory Equation of State. *Ind. Eng. Chem. Res.* 2017, 56(14), 4119-4135.
- Chapter 3: Sauer, E.; Gross, J. Prediction of Adsorption Isotherms and Selectivities: Comparison between Classical Density Functional Theory Based on the PC-SAFT Equation of State and Ideal Adsorbed Solution Theory. *Langmuir.* **2019**, accepted.
- Chapter 4: Sauer, E.; Terzis, A.; Theiss, M.; Weigand, B.; Gross, J. Prediction of Contact Angles and Density Profiles of Sessile Droplets Using Classical Density Functional Theory Based on the PCP-SAFT Equation of State. *Langmuir.* 2018, 34(42), 12519-12531.

The chapters 2 to 4 present literal quotes of the published work. Any addition with respect to the published work is marked. Any deletion is indicated with square brackets as ,[...]'. Cross-references between chapters of this thesis, which are added to the published version of the text to increase readability, are marked by square brackets. The Supporting Information to the single publications are presented in the Appendix of this thesis.

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# Chapter 1

## Introduction

Efficient process design in chemical engineering requires precise models for thermodynamic properties and phenomena. During the last decades, accurate and predictive models have been developed to characterize properties of homogeneous fluid systems. Thermodynamic properties of states with inhomogeneously distributed molecules, like interfacial tensions and adsorption isotherms, are additionally required for many technical applications. It is desirable to transfer the success achieved in the development of bulk phase properties to the modeling of inhomogeneous fluid systems. A model for inhomogeneous systems should be accurate, but also relatively simple in its mathematical form to achieve tolerable computation times, because process design calculations can be very tedious. A precise and predictive model that is applicable to various types of thermodynamic phenomena like interfacial tensions, wetting, and adsorption is desirable.

To harness the advances made in the characterization of bulk phase systems, this thesis proposes a model for inhomogeneous systems as a generalization of an accurate and widely used equation of state (EoS) with excellent extrapolative behavior, namely the Perturbed-Chain Polar Statistical Associating Fluid Theory (PCP-SAFT). The PCP-SAFT model is physically-based, with sound roots in fluid theories from statistical mechanics. It is rather widely used in industry and academia. For inhomogeneous systems the connection with PCP-SAFT furthermore has the advantage that a comprehensive number of pure component and binary mixture parameters published in the literature are directly available for the model. This also explains the meaning of predictiveness in this context: The model for inhomogeneous systems is predictive, if only parameters adjusted to bulk phase properties are used for the characterization of inhomogeneous systems. Corresponding parameters are commonly adjusted to bulk phase densities and vapor pressures.

#### **1.1 PCP-SAFT** Equation of State

SAFT models are a class of modern EoS based on the first-order thermodynamic perturbation theory (TPT1) proposed by Wertheim [1–4]. The first developed SAFT model was presented by Chapman and coworkers [5–8] and since then several SAFT versions were published like SAFT-HR [9, 10], soft-SAFT [11, 12], SAFT for potentials of variable range (SAFT-VR) [13, 14], Perturbed-Chain SAFT [15, 16], and SAFT- $\gamma$  Mie [17, 18]. Because SAFT equations are derived from statistical mechanics, they are elegantly formulated in terms of the Helmholtz energy A. For PCP-SAFT the Helmholtz energy is separated as

$$\tilde{a} = \tilde{a}^{\mathrm{id}} + \tilde{a}^{\mathrm{hs}} + \tilde{a}^{\mathrm{hc}} + \tilde{a}^{\mathrm{disp}} + \tilde{a}^{\mathrm{assoc}} + \tilde{a}^{\mathrm{mp}}$$
(1.1)

where  $\tilde{a} = \frac{A}{NkT}$  is the reduced Helmholtz energy, N is the number of molecules, k is Boltzmann's constant, and T is the temperature. The superscripts {id, hs, hc, disp, assoc, mp} denote ideal gas, hard-sphere, hard-chain, dispersion, association, and multipolar contributions, respectively. Most summands in eq. (1.1) represent results from perturbation theories with the objective to obtain a certain target fluid from a corresponding reference fluid (e.g. a Barker and Henderson [19, 20] perturbation theory is applied on a hard-chain reference fluid to obtain chain molecules exhibiting attractive interactions [16]). Fig. 1.1 shows schematically the molecular model of PCP-SAFT, decomposed into contributions given in eq. (1.1). The mathematical expression of the ideal gas contribution is often times



Figure 1.1: Schematic depiction of molecules and intermolecular interactions related to fluid systems characterized by Helmholtz energy functional contributions in eq. (1.1). Depictions from left to right: ideal gas fluid, hard-sphere fluid, hard-chain fluid, dispersive chain fluid, dispersive chain fluid with associative interactions, dispersive chain fluid with associative and multipolar interactions.

not required, because for derivatives or differences of the Helmholtz energy the ideal gas contribution vanishes or simplifies to exactly known contributions. To add hard-sphere repulsive interactions to the fluid system, the hard-sphere EoS from Boublík [21] and Mansoori et al. [22] is applied. With TPT1 [1–8] the hard-sphere segments are joined together to form tangentially bonded chain-like molecules. The resulting hard-chain reference fluid is used for a second order Barker and Henderson [19, 20] perturbation theory, where a model for radial distribution functions of hard-chain molecules was applied [23]. The resulting target fluid [16] exhibits repulsive and dispersive interactions and is characterized by the pure component parameters  $m_i$  (number of segments composing the molecule),  $\sigma_i$  (segment diameter), and  $\varepsilon_i$  (dispersive energy), whereas *i* refers to the type of molecule.

Intermolecular interactions due to hydrogen bonds are considered by the association contribution [24]. The applied perturbation theory is based on TPT1 and is presented by Chapman et al. [8] and Huang and Radosz [10]. Two additional pure component parameters are introduced to describe the effects of associating interactions:  $\varepsilon^{A_iB_i}$  and  $\kappa^{A_iB_i}$  as the association energy and the effective association volume, respectively. Multipolar interactions consider dipole and quadrupole moments and the Helmholtz energy contribution  $\tilde{a}^{mp}$  is separated into contributions due to dipole-dipole [25], dipole-quadrupole [26], and quadrupole-quadrupole [27] interactions. Each of these contributions has been developed as a third-order perturbation theory, where a non-polar two-centered Lennard-Jones (LJ) fluid served as reference fluid. The dipole moment  $\mu_i$  and the quadrupole moment  $Q_i$  are used as pure component parameters.

#### **1.2** Classical Density Functional Theory

The approach applied in this thesis to characterize inhomogeneous fluid systems is the Classical Density Functional Theory (DFT). While the theoretical background of DFT was developed for electronic systems [28, 29] in the framework of quantum mechanics, the concepts were transferred to statistical mechanics [30, 31], where atomic or molecular number densities are studied instead of electron densities. The basic equation of DFT relates the functional  $\Omega_V$  with the intrinsic Helmholtz energy functional F according to

$$\Omega_V[\boldsymbol{\rho}(\mathbf{r})] = F[\boldsymbol{\rho}(\mathbf{r})] + \sum_i \int \rho_i(\mathbf{r}) \{V_i^{\text{ext}}(\mathbf{r}) - \mu_i\} \mathrm{d}\mathbf{r}$$
(1.2)

where  $\mathbf{r}$  is the spatial coordinate,  $\boldsymbol{\rho}(\mathbf{r}) = \{\rho_1(\mathbf{r}), \rho_2(\mathbf{r}), ...\}$  are the number density profiles,  $\mathbf{V}^{\text{ext}}(\mathbf{r}) = \{V_1^{\text{ext}}(\mathbf{r}), V_2^{\text{ext}}(\mathbf{r}), ...\}$  the external potentials, and  $\boldsymbol{\mu} = \{\mu_1, \mu_2, ...\}$ the chemical potentials. Here,  $\rho_i(\mathbf{r})$  characterizes the spatial distribution of molecules of species *i*. For given *T*, *V* and  $\boldsymbol{\mu}$  the thermodynamic equilibrium is determined by a minimization of  $\Omega_V$ , where in the equilibrium state  $\Omega_V$  is equal to the grand potential  $\Omega$ . Since the DFT formalism has been derived in the grand canonical ensemble, the first derivative of  $\Omega$  is zero in the equilibrium state. The functional derivative of eq. (1.2) leads to the Euler-Lagrange equation

$$0 = \frac{\delta F\left[\boldsymbol{\rho}(\mathbf{r})\right]}{\delta \rho_j(\mathbf{r}^*)} + V_j^{\text{ext}}(\mathbf{r}^*) - \mu_j$$
(1.3)

Introducing residual quantities  $\mu_j^{\text{res}} = \mu_j - \mu_j^{\text{id}}$  and  $F^{\text{res}} = F - F^{\text{id}}$  gives

$$\rho_j(\mathbf{r}^*) = \rho_j^{\text{bulk}} \exp\left(\frac{1}{kT} \left[\mu_j^{\text{res}} - \frac{\delta F^{\text{res}}\left[\boldsymbol{\rho}(\mathbf{r})\right]}{\delta \rho_j(\mathbf{r}^*)} - V_j^{\text{ext}}(\mathbf{r}^*)\right]\right)$$
(1.4)

where the ideal gas contribution of the chemical potential

$$\mu_j^{\rm id} = kT \ln \left( \rho_j^{\rm bulk} \Lambda_j^3 \right) \tag{1.5}$$

and the first derivative

$$\frac{\delta F^{\rm id}\left[\boldsymbol{\rho}(\mathbf{r})\right]}{\delta \rho_j(\mathbf{r}^*)} = kT \ln\left(\rho_j(\mathbf{r}^*)\Lambda_j^3\right) \tag{1.6}$$

was used. Eq. (1.4) is exact and is used to determine density profiles of the grand canonical ensemble in the thermodynamic equilibrium. However, a precise expression of the Helmholtz energy functional is unknown for most systems of practical interest [32] and therefore models for  $F^{\text{res}}$  have to be developed and evaluated in terms of predictiveness, accuracy and simplicity.

## 1.3 Helmholtz Energy Functionals based on SAFT Equations of State

The residual part of the Helmholtz energy functional can be separated according to types of molecular interactions similar to eq. (1.1)

$$F^{\text{res}}\left[\boldsymbol{\rho}(\mathbf{r})\right] = F^{\text{hs}}\left[\boldsymbol{\rho}(\mathbf{r})\right] + F^{\text{hc}}\left[\boldsymbol{\rho}(\mathbf{r})\right] + F^{\text{disp}}\left[\boldsymbol{\rho}(\mathbf{r})\right] + F^{\text{assoc}}\left[\boldsymbol{\rho}(\mathbf{r})\right] + F^{\text{mp}}\left[\boldsymbol{\rho}(\mathbf{r})\right]$$
(1.7)

Note that the order of contributions depicted in eq. (1.7) does not necessarily define the sequence of development: E.g. in the formalism of SAFT-VR, Wertheim's TPT1 is applied to a reference monomer fluid defined by repulsive and dispersive interactions and leads to an expression of the Helmholtz energy of the chain contribution. A different sequence is used for PC-SAFT [16] and the SAFT- $\gamma$  version developed by Ghobadi and Elliott [33]. Here, a hard-chain fluid serves as a reference for a perturbation theory to develop a Helmholtz energy for the dispersive contribution.

#### **1.3.1** Hard-Sphere Contribution

An inhomogeneous hard-sphere fluid is for most applications accurately described by the Helmholtz energy functionals derived from Fundamental Measure Theory (FMT). The original version of FMT was developed by Rosenfeld [34] and improved functionals are available today, e.g. the White-Bear version of FMT [35, 36]. All FMT functionals depend

on the FMT weighted densities

$$n_{\alpha}^{\text{FMT}}(\mathbf{r}) = \sum_{i} \int \rho_{i}(\mathbf{r}_{1}) w_{i,\alpha}^{\text{FMT}}(\mathbf{r} - \mathbf{r}_{1}) \mathrm{d}\mathbf{r}_{1}$$
(1.8)

where the right-hand side of eq. (1.8) is the sum of convolutions of the FMT weight function  $w_{i,\alpha}^{\text{FMT}}$  and corresponding density profiles. Three basic weight functions are used

$$w_{i,2}^{\text{FMT}} = \delta \left( R_i - r \right) \tag{1.9}$$

$$w_{i,3}^{\text{FMT}} = \Theta\left(R_i - r\right) \tag{1.10}$$

$$\mathbf{w}_{i,2}^{\text{FMT}} = \frac{\mathbf{r}}{r} \delta\left(R_i - r\right) \tag{1.11}$$

with  $\delta(r)$  as Dirac-delta distribution,  $\Theta(r)$  as Heaviside step function, and  $R_i$  as the radius of the hard-sphere of species *i*. The boldface typesetting indicates that  $\mathbf{w}_{i,2}^{\text{FMT}}$  is a vectorial, whereas  $w_{i,2}^{\text{FMT}}$  and  $w_{i,3}^{\text{FMT}}$  are scalar weighting functions.

#### 1.3.2 Chain Contribution

For the Helmholtz energy functional of the chain contribution two approaches are typically used in the literature. Yu and Wu [37] developed a functional based on the Helmholtz energy density for chain formation known for homogeneous phases by using FMT weighted densities. The chain contribution presented by Tripathi and Chapman [38, 39] is derived from an inhomogeneous expression of the Helmholtz energy for the association contribution based on TPT1. The limit of complete association leads to the expression of the functional for chain connectivity. The final expression contains two weighted densities

$$\bar{\rho}_i^{\rm hc}(\mathbf{r}) = \frac{3}{4\pi d_i^3} \int \rho_i(\mathbf{r}_1) \Theta\left(d_i - |\mathbf{r} - \mathbf{r}_1|\right) \mathrm{d}\mathbf{r}_1 \tag{1.12}$$

$$\lambda_i^{\rm hc}(\mathbf{r}) = \frac{1}{4\pi d_i^2} \int \rho_i(\mathbf{r}_1) \delta\left(d_i - |\mathbf{r} - \mathbf{r}_1|\right) \mathrm{d}\mathbf{r}_1 \tag{1.13}$$

where the weighting functions look similar to FMT versions, but with the hard-sphere diameter  $d_i$  used as a weighting radius. The functional of Tripathi and Chapman is more detailed compared to the model of Yu and Wu, because individual segment density profiles  $\rho_{\alpha}^{\text{seg}}(\mathbf{r})$  of segment  $\alpha$  of a chain characterizing the spatial distribution of segments are used instead of molecular density profiles. A later modification by Jain et al. [40] led to an improvement of the model in terms of stoichiometry of the segmental distributions.

#### **1.3.3** Dispersion Contribution

Helmholtz energy functionals for fluids exhibiting long-ranged attractive interactions can be developed in various ways. Starting at a general expression for the dispersion contribution

$$F^{\text{disp}}\left[\boldsymbol{\rho}(\mathbf{r})\right] = \int f^{\text{disp}}\left[\boldsymbol{\rho}(\mathbf{r})\right] d\mathbf{r}$$
(1.14)

that defines  $f^{\text{disp}}$  as the dispersive Helmholtz energy density, the simplest model for  $F^{\text{disp}}$  is achieved by assuming the local density approximation (LDA). Here, the Helmholtz energy density, which is in general a functional of the density profiles, is approximated as a function of the local values of the density profiles

$$f^{\text{disp}}\left[\boldsymbol{\rho}(\mathbf{r})\right] \approx f^{\text{disp}}\left(\boldsymbol{\rho}(\mathbf{r})\right) = \rho(\mathbf{r})\tilde{a}^{\text{disp}}(\boldsymbol{\rho}(\mathbf{r}))$$
(1.15)

where  $\rho(\mathbf{r})$  is the total local density profile according to  $\rho(\mathbf{r}) = \sum_{i} \rho_i(\mathbf{r})$ . Eq. (1.15) shows that a reduced Helmholtz energy of a bulk phase EoS can directly and easily be applied due to the LDA. LDA, however, can lead to strong inaccuracies and serious problems in the DFT formalism. Only when the density profile is slowly varying enough can LDA be a reasonable assumption [41]. Furthermore, very high local density values can occur at solid-fluid interfaces. These local values can easily exceed the maximum packing fraction of hard-spheres and have therefore no meaningful representation in homogeneous systems. Also, LDA approaches are not able to reproduce the oscillating behavior of density profiles in planar solid-fluid interfaces. LDA was applied on the residual Helmholtz energy functional by Lu et al. [42] to study pure component surface tensions of polar and associating fluids. Recently, a study of adsorption isotherms by Butz et al. [43] was presented that formulated a residual Helmholtz energy functional using LDA with PCP-SAFT and Peng-Robinson EoS, respectively.

#### 1.3.3.1 Weighted Density Approximation

In the literature [41, 44, 45] the weighted density approximation (WDA) is generally introduced as

$$F[\boldsymbol{\rho}(\mathbf{r})] = \int \rho(\mathbf{r})\tilde{a}\left(\bar{\boldsymbol{\rho}}(\mathbf{r})\right) d\mathbf{r}$$
(1.16)

where the reduced Helmholtz energy  $\tilde{a}$  is assumed as a function of weighted densities  $\bar{\rho}(\mathbf{r}) = \{\bar{\rho}_1(\mathbf{r}), \bar{\rho}_2(\mathbf{r}), ...\}$  defined as

$$\bar{\rho}_i(\mathbf{r}) = \int \rho_i(\mathbf{r}_1) w_i(\mathbf{r} - \mathbf{r}_1) \mathrm{d}\mathbf{r}_1$$
(1.17)

with  $w_i$  as the weighting function. In several WDA approaches [46–48]  $w_i$  itself depends on  $\bar{\rho}_i$ , which makes eq. (1.17) only implicitly solvable. Although eq. (1.16) is the most frequently used WDA variant, other versions are also present in the literature. Instead of formulating  $\tilde{a}$  as a function of  $\bar{\rho}(\mathbf{r})$ , the Helmholtz energy density can be defined as  $\bar{\rho}(\mathbf{r})$ dependent [49, 50]:  $f(\bar{\rho}(\mathbf{r})) = \bar{\rho}(\mathbf{r}) \tilde{a}(\bar{\rho}(\mathbf{r}))$ . Alternatively, a distinction between species contributions can be introduced [51]

$$F[\boldsymbol{\rho}(\mathbf{r})] = \sum_{i} \int \rho_{i}(\mathbf{r}) \tilde{a}_{i} \left( \bar{\boldsymbol{\rho}}(\mathbf{r}) \right) d\mathbf{r}$$
(1.18)

Like for LDA approaches, bulk phase EoS are used to model  $\tilde{a}$  or  $\tilde{a}_i$ , which means that the inhomogeneity of the system is captured by the weighted densities. Therefore, the challenge of WDA development is to find a weighting function for the chosen EoS that models the properties and the behavior of the Helmholtz energy functional correctly. The problems discussed with LDA do not occur for WDA approaches. Oscillating density profiles in solid-fluid interfaces can be described and very high local density values are not problematic due to the the smoothing character of the convolution in eq. (1.17).

Müller and MacDowell [52] applied Wertheim's TPT1 using a monomeric LJ fluid as reference system in the context of self-consistent field theory. A WDA was used to model the residual Helmholtz energy functional of the reference system. Müller et al. [53] reported that an explicit decomposition of the functional of the reference system into a repulsive and a dispersive contribution with different weighting functions is crucial. In both publications various weighting functions were tested.

Ye et al. [54] studied density profiles of square-well (SW) chains in confined media.  $F^{\text{res}}$  was separated into a hard-sphere and a dispersive contribution based on SAFT-VR and both were modeled using WDA. Heaviside step functions are used for the weighting functions to obtain weighted densities as averages of density profiles within a spherical region using eq. (1.17). The radius of the spherical region was chosen to be  $\sigma$  for the hard-sphere and 1.5 $\sigma$  for the dispersive contribution, respectively.

A Helmholtz energy functional focused on water systems was developed by Hughes et al. [55]. The dispersion contribution is based on SAFT-VR, eq. (1.16), and an effective local packing fraction that serves as weighted density. The weighting function is given by an exponential relation and includes a model parameter that was adjusted to experimental surface tension data. In the subsequent work by Krebs et al. [56] water and aqueous solutions were studied with an improved model for the association contribution of the Helmholtz energy functional.

Shen et al. [57] presented a dispersion contribution based on WDA from Ye et al. [54] (assuming a Heaviside weight of range  $1.5 \sigma$ ) but with PC-SAFT as bulk phase EoS. The model was used to study adsorption isotherms and density profiles of pure LJ and SW chains in confined systems. In a following work, Shen et al. [51] extended the model to mixtures and proposed a functional according to eq. (1.18). Besides the weighting

function of Ye et al., a potential dependent weighting was applied [49]

$$w^{\text{disp}}(\mathbf{r}) = \frac{\phi^{\text{disp}}(\mathbf{r})}{\int \phi^{\text{disp}}(\mathbf{r}_1) d\mathbf{r}_1}$$
(1.19)

with  $\phi^{\text{disp}}$  as the attractive part of the LJ potential. The comparison of results from both models with experimental data of methane and carbon dioxide adsorption isotherms showed a better performance of the model with the weighting function proposed by Ye et al. Further adsorption isotherms and pore size distributions were studied subsequently [58].

Bernet et al. [59] proposed a generalization of the FMT approach for intermolecular potentials containing an attractive part. The formalism was applied to SAFT-VR for a SW potential.

#### 1.3.3.2 Perturbation Theory

Due to the origins of SAFT EoS in perturbation theories, an obvious starting point in the development of a dispersion contribution is a perturbation expansion. The perturbation theory provides a description for the difference between the Helmholtz energy functional of a target and a reference fluid.

$$\Delta F^{\rm PT}\left[\boldsymbol{\rho}(\mathbf{r})\right] = F^{\rm target}\left[\boldsymbol{\rho}(\mathbf{r})\right] - F^{\rm ref}\left[\boldsymbol{\rho}(\mathbf{r})\right]$$
(1.20)

where the difference  $\Delta F^{\text{PT}}$  can be identified as the dispersion contribution  $F^{\text{disp}}$  if the target fluid is defined by dispersive and repulsive interactions and the reference fluid is governed by repulsive interactions only. The intermolecular pair potential of the target fluid  $\phi_{\alpha_i\beta_j}^{\text{target}}$  is separated into the pair potential of the reference fluid  $\phi_{\alpha_i\beta_j}^{\text{ref}}$  and the perturbation  $\phi_{\alpha_i\beta_j}^{\text{PT}}(r) = \phi_{\alpha_i\beta_j}^{\text{target}}(r) - \phi_{\alpha_i\beta_j}^{\text{ref}}(r)$ , where spherical symmetric potentials are assumed. The subscripts  $\alpha_i$  and  $\beta_j$  refer to segment  $\alpha$  in molecule *i* and segment  $\beta$  in molecule *j*, respectively. An integration path can be ensured by defining a coupling parameter  $\lambda$  according

$$\phi_{\lambda,\alpha_i\beta_j}(r) = \phi_{\alpha_i\beta_j}^{\text{ref}}(r) + \lambda \phi_{\alpha_i\beta_j}^{\text{PT}}(r)$$
(1.21)

which determines a continuous transition from reference to target potential between the limits  $\lambda = 0$  and 1. The dispersion contribution to the Helmholtz energy functional can then be derived exact, as [41, 45]

$$F^{\text{disp}} = \frac{1}{2} \sum_{i} \sum_{j} \sum_{\alpha_{i}} \sum_{\beta_{j}} \int_{0}^{1} \int \int \rho_{\alpha_{i}}^{\text{seg}}(\mathbf{r}_{1}) \rho_{\beta_{j}}^{\text{seg}}(\mathbf{r}_{2}) g_{\lambda,\alpha_{i}\beta_{j}}(\mathbf{r}_{1},\mathbf{r}_{2}) \phi_{\alpha_{i}\beta_{j}}^{\text{PT}}(\hat{r}) \mathrm{d}\mathbf{r}_{1} \mathrm{d}\mathbf{r}_{2} \mathrm{d}\lambda \quad (1.22)$$

where  $g_{\lambda,\alpha_i\beta_j}$  is the pair correlation function of an inhomogeneous fluid interacting with the pair potential  $\phi_{\lambda,\alpha_i\beta_j}$ . Further,  $\hat{r} = |\mathbf{r}_1 - \mathbf{r}_2|$  is the segment-segment distance. Note that  $g_{\lambda,\alpha_i\beta_j}(\mathbf{r}_1,\mathbf{r}_2)$  does not only depend on coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , but is a functional of the corresponding segment density profiles. For the regular PCP-SAFT model, where molecular chains are composed of identical segments, eq. (1.22) can be simplified by assuming  $g_{\lambda,\alpha_i\beta_j} \approx g_{\lambda,ij}$  and by further assuming all segments of a molecule to have the same local density profiles

$$\rho_i(\mathbf{r}) = \frac{1}{m_i} \sum_{\alpha_i} \rho_{\alpha_i}^{\text{seg}}(\mathbf{r})$$
(1.23)

This leads to

$$F^{\text{disp}} = \frac{1}{2} \sum_{i} \sum_{j} \int_{0}^{1} \int \int m_{i} \rho_{i}(\mathbf{r}_{1}) m_{j} \rho_{j}(\mathbf{r}_{2}) g_{\lambda,ij}(\mathbf{r}_{1},\mathbf{r}_{2}) \phi_{ij}^{\text{PT}}(\hat{r}) \mathrm{d}\mathbf{r}_{1} \mathrm{d}\mathbf{r}_{2} \mathrm{d}\lambda$$
(1.24)

where  $\phi_{ij}^{\text{PT}} = \phi_{\alpha_i \beta_j}^{\text{PT}}$  follows directly for homonuclear chains. The above assumptions imply that differences in spatial distributions of terminal segments and segments located in the center of a chain are neglected.

#### 1.3.3.3 Mean-Field Approximation

Finding a suitable approximation for  $g_{\lambda,ij}$  is the major challenge in developing Helmholtz energy functionals using perturbation theories, since accurate models of pair correlation functions of inhomogeneous systems are unknown. Applying a van-der-Waals-like approximation with  $g_{\lambda,ij} \approx \Theta(\hat{r} - d_{ij})$  [60] leads to

$$F^{\text{disp}} = \frac{1}{2} \sum_{i} \sum_{j} \int \int_{\hat{r} > d_{ij}} m_i \rho_i(\mathbf{r}_1) m_j \rho_j(\mathbf{r}_2) \phi_{ij}^{\text{PT}}(\hat{r}) d\mathbf{r}_1 d\mathbf{r}_2$$
(1.25)

where  $d_{ij}$  is a repulsive diameter related to the chosen reference fluid. Eq. (1.25) is the dispersion contribution to the Helmholtz energy functional in the mean-field approximation (MFA). According to Tang et al. [60] MFA is qualitatively incorrect at low densities and quantitatively inaccurate at intermediate and high densities. Nevertheless, MFA is somewhat valuable due to its simplicity and can serve as a first step during the modeling process.

Helmholtz energy functionals using MFA in the SAFT or related context were applied by several authors. Blas et al. [61] developed a Helmholtz energy functional by extrapolating the SAFT-HS [62] EoS to inhomogeneous systems. While all other Helmholtz energy contributions are treated locally, the dispersion contribution is based on MFA to obtain an expression consistent with SAFT-HS. The functional was applied to vapor-liquid interfaces [61, 63] to study density profiles and surface tensions. Bryk et al. [64] proposed a Helmholtz energy functional for binary monomer-polymer mixtures. The functional is based on FMT, the chain contribution of Yu and Wu [37], and MFA for the dispersion contribution. Bryk et al. studied phase diagrams, vaporliquid interfaces in terms of shape of the density profiles and enrichment effects, wetting transitions and adsorption in slit-shaped pores.

Chapman and coworkers proposed Helmholtz energy functionals, denoted as Interfacial Statistical Associating Fluid Theory (iSAFT), in a variety of publications that take the dispersion contribution in a MFA into account. The chain contribution developed by Tripathi and Chapman [38, 39] was used to study density profiles of molecular segments in confined media. Dominik et al. [65] presented DFT results for vapor-liquid interfaces and surface tension. Studies of heteronuclear chains using iSAFT revealed that resulting density profiles of molecular segments do not satisfy stoichiometry. Therefore, Jain et al. [40] developed a modified iSAFT where a stoichiometric distribution is enforced within the derivation of the chain contribution. The functional was applied to lipids near surfaces, lipid bilayers, and copolymer films and in a subsequent work to symmetric diblock copolymers [66]. Bymaster et al. [67] proposed a functional for LJ molecules with four associating sites and studied structure and interfacial properties of water dependent on solutes of different sizes. The modified version of iSAFT is extended to associating polyatomic molecular systems by Bymaster and Chapman [68] where the theory from Segura et al. [69] was used as association contribution. In a very recent work, Liu et al. [70] applied modified iSAFT to investigate alkane systems confined in graphite pores.

Xu et al. [71] constructed a Helmholtz energy functional to investigate polymer-carbon dioxide mixtures. A short-range contribution, that comprises repulsive and attractive interactions, is defined by WDA using Peng-Robinson as bulk EoS and FMT weighted densities. Long-ranged interactions are added to the model by an MFA-like dispersion contribution. The long-range term vanishes for homogeneous systems, due to density differences incorporated in the formulation. In the subsequent work [72], a similar formalism with PC-SAFT instead of Peng-Robinson was proposed. A comparison with experimental data showed that the PC-SAFT functional is superior in terms of interfacial tensions and solubility of carbon-dioxide.

#### **1.3.3.4** Further Models based on Approximations of Perturbation Terms

Eqs. (1.22) or (1.24) serve as starting points for perturbation expansion methods such as the Barker and Henderson [19, 20] (BH) or the Weeks-Chandler-Anderson [73] (WCA) perturbation theory. The  $\lambda$ -integral is transformed into a series expansion where higher order terms are neglected. The first-order term of eq. (1.24) reads

$$F_1^{\text{disp}} = \frac{1}{2} \sum_i \sum_j \int \int m_i \rho_i(\mathbf{r}_1) m_j \rho_j(\mathbf{r}_2) g_{ij}^{\text{ref}}(\mathbf{r}_1, \mathbf{r}_2) \phi_{ij}^{\text{PT}}(\hat{r}) d\mathbf{r}_1 d\mathbf{r}_2$$
(1.26)

with  $g_{ij}^{\text{ref}}$  as pair correlation function of the inhomogeneous reference fluid. Writing the pair distribution function in terms of the total correlation function  $h_{ij}$ , as  $h_{ij}(\mathbf{r}_1, \mathbf{r}_2) = g_{ij}(\mathbf{r}_1, \mathbf{r}_2) - 1$ , allows using a mean-field approach for part of  $g_{ij}^{\text{ref}}$ . One obtains a separation [44], as

$$F_1^{\rm disp} = F_1^{\rm sr} + F_1^{\rm lr} \tag{1.27}$$

where superscripts sr and lr refer to short-ranged and long-ranged, respectively.  $F_1^{\rm lr}$  is now identical to the mean-field approximation and  $F_1^{\rm sr}$  reads

$$F_1^{\rm sr} = \frac{1}{2} \sum_i \sum_j \int \int m_i \rho_i(\mathbf{r}_1) m_j \rho_j(\mathbf{r}_2) h_{ij}^{\rm ref}(\mathbf{r}_1, \mathbf{r}_2) \phi_{ij}^{\rm PT}(\hat{r}) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$
(1.28)

Gloor et al. [74] proposed a model, referred to as SAFT-VR MF DFT, where the firstorder BH perturbation term is separated according to eq. (1.27). The short-range part and the second-order term was approximated using LDA and SAFT-VR. An extension to mixtures was presented by Llovell et al. [75]. Malheiro et al. [76] also used SAFT-VR as bulk reference and separated  $F_1^{\text{disp}}$  with eq. (1.27). WDA was applied to  $F_1^{\text{sr}}$  and the BH second-order term  $F_2^{\text{disp}}$ . A FMT version and a coarse-grained version, where a weighted density similar to eq. (1.12) was used, were suggested. Comparisons with results from MC simulations in slit-shaped pores showed the superiority of the coarse-grained approach. Malheiro et al. [77] applied the coarse-grained version also to study water adsorption in confined media.

The mean-value theorem for integrals is another way to simplify eq. (1.26)

$$F_1^{\text{disp}} = \frac{1}{2} \sum_i \sum_j g_{ij}^{\text{ref}}(\boldsymbol{\rho}^{\text{eff}}) \int \int m_i \rho_i(\mathbf{r}_1) m_j \rho_j(\mathbf{r}_2) \phi_{ij}^{\text{PT}}(\hat{r}) d\mathbf{r}_1 d\mathbf{r}_2$$
(1.29)

with  $g_{ij}^{\text{ref}}$  evaluated as a function of effective densities  $\rho^{\text{eff}}$ . Kahl and Winkelmann [78] applied the mean-value theorem to develop the modified PT-LJ-SAFT DFT based on WCA perturbation theory. A temperature, density, and segment diameter dependent function was defined to model  $g_{ij}^{\text{ref}}$ . Density profiles of vapor-liquid interfaces and surface tensions of pure LJ chain molecules were studied. Various variants based on the mean-value theorem were investigated and compared by Bernet et al. [79].

Additional approaches are based on the idea that the pair correlation function in eq. (1.26) can be approximated by the radial distribution function of the corresponding bulk reference fluid  $g_{ij}^{\text{ref,bulk}}$ . This can be achieved with  $g_{ij}^{\text{ref,bulk}}$  evaluated with appropriate

mean densities [80]

$$g_{ij}^{\text{ref}}(\mathbf{r}_1, \mathbf{r}_2) \approx g_{ij}^{\text{ref,bulk}}(\hat{r}; \hat{\boldsymbol{\rho}})$$
(1.30)

A simple approximation of the mean densities  $\hat{\rho} = {\hat{\rho}_1, \hat{\rho}_2, ...}$  is the arithmetic average [81, 82]

$$\hat{\rho}_i = \frac{1}{2} \left( \rho_i \left( \mathbf{r}_1 \right) + \rho_i \left( \mathbf{r}_2 \right) \right) \tag{1.31}$$

Gloor et al. [74] developed the SAFT-VR DFT functional by introducing these approximations to the first-order BH term, while keeping the second-order term on a LDA level. Comparisons of results from SAFT-VR DFT and SAFT-VR MF DFT with MC results verified the superiority of SAFT-VR DFT regarding vapor-liquid interfacial systems. A subsequent work [83] showed that surface tensions can be incorporated in the adjustment of SAFT-VR pure component parameters, which is especially of advantage for associating components. Llovell et al. [75] applied the SAFT-VR DFT for mixtures and confirmed the superiority over SAFT-VR MF DFT. The functional was applied to mixtures associated to enhanced oil recovery systems [84] and to vapor-liquid interfacial properties of SW chain fluids [85].

Gross [86] introduced eqs. (1.30) and (1.31) to develop a dispersion contribution based on the first-order term of the BH perturbation theory. The same treatment was applied to the second-order term, but a comparison of calculated surface tensions showed a negligible influence of the second-order term. To obtain consistency with PC-SAFT a locally defined correction was adopted. A comparison with a MFA dispersion contribution showed that the proposed functional has a better temperature behavior. The model was extended to mixture systems and interfacial tensions of vapor-liquid [87] and liquid-liquid [88] equilibria and transport resistivities [89] were investigated. An improved description in the critical region using a renormalization group theory was presented by Tang and Gross [90].

A dispersion contribution based on SAFT-VR was presented by Schindler et al. [91]. The pair correlation function in the first- and second-order term of the perturbation theory was approximated using WDA

$$g_{ij}^{\text{ref}}(\mathbf{r}_1, \mathbf{r}_2) \approx g_{ij}^{\text{ref,bulk}}\left(\mathbf{r}_2; n_3^{\text{FMT}}(\mathbf{r}_2)\right)$$
(1.32)

Density profiles of SW chains in confined media were investigated. Mitchell et al. [92] calculated a pore size distribution for a activated carbon system and predicted adsorption isotherms for several n-alkanes accurately.

In the SAFT- $\gamma$  functional developed by Ghobadi and Elliott [93] the pair correlation functions itself is approximated by arithmetic averaging

$$g_{\alpha_i\beta_j}^{\text{ref}}(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{1}{2} \left( g_{\alpha_i\beta_j}^{\text{ref,bulk}}(\mathbf{r}_1; n_{3,\alpha_i\beta_j}^{\text{eff}}(\mathbf{r}_1)) + g_{\alpha_i\beta_j}^{\text{ref,bulk}}(\mathbf{r}_2; n_{3,\alpha_i\beta_j}^{\text{eff}}(\mathbf{r}_2)) \right)$$
(1.33)

where  $n_{3,\alpha_i\beta_j}^{\text{eff}}$  is related to weighted densities from FMT. The subscripts  $\alpha_i$  and  $\beta_j$  are used, because the SAFT- $\gamma$  distinguishes between molecular segments. The approximation is introduced in the first-, second-, and third-order term of the WCA perturbation theory. In a subsequent work [94], the approach was extended to molecules with partial charges.

#### **1.4** Scope and Outline of this thesis

The goal of this thesis is to develop a Helmholtz energy functional in the framework of DFT and to investigate its predictive capabilities when applied to a variety of inhomogeneous systems. A new functional model based on PCP-SAFT EoS is directly applicable to various pure component and mixture systems, due to the high number of PCP-SAFT parameters available in the literature. The PCP-SAFT functional previously proposed by Gross [86] for pure components and extended by Klink and Gross [87] for mixtures is very successful in the prediction of properties of liquid-fluid interfaces. However, the locally modeled correction term, that ensures consistency with PCP-SAFT, in the dispersion contribution is inappropriate for solid-fluid interfaces.

The newly proposed Helmholtz energy functional is suitable for fluid interfaces (vaporliquid and liquid-liquid equilibria) and for solid-fluid interfaces. Simplicity, accuracy, predictivity, good extrapolative behavior, and consistency with PCP-SAFT are desired properties of the suggested model. The WDA is an excellent choice with respect to consistency, because the functional translates naturally to the bulk EoS for constant density profiles. Furthermore, WDA provides a relatively simple expression for the dispersion contribution that can be implemented into very efficient code with the help of Fast Fourier transforms. The investigation of accuracy, predictivity, and extrapolative capabilities of the presented models is a central part of this thesis.

In Chapter 2, two variants of the dispersion contribution are proposed and discussed. For each variant a universal model parameter is introduced and adjusted to experimental surface tension data of pure *n*-alkanes. The transferability of the developed models is tested using results obtained from MC simulations of a molecularly thin liquid film on a planar solid substrate. Results obtained from the superior model are compared to experimental interfacial tensions of mixture liquid-fluid interfaces and to density profiles of confined systems obtained from MC simulations.

Chapter 3 extends the application of the Helmholtz energy functional to confined systems. Adsorption isotherms and selectivities from Transition Matrix MC techniques are used to examine the accuracy and the predictive capabilities of the model. Two different types of systems were studied. The first comprises clearly defined systems, where fluid-fluid as well as solid-fluid interactions are based on LJ interactions. Results are presented for pores with a slit-shaped and a cylindrical geometry. The second type characterizes more realistic systems: fluids composed of methane-n-butane mixtures in graphite-like pores.

In Chapter 4, argon and ethane nanodroplets on planar solid substrates are studied. The DFT formalism is extended with a Lagrange multiplier approach to fix the number of molecules in the system. A comparison of density profiles and contact angles obtained from MC and DFT methods is presented. Contact angles of nanodroplets of different sizes are related to results from Young's equation. The solid-fluid interactions between a polytetrafluoroethylene solid substrate and various liquid substances are modeled with an external potential. The transferability of the external potential to other species by using Berthelot-Lorentz combining rules is shown.

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# Chapter 2

# Classical Density Functional Theory for Liquid-Fluid Interfaces and Confined Systems: A Functional for the Perturbed-Chain Polar Statistical Associating Fluid Theory Equation of State

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## 2.1 Introduction

Interfacial properties of vapor liquid equilibria (VLE) and liquid-liquid equilibria (LLE), such as the interfacial tension, are essential for many technical applications. The study of solid-fluid interfaces is required to describe fluids in confinement (porous materials) and the predicted physical properties are for example adsorption isotherms, wetting phenomena, or the shift of phase equilibria due to confinement. As a unifying factor, all of these applications regard fluids as inhomogeneous systems which means that the oneparticle density varies in spacial coordinates. A powerful approach for the description of inhomogeneous liquid-fluid and solid-fluid interfaces is the classical density functional theory (DFT). A comprehensive discussion of the mathematical background of DFT is provided by Evans [1] and a compilation of possible applications is presented by Davis [2], Löwen [3], and Wu [4].

The applied Helmholtz energy functional determines the accuracy of DFT predictions. Several types of approximations for the Helmholtz energy functional have been proposed, such as density expansion, integral equation theories and perturbation approaches. A detailed overview is given in the reviews of Vanderlick et al. [5], Evans [6], Wu and Li [7], and Emborsky et al. [8]. Many DFT developments take a successful equation of state for bulk phases as a starting point and construct a suitable Helmholtz energy functional. In other cases, fluid theories are natively formulated in a functional form, as e.g. the first-order mean-spherical approximation of Tang and Wu [9].

In several works Helmholtz energy functionals have been developed by extending an expression of the Helmholtz energy initially developed for bulk phases. The simplest approach is the local density approximation (LDA), where the Helmholtz energy density  $F[\rho(\mathbf{r})] = \int f[\rho(\mathbf{r})] d\mathbf{r}$  of an inhomogeneous system with density profile  $\rho(\mathbf{r})$  is calculated using the bulk phase Helmholtz energy density evaluated at the value of the local density, i.e.  $f[\rho(\mathbf{r})] \approx f(\rho(\mathbf{r}))$ . The round brackets indicate, that f is a function of  $\rho$  whereas the square brackets define f as a functional. This approach is insufficient for most applications, especially if strongly oscillating density profiles occur and the values of local densities exceed the maximal packing fraction.

A significantly more successful approach is the weighted density approximation (WDA), where an appropriate bulk phase Helmholtz energy density is evaluated with a coarse grained or smoothed density. This so-called weighted density is obtained by averaging the one-particle density in defined regions and thus carries information of the inhomogeneity of the system. Note that the WDA is not limited to Helmholtz energy functionals, but has been used for other quantities such as direct correlation functions [6].

A WDA can be applied to Helmholtz energy expressions for bulk phase properties. The family of Statistical Associating Fluid Theory (SAFT) models is a prominent and promising choice due to reliable results obtained from SAFT EoS for many applications. SAFT models are usually based on the first-order thermodynamic perturbation theory (TPT1) introduced by Wertheim [10–13]. After the first development of the SAFT framework [14–17] several variants were proposed, such as soft-SAFT [18, 19], for potential of variable range (SAFT-VR) [20, 21], Perturbed-Chain SAFT (PC-SAFT) [22, 23], and SAFT- $\gamma$  Mie [24, 25]. We recommend the reviews of Müller and Gubbins [26], Economou [27], Paricaud et al. [28], and Tan et al. [29] for a detailed study of SAFT. A

review of how Wertheim developed the TPT is given in ref. [30].

Wertheim's [10-13] perturbation theory has been applied to inhomogeneous systems by several groups. Kierlik and Rosinberg [31, 32] presented a TPT1 functional and studied the behavior of polyatomic molecules in slit-shaped pores [33]. Segura and Chapman [34] performed Monte Carlo (MC) simulations of spherical molecules with four association sites confined near solid surfaces. They developed a model for determining monomer fractions (i.e. the fraction of molecules not associatively bonded) using Wertheim's theory and evaluated the theory using MC results. Segura et al. [35] presented and compared two methods for spherical associating molecules. The first method used an inhomogeneous form of Wertheim's theory whereas the second methods applied Tarazona's [36] weighted density to make the functional a simple extension of Wertheim's theory for bulk phases. A similar model has been applied to study the adsorption on surfaces with association sites [37]. Yu and Wu applied TPT1 to inhomogeneous systems and used the weighted densities of FMT [38–40] to develop functionals for associating interactions [41] and chain connectivity [42]. It has been applied successfully to confined systems and interfacial tensions [43]. Müller et al. [44] applied TPT1 to model Lennard-Jones chain molecules in inhomogeneous systems and used the WDA to formulate the Helmholtz energy functional. Their results show, that the ranges of the WDA for the repulsive interactions and the WDA for attractive contributions are different.

A SAFT-variant applicable to inhomogeneous systems has been presented by Tripathi and Chapman [45, 46] and is referred to as iSAFT. It models molecules as chains where the Helmholtz energy due to chain formation is developed from the association contribution in the limit of complete association and provides an accurate description of polymeric systems in confined media [45, 46] and experimental surface tensions [47]. Jain et al. [48] modified iSAFT by ensuring that overall stoichiometry is satisfied by the density profiles and thus made iSAFT applicable to heteronuclear molecules. Subsequently, Bymaster and Chapman [49] extended the theory to model associating molecular chains.

In several works SAFT EoS have been used as a basis in the development of DFTs. A DFT study of VLE interfaces was presented by Jackson and co-workers [50, 51]. The proposed functional of the Helmholtz energy models the hard-sphere, chain, and association contributions at the LDA level whereas dispersive interactions are described as a mean-field approximation approach. In a subsequent study, Gloor et al. [52] developed and compared two additional Helmholtz energy functionals based on the SAFT-VR [20] EoS. The first functional describes the first-order dispersion term as a nonlocal perturbation theory and approximates the pair correlation function as a bulk phase radial distribution function. In the second variant, the first-order term is separated in a short range contribution, approximated with the LDA, and a long range contribution, where the pair correlation function function is set to unity (mean field theory). Both functionals show good

agreement with surface tensions of molecular simulations and experimental data. Gloor et al. [53] presented an approach, where experimental surface tensions are considered in the objective function of the adjustment of SAFT-VR pure component parameters.

The SAFT-FMT-DFT approach proposed by Schindler et al. [54] is also based on the SAFT-VR EoS. The chain contribution of the functional is based on the work of Yu and Wu [42]. The dispersion contribution is modeled via a second-order nonlocal perturbation theory where the pair correlation function is calculated using a weighted density of the FMT contribution. The functional is compared with results of MC simulations for confined systems defined by different external potentials. In subsequent work [55], the functional was tested against experimental data of adsorption isotherms for several n-alkanes accounting also for the pore size distributions.

Malheiro et al. [56] presented and compared two additional functionals based on the SAFT-VR EoS for spherical components. Both approaches model the dispersion contribution of the Helmholtz energy functional via a WDA. The first approach uses the weighted densities obtained by the FMT term whereas the second approach uses a separately defined weighted density with Heaviside averaging. The second approach is superior and describes density profiles of confined systems very accurately. Subsequently [57], the model extended by an association contribution according to Yu and Wu [41] and water was described in confined systems.

An EoS similarly to the SAFT- $\gamma$  [24] EoS has been constructed by Ghobadi and Elliott [58] as a third-order Weeks-Chandler-Andersen [59] perturbation theory. Based on this EoS, a DFT framework has been developed that is applicable to confined systems and vapor-liquid interfaces [60]. Because of its group-contribution structure analogous to the SAFT- $\gamma$  EoS, it is able to describe fused heteronuclear chains and it provides density profiles for all involved segment types. An extension of the DFT framework [61] to molecules with partial charges was established by including an association model according to Bymaster and Chapman [49].

Several studies used the PC-SAFT EoS as a basis for constructing Helmholtz energy functionals. In previous work of our group [62], we followed the work of Gloor et al. [52] and modeled the dispersion contribution as a nonlocal perturbation theory. To establish consistency with the PC-SAFT EoS a locally treated correction term was added. A comparison between a first- and a second-order dispersion functional showed nearly no difference in the calculation of surface tensions. The approach was extended to mixtures to describe interfacial tensions of vapor-liquid [63] and liquid-liquid phase equilibria [64]. A renormalization group theory was applied to ensure very good agreement in the vicinity of the critical point [65]. Von Müller and Leonhard applied the approach to surface tensions using PC-SAFT parameters obtained from quantum mechanical calculations [66].

Shen et al. [67] presented a PC-SAFT-based Helmholtz energy functional referred to as

hybrid PC-SAFT DFT. The dispersion contribution uses weighted densities proposed by Ye et al. [68], where the density is averaged within a local sphere with radius  $1.5\sigma$ . Density profiles in slit-shaped pores and adsorption isotherms were found in good agreement to results from molecular simulations and experimental data, respectively. Subsequently, an extension to mixtures and the influence of a WDA Lennard-Jonesian averaging were presented [69]. Also pore size distributions were included into the model [70].

In this work two variants of a dispersion contributions to the Helmholtz energy functional are presented and compared. The superior variant is further evaluated by comparisons with experimental interfacial tensions and with density profiles obtained by MC simulations for solid-fluid interfaces.

## 2.2 Classical Density Functional Theory

The basic equation within DFT is the relation between the grand potential  $\Omega$  and the intrinsic Helmholtz energy F, as [1, 71]

$$\Omega\left[\rho_k\right] = F\left[\rho_k\right] + \sum_{i}^{N_c} \int \rho_i(\mathbf{r}) \{V_i^{\text{ext}}(\mathbf{r}) - \mu_i\} \mathrm{d}\mathbf{r}$$
(2.1)

where the density  $\rho_i$  of species *i* depends on the positional vector **r**, and  $\Omega$  and *F* are functionals of all densities  $\rho_k$  of the inhomogeneous system, and further  $N_c$  is the number of components. In this work, we use *k* as an generic index and  $\rho_k(\mathbf{r})$  refers to the vector of all species-density profiles.

The integration is carried out over the volume V of the system. The external potential  $V_i^{\text{ext}}(\mathbf{r})$  describes interactions between a molecule of component *i* at position  $\mathbf{r}$  and an external field. For a system with given temperature *T*, volume V and chemical potentials  $\mu_i$ , thermodynamic equilibrium requires  $\Omega$  to be minimal with respect to all internal degrees of freedom, such as the density profiles  $\rho_k(\mathbf{r})$ . In fact, it is appropriate to speak of  $\Omega$  as the grand potential only in its minimized state with respect to internal degrees of freedom, i.e. the density profiles  $\rho_k(\mathbf{r})$  in our case. The first functional derivative of  $\Omega$  with respect to the  $\rho_j$  is thus zero for all components *j* 

$$\frac{\delta\Omega\left[\rho_k\right]}{\delta\rho_j(\mathbf{r}^*)} = 0 \tag{2.2}$$

The equilibrium condition applied to eq. (2.1) leads to

$$0 = \frac{\delta F\left[\rho_k\right]}{\delta \rho_j(\mathbf{r}^*)} + V_j^{\text{ext}}(\mathbf{r}^*) - \mu_j^{\text{b}}$$
(2.3)

All inhomogeneous systems shown in this work are connected to bulk phases (superscript b). Because when thermodynamic equilibrium prevails, the chemical potentials are uniform over space and therefore  $\mu_j = \mu_j^{\rm b}$ . Separating F and  $\mu_j^{\rm b}$  into an ideal gas (id) and a residual (res) contribution leads to

$$\rho_j(\mathbf{r}^*) = \rho_j^{\rm b} \exp\left[\frac{\mu_j^{\rm res,b}}{kT} - \frac{\delta^{F^{\rm res}[\rho_k]/kT}}{\delta\rho_j(\mathbf{r}^*)} - \frac{V_j^{\rm ext}(\mathbf{r}^*)}{kT}\right]$$
(2.4)

where k is Boltzmann's constant. In eq. (2.4) we canceled the de Broglie wavelength  $\Lambda_i$ from the functional derivative of the ideal gas Helmholtz energy

$$F^{\rm id}\left[\rho_k\right] = kT \sum_{i}^{N_c} \int \rho_i(\mathbf{r}) \{\ln\left(\rho_i(\mathbf{r})\Lambda_i^3\right) - 1\} \mathrm{d}\mathbf{r}$$
(2.5)

and from the ideal gas chemical potential

$$\mu_j^{\rm id,b} = kT \ln \left(\rho_j^{\rm b} \Lambda_j^3\right) \tag{2.6}$$

Ideal gas here refers to molecular species in a state where intermolecular interactions do not exist. The connectivity of segments to form chains (molecules) is considered using Wertheim's perturbation theory [10–13] within the chain term, described below. Details are given in Appendix D.

#### 2.2.1 Application: Interfacial Tensions

We briefly summarize how the surface tension between vapor and liquid phases (VLE) of mixtures as well as the interfacial tension of two liquid phases (LLE) were calculated in this work. A more comprehensive description of the general calculation procedure is given by Klink and Gross [63]. For given temperature T (pure components) or given temperature Tand pressure p (binary mixtures) the phase equilibrium is determined with the PCP-SAFT EoS. The phase equilibrium calculation delivers the required bulk chemical potentials  $\mu_j^{\text{res,b}}$ as well as bulk densities  $\rho_j^{\text{b}}$  for both coexisting phases. We consider planar interfaces using a cylindrical coordinate system, with z-coordinate normal to the interface. The density varies only along the z-coordinate and one can perform simple one-dimensional DFT calculations for the interfacial tensions.

Eq. (2.4) is solved iteratively using a damped direct substitution scheme (Picard iteration). The starting profile of the partial densities are generated using a hyperbolic tangent function proposed by Klink et al. [64]

$$\rho_j^{(0)}(z) = \frac{1}{2} \left( \rho_j^{\rm b,P1} + \rho_j^{\rm b,P2} \right) + \frac{1}{2} \left( \rho_j^{\rm b,P1} - \rho_j^{\rm b,P2} \right) \tanh\left( 0.6 \frac{z}{\sigma_j} \right)$$
(2.7)

where the coexisting phases are denoted by P1 and P2 and  $\sigma_j$  is the PCP-SAFT segment size parameter.

For converged density profiles defining the equilibrium state, the interfacial tension can be calculated using

$$\gamma = \int \left( f\left[\rho_k(z)\right] - \sum_i^{N_c} \mu_i \rho_i(z) + p^{\rm b} \right) \mathrm{d}z \tag{2.8}$$

with  $p^{b}$  as the scalar valued pressure of bulk phases in phase equilibrium, which is equal to the normal pressure for planar interfaces. The Helmholtz energy density  $f[\rho_{k}(z)]$  is defined by

$$F[\rho_k] = A \int f[\rho_k(z)] dz$$
(2.9)

where A is the area of the considered planar interface.

## 2.2.2 Application: Confined Systems

The DFT is a powerful framework also for studying the behavior of fluids in confinement. We assume solid walls, which determine the geometry of the confinement, to be perfectly plain (without roughness) and chemically homogeneous. We focus on graphite-like slitshaped pores. With these assumptions, density profiles vary only along the z-coordinate, where the z-axis points perpendicular to the planar wall. The same one-dimensional implementation used for the calculation of interfacial tensions can be used for these slitshaped pores.

The intermolecular interactions within the fluid phase is covered by the intrinsic Helmholtz energy, whereas molecular solid-fluid interactions are described through the external potential  $V_j^{\text{ext}}$  acting on fluid molecules of species j. For the external potential, in this work we use the 9-3 potential

$$V_{js}^{\text{ext}}(z) = \varepsilon_{js} \left[ \left( \frac{\sigma_{js}}{z} \right)^9 - \left( \frac{\sigma_{js}}{z} \right)^3 \right]$$
(2.10)

where the subscripts j and s denote the fluid component and the solid species, respectively. Binary solid-fluid interaction parameters are defined by the Berthelot-Lorentz combining rules  $\sigma_{js} = \frac{1}{2}(\sigma_{jj} + \sigma_{ss})$  and  $\varepsilon_{js} = \sqrt{\varepsilon_{jj}\varepsilon_{ss}}$ , where  $\varepsilon$  denotes dispersive energy parameters. Furthermore, we apply the frequently used external 10,4,3 potential proposed by Steele [72], as

$$V_{js}^{\text{ext}}(z) = 2\pi\rho_{s}\varepsilon_{js}\sigma_{js}^{2}\Delta\left[\frac{2}{5}\left(\frac{\sigma_{js}}{z}\right)^{10} - \left(\frac{\sigma_{js}}{z}\right)^{4} - \frac{\sigma_{js}^{4}}{3\Delta\left(z+0.61\Delta\right)^{3}}\right]$$
(2.11)

The solid phase is thereby described as a stack of lattice planes, assumed as idealized basal graphite planes. The distance between lattice planes is defined by distance parameter  $\Delta$  and the overall density of the solid phase is  $\rho_{\rm s}$ . Interactions of the fluid molecules with the topmost lattice plane (adjacent to the fluid phase) leads to the first and second term on the right hand side of eq. (2.11). The subjacent lattice planes interact with the fluid molecules according to the third term. The z coordinate is defined as the distance between the center of a solid particle on the topmost lattice plane and the center of a fluid molecule. A parameter set [72, 73] for a graphite solid phase is given:  $\sigma_{\rm ss} = 3.40$  Å,  $\varepsilon_{\rm ss}/k = 28.0$  K,  $\Delta = 3.35$  Å and  $\rho_{\rm s} = 0.114$  Å<sup>-3</sup>.

The external field acting on a molecule of type j at position z resulting from the solid-phase on both sides of the slit-shaped pore is obtained by superposition

$$V_{j}^{\text{ext}}(z) = V_{js}^{\text{ext}}(z) + V_{js}^{\text{ext}}(H-z)$$
(2.12)

where H is the distance between the centers of the topmost wall particles of both planar walls.  $V_{js}^{\text{ext}}(z)$  describes the interaction of a fluid molecule with the solid phase on the left side and  $V_{js}^{\text{ext}}(H-z)$  with the solid phase on the right side.

The grand potential  $\Omega$  is minimal with respect to the equilibrium density profiles  $\rho_k(\mathbf{r})$ for defined variables T, V and  $\mu_k$ . We choose the input variables by (hypothetically) connecting the inhomogeneous system to a bulk phase system. The natural variables are then given as thermodynamic equilibrium conditions of the connected bulk phase,  $T = T^{\rm b}$ and  $\mu_i = \mu_i^{\rm b}$ . The temperature  $T^{\rm b}$  (and volume V) of the considered system are usually easy to define, whereas the chemical potentials need to be determined from the EoS by considering the bulk phase system at given (T, p).

## 2.3 Helmholtz Energy Functional

The Helmholtz energy functional entirely determines the quality of DFT predictions. In this section, we propose a new Helmholtz energy functional that is consistent with the PCP-SAFT EoS. More specifically, we present a new functional term for the dispersive (attractive) interactions, which is suitable for both, confined systems and for VLE or LLE interfaces. At the same time the new functional can be solved very efficiently compared to our previous work [62, 63].

In accordance with the structure of the PCP-SAFT EoS, we consider a functional composed of several contributions

$$F^{\rm res}[\rho_k] = F^{\rm hs}[\rho_k] + F^{\rm hc}[\rho_k] + F^{\rm disp}[\rho_k] + F^{\rm assoc}[\rho_k] + F^{\rm mp}[\rho_k]$$
(2.13)

where the superscripts (hs, hc, disp, assoc, and mp) denote hard-sphere, chain, dispersion,

association, and multipolar contributions, respectively. To provide a DFT that is consistent with the PCP-SAFT EoS it is required that all contributions of eq. (2.13) simplify to the corresponding contributions [23, 74–77] of the reduced Helmholtz energy  $\tilde{a} = F/NkT$ for homogeneous phases, with N as the total number of molecules in the system. This section is focused on the proposed dispersion contribution, but a short description of all contributions in eq. (2.13) is given.

## 2.3.1 The Hard-Sphere Contribution

The fundamental measure theory (FMT) originally proposed by Rosenfeld [38] and simultaneously modified by Roth et al. [39] and Yu and Wu [40] very accurately describes the behavior of inhomogeneous hard-sphere systems. The bulk EoS that corresponds to the modified FMT [39, 40] is the hard-sphere EoS proposed by Mansoori et al. [78]. The modified FMT is thus consistent with the PCP-SAFT hard-sphere contribution. In the Appendix of previous work [62] we formulated the modified FMT integrals for onedimensional cylindrical coordinate systems, where the density profile depends only on the z coordinate. Unfortunately we presented an erroneous equation and discuss the correction of the error in Appendix A.

#### 2.3.2 The Chain Contribution

The chain contribution to the Helmholtz functional used in this work has been developed by Tripathi and Chapman [45, 46] and is based on Wertheim's first order perturbation theory [10–13]. The here considered version of PCP-SAFT EoS regards nonspherical molecules as chains of equal spherical segments (homonuclear chains). The corresponding chain functional reads

$$\frac{F^{\rm hc}\left[\rho_k\right]}{kT} = \sum_i (m_i - 1) \int \rho_i(\mathbf{r}) \left(\ln \rho_i(\mathbf{r}) - 1\right) d\mathbf{r} - \sum_i (m_i - 1) \int \rho_i(\mathbf{r}) \left(\ln \left[y_{ii}^{\rm dd}(\bar{\rho}_k^{\rm hc}(\mathbf{r}))\lambda_i(\mathbf{r})\right] - 1\right) d\mathbf{r}$$
(2.14)

The ideal gas reference state used by Tripathi and Chapman [46] (and natively obtained from Wertheim's theory) is the ideal gas state of nonbonded segments. The chain functional in eq. (2.14) differs from the chain functional of Tripathi and Chapman [46] because the ideal gas reference state used in the PCP-SAFT formalism is defined for complete molecules. The difference between both functionals ensures the consistency with the chain contribution of the PCP-SAFT EoS. For further details see Appendix D.

In the derivation of eq. (2.14),  $\rho_i$  is an average of density profiles of segments in molecule *i*. Therefore, eq. (2.14) does not provide density profiles of individual segments

in a molecule. For some cases, like for surfactants, a distinction between density profiles of individual segments is an interesting perspective. An extension of the theory to heteronuclear molecules is described in the work of Jain et al. [48]. This DFT concept is appealing for heteronuclear chains, used for example in group-contribution methods [79].

## 2.3.3 The Contribution from Dispersive Attractions

A dispersive term compatible with the PCP-SAFT EoS has been proposed in earlier work [62, 63]. This earlier term has strengths in the accuracy of predictions, that are possible for interfacial tensions of pure substances and mixtures. At the same time, there are disadvantages, namely the functional is not suited for interfaces to solids, where significant local fluctuations of the single-particle density occur. Second, the term is rather involved, both in implementation and in computational cost. We here strive to alleviate these deficiencies with a new term that is suitable for systems with confining solid-fluid interfaces while at the same time maintaining the accuracy of our earlier functional term. In this section, the structure of an alternative contribution  $F^{\text{disp}}[\rho_k]$  is suggested. A discussion of benefits and disadvantages of the former and the new dispersion contribution as well as a comparison between them is given in the Results and Discussion section.

#### 2.3.3.1 Definition of Weighted Densities for Dispersion of PCP-SAFT EoS

For the weighted densities, we adopt the formulation proposed by Tarazona [80, 81]

$$\bar{\rho}_i(\mathbf{r}_1) = \int \rho_i(\mathbf{r}_2) w_i(|\mathbf{r}_1 - \mathbf{r}_2|) \mathrm{d}\mathbf{r}_2$$
(2.15)

where  $\bar{\rho}_i$  is the weighted density of component *i* for position  $\mathbf{r}_1$  and  $w_i$  is the corresponding normalized weighting function. In several works [36, 82, 83], a density dependent weighting function has been proposed. Our aim is to keep the dispersion contribution as simple as possible and therefore no density dependence is introduced. We define the normalized weighting function of component *i* as

$$w_i(r) = \frac{\Theta \left[\psi d_i - r\right]}{\int \Theta \left[\psi d_i - |\mathbf{r}_3|\right] d\mathbf{r}_3}$$
(2.16)

with  $d_i$  as the temperature dependent effective repulsive (hard-sphere) diameter and  $\Theta$ as the Heaviside function. We summarize the basis to the weighted density approach in Appendix C and reveal the involved assumptions. The Appendix shows that other weight functions are possible (and are in fact more obvious than a Heaviside-weight), however we value the simplicity of the Heaviside function, particularly because Heavisideweighted densities are already required for the Fundamental Measure Theory. That choice ensures a simple implementation and high computational efficiency. In Appendix C, we discuss other choices, such as a weight according to the attractive part of the Lennard-Jones potential or a square-well potential and we mention that the considered alternative choices gave no advantage for our applications. We introduced the parameter  $\psi$ , which scales the size of the averaging space, analogously to Ye et al. [68]. Instead of defining  $\psi = 1.5$ , we interpret  $\psi$  as an universal but (one time) adjustable model parameter. Because of the long-ranged nature of dispersive interactions it is sensible to assume that  $\psi$  values are larger than 1. With the weighting function the weighted density used in this work is

$$\bar{\rho}_i(\mathbf{r}_1) = \frac{3}{4\pi\psi^3 d_i^3} \int \rho_i(\mathbf{r}_2) \Theta\left[\psi d_i - |\mathbf{r}_1 - \mathbf{r}_2|\right] \mathrm{d}\mathbf{r}_2 \tag{2.17}$$

#### 2.3.3.2 Structure of the New Dispersion Contribution

The basic idea behind WDA is to cast a model valid for homogeneous systems into functional form, applicable to inhomogeneous systems. In our case, the reduced dispersion contribution to the Helmholtz energy  $\tilde{a}^{\text{disp}}$  has to be written in functional form. We suggest two simple and straightforward variants of the functional, noting that several more variants are conceivable. In variant WDA1 the full Helmholtz energy density is modeled via weighted densities so that

$$\frac{F^{\text{disp},1}\left[\rho_{k}\right]}{kT} = \int \bar{\rho}(\mathbf{r}_{1})\tilde{a}^{\text{disp}}(\bar{\rho}_{k}(\mathbf{r}_{1}))\mathrm{d}\mathbf{r}_{1} \qquad (\text{WDA1})$$
(2.18)

where  $\tilde{a}^{\text{disp}}$  is a function of all weighted densities at position  $\mathbf{r}_1$  and  $\bar{\rho}$  is the locally defined total weighted density

$$\bar{\rho}(\mathbf{r}_1) = \sum_j \bar{\rho}_j(\mathbf{r}_1) \tag{2.19}$$

For variant WDA2  $\tilde{a}^{\text{disp}}$  is multiplied by the local value of the density  $\rho$  instead of  $\bar{\rho}$ , which leads to

$$\frac{F^{\text{disp},2}\left[\rho_{k}\right]}{kT} = \int \rho(\mathbf{r}_{1})\tilde{a}^{\text{disp}}(\bar{\rho}_{k}(\mathbf{r}_{1}))\mathrm{d}\mathbf{r}_{1} \qquad (\text{WDA2})$$
(2.20)

WDA models in form of eq. (2.20) are dominant in the literature. Earlier studies with strongly oscillating density profiles showed that, in combination with eq. (2.16), the influence of the local density  $\rho(\mathbf{r}_1)$  in eq. (2.20) leads to insufficient results. As a result, eq. (2.18) has been introduced as an alternative model, where the direct influence of  $\rho(\mathbf{r}_1)$ is reduced. An approach similar to eq. (2.18) was proposed also by Peng and Yu [84, 85].

The formulation of variant WDA2 is closely related to the approach presented by Shen et al. [69]. Their model is for pure component systems equal to eq. (2.20) but both models differ slightly for mixtures. Note, the similarity of both approaches concern the structure of eq. (2.20). But we will use a different definition for the weighted densities, compared to Shen et al. so that results for pure components from both approaches differ in any practical calculation. A comparison with the Shen et al. functional is shown in Appendix B. Note that two additional WDA approaches have been derived that were discarded due to insufficient accuracy in confined systems. The derivation and discussion is presented in Appendix C.

The evaluation of  $\tilde{a}^{\text{disp}}$  with weighted densities is

$$\tilde{a}^{\text{disp}}(\bar{\rho}_k(\mathbf{r}_1)) = -2\pi\bar{\rho}(\mathbf{r}_1)I_1(\bar{\eta},\bar{m})\overline{m^2\varepsilon\sigma^3} - \pi\bar{\rho}(\mathbf{r}_1)\bar{m}C_1I_2(\bar{\eta},\bar{m})\overline{m^2\varepsilon^2\sigma^3}$$
(2.21)

with the mean segment number

$$\bar{m} = \sum_{i} \bar{x}_{i} m_{i} \tag{2.22}$$

where  $m_i$  is the PC-SAFT segment number. The abbreviations  $\overline{m^2 \varepsilon \sigma^3}$ ,  $\overline{m^2 \varepsilon^2 \sigma^3}$  and  $C_1$  calculate as [23]

$$\overline{m^2 \varepsilon^n \sigma^3} = \sum_i \sum_j \bar{x}_i \bar{x}_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT}\right)^n \sigma_{ij}^3$$
(2.23)

and

$$C_1 = \left[1 + \bar{m}\frac{8\bar{\eta} - 2\bar{\eta}^2}{\left(1 - \bar{\eta}\right)^4} + (1 - \bar{m})\frac{20\bar{\eta} - 27\bar{\eta}^2 + 12\bar{\eta}^3 - 2\bar{\eta}^4}{\left[(1 - \bar{\eta})(2 - \bar{\eta})\right]^2}\right]^{-1}$$
(2.24)

The packing fraction  $\bar{\eta}$  and the mole fraction  $\bar{x}_i$  are locally defined as

$$\bar{\eta} = \frac{\pi}{6} \sum_{i} \bar{\rho}_i(\mathbf{r}_1) m_i d_i^3 \tag{2.25}$$

$$\bar{x}_i = \frac{\bar{\rho}_i(\mathbf{r}_1)}{\bar{\rho}(\mathbf{r}_1)} \tag{2.26}$$

The parameters  $\sigma_{ij}$  and  $\varepsilon_{ij}$  are defined by Lorentz-Berthelot combining rules using PC-SAFT segment diameters  $\sigma_{ii}$  and PC-SAFT potential depth  $\varepsilon_{ii}$ , respectively.

#### 2.3.3.3 Evaluation of WDA Variants

In the previous paragraph we presented two dispersion functionals. We treat  $\psi$  for both variants as (one time) adjustable and subsequently universal model constant and evaluate whether the dispersion functional maintains its predictive qualities for a variety of applications. We adjusted the values of the  $\psi$  parameters for both variants by minimizing the root mean square (%RMS) deviations of calculated surface tensions from experimental values. Because of the known overestimation of critical points by the PCP-SAFT EoS, we omitted experimental data points at temperatures above  $0.95 \cdot T_c$ , where  $T_c$  is the critical temperature of the considered substance. The calculated surface tensions were obtained

according to the procedure described above. PCP-SAFT pure component parameters were taken from Gross and Sadowski [23] and are listed as Supporting Information.

Both variants show a similar accuracy in the correlation of the experimental data. The %RMS (%AAD) values obtained are 4.24 % (2.63 %) and 4.01 % (2.06 %) for WDA1 and WDA2, respectively. The performance of both WDA variants is comparable, however WDA2 is slightly better for surface tensions of n-alkanes. The optimized values of the parameters are  $\psi_{WDA1} = 1.3862$  and  $\psi_{WDA2} = 1.8738$ . We studied whether  $\psi$  depends on the segment number  $m_i$  and have not found strong segment number dependence. A graphical description of the adjustment results are shown in the Results and Discussion section.

#### 2.3.4 The Associative Attraction

In previous work on interfacial tensions of liquid-liquid equilibria, we adopted the LDA for the association term [64]. The density profile in such systems is rather smooth, as opposed to solid-fluid interfaces, so that we assumed the LDA to be sufficient for the association term. In the meantime we came to the conclusion that the LDA is not adequate, even for fluid interfaces. For solid-fluid interfaces, deficiencies of the LDA are amplified. We now describe the association contribution to the Helmholtz functional with the WDA functional presented by Yu and Wu [41]. An advantage of this functional is that within a DFT calculation no further weighted densities need to be calculated because it is based on scalar as well as vector-weighted densities defined by the FMT.

With some generalizations and minor modifications to the functional presented by Yu and Wu [41], based on Wertheim's TPT [10–13] and the extension of Chapman et al. [15] we obtain a functional consistent with the PCP-SAFT association contribution. The associative Helmholtz energy functional is

$$F^{\text{assoc}}\left[\rho_{k}\right] = \int f^{\text{assoc}}\left[\rho_{k}\right] \mathrm{d}\mathbf{r}$$
(2.27)

with the associative Helmholtz energy density

$$f^{\text{assoc}}[\rho_k] = kT \sum_i \frac{n_{0i}}{m_i} \xi_i \sum_{A_i}^{\{A_i\}} N_{A_i} \left( \ln \chi^{A_i}(\mathbf{r}) - \frac{\chi^{A_i}(\mathbf{r})}{2} + \frac{1}{2} \right)$$
(2.28)

where the outer sum runs over all components and the inner sum runs over all types of association sites  $A_i$  of species *i*. Further,  $N_{A_i}$  is the number of association sites of type  $A_i$ and  $\chi^{A_i}(\mathbf{r})$  is the locally defined monomer-fraction of type  $A_i$  (i.e. fraction of nonbonded association sites), calculated as

$$\chi^{A_i}(\mathbf{r}) = \left[1 + \sum_j \frac{n_{0j}}{m_j} \xi_j \sum_{B_j} N_{B_j} \chi^{B_j}(\mathbf{r}) \Delta^{A_i B_j}(\mathbf{r})\right]^{-1}$$
(2.29)

with  $\Delta^{A_i B_j}(\mathbf{r})$  as the locally defined association strength between association sites  $A_i$  and  $B_j$ 

$$\Delta^{A_i B_j}(\mathbf{r}) = \sigma_{ij}^3 \kappa^{A_i B_j} \left[ \exp\left(\frac{\varepsilon^{A_i B_j}}{kT}\right) - 1 \right] g_{ij}^{\rm hs}(n_\alpha)$$
(2.30)

with  $\kappa^{A_iB_j}$  and  $\varepsilon^{A_iB_j}$  as the adjustable association parameters. The radial distribution function of hard-spheres is given as

$$g_{ij}^{\rm hs}(n_{\alpha}) = \frac{1}{1-n_3} + d_{ij}\frac{n_2\xi}{2(1-n_3)^2} + d_{ij}^2\frac{n_2^2\xi}{18(1-n_3)^3}$$
(2.31)

The factors  $\xi$  and  $\xi_i$  as well as the component-wise weighted densities  $n_{\alpha i}$  are defined according to Yu and Wu [41]

$$\xi = 1 - \frac{\mathbf{n}_{V2} \cdot \mathbf{n}_{V2}}{n_2^2} \tag{2.32}$$

$$\xi_i = 1 - \frac{\mathbf{n}_{V2i} \cdot \mathbf{n}_{V2i}}{n_{2i}^2} \tag{2.33}$$

$$n_{\alpha i} = n_{\alpha i}(\mathbf{r}) = m_i \int \rho_i(\mathbf{r}') w_{\alpha i}^{\text{FMT}}(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \quad \text{with} \ \alpha = \{0, 2, 3, V2\}$$
(2.34)

where  $w_{\alpha i}^{\text{FMT}}$  are weights defined by the FMT [38]. The overall weighted densities  $n_{\alpha} = \sum_{i} n_{\alpha i}$  are the same weighted densities used in the FMT functionals [38–40, 86].

#### 2.3.5 The Multipolar Attraction

Multipolar interactions between molecules are taken into account using the weighted densities defined above, with

$$\frac{F^{\mathrm{mp}}\left[\rho_{k}\right]}{kT} = \int \bar{\rho}(\mathbf{r})\tilde{a}^{\mathrm{mp}}\left(\bar{\rho}_{k}(\mathbf{r})\right) \mathrm{d}\mathbf{r}$$
(2.35)

where  $\tilde{a}^{mp}$  is the sum of the bulk phase dipole-dipole [76], dipole-quadrupole [75], and quadrupole-quadrupole [77] contribution.

## 2.4 Results and Discussion

The objective of this work is to propose a simple Helmholtz energy functional that can be used to predict interfacial tensions as well as density profiles of fluids in confined systems. In this section, the two variants of the dispersion contribution presented above are compared to experimental data and to results from molecular simulations. A model constant  $\psi$ , adjusted to vapor-liquid surface tensions of n-alkanes, has gone into both variants of the Helmholtz energy functional. First, we compare results of both variants to the density profile for liquid (adsorbed) film on a solid wall obtained by MC simulations. This case allows us to discriminate clearly between both models and choose the superior variant. Subsequently, we demonstrate the transferability of the so-obtained functional to confined systems. Finally, we assess predictions of the models for interfacial tensions of pure components and mixtures, in comparison to experimental data. Also a comparison between the suggested functional of this work,  $F^{disp}$  to results from our earlier work [62–64] is provided. We note, the focus of this work is on evaluating the dispersion functional. Substances with strong associative (hydrogen bonding) or polar interactions are not considered.

We use experimental data for the validation of interfacial tensions. Experimental data for assessing the theory for confined systems would also be desirable. Experimental adsorption isotherms, for example, should be appropriate in this context. A meaningful comparison between DFT and experimental adsorption isotherm data, however, necessitates detailed knowledge of the solid surface. The solid would need to be characterized in the geometrical shape of pores, the pore size distribution, and the (effective) solidfluid interaction [87]. This detail is not available for typical porous materials and we thus compare density profiles from DFT calculations with density profiles obtained from MC simulations, where we have full control over pore-shape and solid-fluid interaction potentials.

#### 2.4.1 Liquid Film on Solid Wall

As a first application of the DFT with the WDA dispersion functional to solid-fluid interfaces we regard a pure component density profile of a Lennard-Jones fluid with the parameters  $\sigma_{jj}$  and  $\varepsilon_{jj}$ . We performed a MC simulation in the grand-canonical ensemble to obtain the density profile. The (9,3)-potential, eq. (2.10), is used as an external potential with the parameters  $\sigma_{js} = \sigma_{jj}$  and  $\varepsilon_{js} = 8 \varepsilon_{jj}$ . A relatively high value for  $\varepsilon_{js}$  leads to strong attractive interaction between solid and fluid molecules. Although the behavior of a fluid component next to a single wall is of interest, a MC simulation within a slit-shaped pore geometry, eq. (2.12), is carried out. The distance between both pore walls is chosen sufficient far,  $H = 35 \sigma_{jj}$ , in order to prevent interactions between particles of the liquid film of one side of the simulation box with particles of the film of the other side of the box. The system size is chosen to be  $30 \sigma_{jj}$  in spatial direction parallel to the solid wall. The cutoff radius is set to the high value of  $r_c = 15 \sigma_{jj}$ , avoiding the need for cutoff corrections. This cutoff value does not limit interactions in the z-direction, normal to the interface, so that the cutoff is active in two of the three dimensions of the system. The dimensionless temperature is set to  $T^* = T \frac{k}{\varepsilon_{jj}} = 0.9$ , and for the excess chemical potential we defined  $\mu_j^* = \mu_j/kT - 3\ln(\Lambda_j/\Lambda) = -4.45$ . The number of particles in the system varies during the simulation between 7000 and 8700. For sampling the single-particle density profile  $\rho(z)$ , we divided the normal coordinate in 1750 slabs of equal width  $\Delta z$ .

The PCP-SAFT model is not a true Lennard-Jones equation of state. The properties of a Lennard-Jones fluid are in practice, however, described very well. A comparison between PC-SAFT and the LJ EoS presented by Johnson et al. [88] with  $0.5 T_c < T^* < 0.9 T_c$ yields deviations of 1.20% and 2.65% in vapor pressure and liquid density, respectively. We thereby use the PC-SAFT parameters as Lennard-Jones parameters, with  $m_i = 1$ . DFT calculations are performed for both variants of the Helmholtz energy functional for the dispersion contribution.



Figure 2.1: Density profile of a Lennard-Jones fluid forming a liquid film on a planar wall at  $T^* = 0.9$  and  $\mu_j^* = -4.45$  (corresponding PC-SAFT bulk phase pressure:  $p^* = 0.01155$ ). Comparison between the DFT calculations of the variants WDA1 and WDA2 and results obtained by MC simulations.

The resulting density profiles of the liquid film are shown in Fig. 2.1. The MC simulation gives a liquid film with a film thickness of approximately  $7\sigma_{jj}$ . A comparison between the WDA1 and the WDA2 variant shows a clear advantage of the WDA1 model. In contrast to WDA2, the WDA1 variant predicts the  $z^*$  position of density peaks and valleys in good agreement to the simulation data. The WDA1 model also captures the amplitude of density oscillations much better than the WDA2 model. Furthermore, the WDA2 variant does not provide a smooth description of the density undulations along the  $z^*$  coordinate, as can be seen in the range  $z^* = 2.7 - 3.3$ . Both models somewhat overestimate the density profile in the range  $z^* = 5 - 8$ . The overall agreement of the WDA1 model to data from MC simulations, however, is very good.

We chose the WDA1 model as our preferred model of the dispersion contribution, due to the better behavior in Fig. 2.1. We find the adsorbed (liquid-like) film regarded in Fig. 2.1 discriminates between different Helmholtz energy functionals in a very sensitive manner, whereas interfacial tensions of pure components were not allowing a meaningful discrimination of models (noting that a model constant  $\psi$  was adjusted to pure component interfacial tensions). The WDA1 model will henceforth be referred to as DFT model.

#### 2.4.2 Confined Systems

To demonstrate the transferability of the defined functional to confined systems we show density profiles for a mixture of two Lennard-Jonesian components. The density profiles of grand-canonical MC simulations are taken from Sokołowski and Fischer [89]. The components are referred to as argon (a) and krypton (k) and defined by the parameters  $\sigma_{aa} = 3.405 \text{ Å}, \ \varepsilon_{aa}/k = 119.8 \text{ K}$  and  $\sigma_{kk} = 3.630 \text{ Å}, \ \varepsilon_{kk}/k = 163.1 \text{ K}$ , respectively. The external potential used by Sokołowski and Fischer [89] is identical to the potential in eq. (2.10), with solid-fluid parameters  $\sigma_{as} = 0.5621\sigma_a, \ \varepsilon_{as} = 23.998\varepsilon_a, \ \sigma_{bs} = 0.588\sigma_a, \ and \ \varepsilon_{bs} = 31.630\varepsilon_{aa}$ . The slit-shaped geometry of the pore in this system is defined by a wall distance of  $H = 5\sigma_{aa}$ .

To obtain DFT density profiles of the binary mixture, two PC-SAFT components are defined by  $m_{\rm a} = 1$ ,  $\sigma_{\rm aa}$ ,  $\varepsilon_{\rm aa}$  and  $m_{\rm k} = 1$ ,  $\sigma_{\rm kk}$ ,  $\varepsilon_{\rm kk}$ , respectively. The DFT calculation was performed using the same external potential and wall distance [89]. The required chemical potentials  $\mu_{\rm a}^{\rm res,b}$  and  $\mu_{\rm k}^{\rm res,b}$  are obtained by PC-SAFT EoS using the given [89] dimensionless bulk (index b) phase temperature  $T^{\rm b} = \frac{\varepsilon_{\rm aa}}{k} T^{\rm b,*}$ , density  $\rho^{\rm b} = \rho^{\rm b,*} \sigma_{\rm aa}^{-3}$  and mole fraction of argon  $x_{\rm a}^{\rm b}$ .

DFT density profiles and results from Sokołowski and Fischer [89] are shown for two different bulk phase conditions in Fig. 2.2 and Fig. 2.3. Only the left side of the profile is presented due to symmetry. In Fig. 2.2, the adsorbed amount in the pore is significantly higher for krypton than for argon. The reason is that the krypton-solid attractive interaction is stronger and the (virtually) connected bulk phase consists of more krypton. In contrast, the system in Fig. 2.3 is defined by a bulk phase with argon as dominant component which leads to a higher adsorption of argon relative to krypton.

The DFT density profiles are in very good agreement with the MC simulation data for both components and both bulk phase conditions. Density peaks and valleys are predicted accurately. These purely predictive results show that the model constant  $\psi$  obtained from experimental n-alkane surface tensions is transferable.

We now proceed to analyze nonmonoatomic (molecular) fluids. We consider ethane using the Transferable Anisotropic Mie (TAMie) [90] force field. The TAMie model rep-



Figure 2.2: Density profile of a Lennard-Jones binary mixture in a slit-shaped pore at  $T^* = 2.0$ ,  $\rho^{b,*} = 0.444$  and  $x_a^b = 0.262$ . Comparison between the DFT calculations (full curve) and results obtained by MC simulations [89] (symbols).



Figure 2.3: Density profile of a Lennard-Jones binary mixture in a slit-shaped pore at  $T^* = 2.0$ ,  $\rho^{b,*} = 0.103$  and  $x_a^b = 0.891$ . Comparison between the DFT calculations (full curve) and results obtained by MC simulations [89] (symbols).

resents fluid phase properties, in particular vapor-liquid equilibria, of ethane in good agreement with experimental data. Ethane is in this force field regarded as two Mieinteraction sites, representing the  $CH_3$ -groups a fixed bond-length apart. Such a model can also be referred to as 'fused dimer' model. The molecular model of the PCP-SAFT EoS, on the other hand, is well-defined for integer values of segment number  $m_i$ . For noninteger values  $1 < m_i < 2$ , the equation of state is in excellent quantitative agreement to a fused dimer model [75]. A geometric interpretation for cases  $1 < m_i < 2$ , however, can not be given and we can therefore not expect DFT to represent accurately the density profile ( $\rho(\mathbf{r})$ ) of the fused dimer model. We take molecular simulations for the TAMie model as a reference and compare results of the DFT approach to evaluate the quality of the dispersion functional.

We regard ethane in a slit-shaped pore. In the MC simulation, the pore is modeled by the external potential  $V_{js}^{\text{ext,MC}}$  using the 10,4,3 potential. The interaction parameters  $\sigma_{js}$  and  $\varepsilon_{js}$  in eq. (2.11) are calculated with the Berthelot-Lorentz combining rules using the graphite solid phase parameters and the TAMie force field parameters of the ethane methyl bead:  $\sigma_{jj} = 3.6463$  Å and  $\varepsilon_{jj}/k = 130.78$  K. The MC simulations are performed in grand-canonical ensemble with a box size of 100 Å in x and y direction and a wall separation distance of H = 36 Å in z direction. To omit cutoff corrections, the cutoff radius is defined to  $r_c = 50$  Å. The number of particles in the simulation box varies during the simulation between 2980 and 3120. A number of 500  $\Delta z$  slabs are used to sample the density profile.

In the MC simulations, the solid wall acts as an external potential on each interactionsite of ethane molecules. Within the DFT and PCP-SAFT EoS framework, the external potential describes the interaction between the solid wall and the entire molecule. The external potential used in the DFT calculations has to be multiplied by the number of segments, which leads to  $V_{js}^{\text{ext,DFT}} = 2V_{js}^{\text{ext,MC}}$  in the case of ethane. The ethane pure component parameters for the DFT calculation are taken from Gross and Sadowski [23].

The density profiles for both calculations are depicted in Fig. 2.4 for the left side of the symmetric system. The figure shows segment density profiles, i.e. the probability of finding a CH<sub>3</sub>-interaction site of ethane within a  $\Delta z$  slab. The MC simulation gives density profiles of these interaction sites due to the direct sampling of bead positions. In contrast, the DFT calculation initially provides molecular density profiles. To obtain the segment density profile of the DFT calculation, the molecular density profile is multiplied with the number of segments, i.e. factor 2.

It is obvious that the profiles do not coincide. The main reason is the significant difference between the molecular models mentioned above. The 'fused dimer' model of the TAMie force field leads to the small peak at position 5.1 Å. At this location methyl beads are sampled that are bound to a methyl bead located at position 3.5 Å, which is the tallest peak. The second small peak is due to ethane molecules oriented perpendicular to the solid wall. For the PCP-SAFT EoS, the segments of an ethane molecule oriented perpendicular to the solid wall give a contribution to the density profile at position of the first peak at 3.5 Å and the second peak at 7 Å, due to the tangentially bonding of segments. Therefore, finding a methyl bead at position 7 Å is more probable for the DFT



Figure 2.4: Density profile of methyl segments of ethane in a slit-shaped pore at T = 250 K and  $\mu_j^* = \mu_j/kT - 3\ln(\Lambda_j/Å) = -8.15$  (corresponding PC-SAFT bulk phase pressure: 11.61 bar). Comparison between the DFT calculation and results obtained by the MC simulation using the TAMie [90] force field.

calculation based on the PCP-SAFT EoS.

The different molecular models do not allow for same density profiles. Nonetheless, the presented functional gives a very good prediction of the adsorbed amount within the slit-shaped pore. The integration over the pore space leads to an averaged segment density

$$\rho_{\rm av} = \frac{1}{H} \int_0^H \rho(z) \mathrm{d}z \tag{2.36}$$

with values of  $\rho_{\rm av}^{\rm MC} = 0.01702 \,\text{\AA}^{-3}$  and  $\rho_{\rm av}^{\rm DFT} = 0.01778 \,\text{\AA}^{-3}$ , respectively. The result can in particular be appreciated when realizing that the corresponding (equilibrium) bulk phase at the same temperature and chemical potential is a vapor phase with a much lower bulk segment density of  $\rho^{\rm b} = 0.00081 \,\text{\AA}^{-3}$ . The strong attractive interaction between fluid and solid phase leads to the formation of a liquid-like phase within the slit-shaped pore.

Repeating the DFT calculation for various chemical potentials  $\mu_j^*$  leads to the adsorption isotherm depicted in Fig. 2.5. In a certain range of  $\mu_j^*$ , the calculated DFT density profile depends on the defined starting profile, leading to an apparent hysteresis phenomenon. We investigated the system similar to the procedure presented by Kierlik et al. [91] to obtain three different curves: By mimicking a pore filling process by increasing the chemical potential starting from a small value leads to results of the adsorption path. The reverse way gives the desorption path curve. The actual thermodynamic equilibrium for each  $\mu_j^*$  corresponds to the minimal grand potential. The results show that the DFT prediction is in very good agreement with MC data over the entire region of chemical potential.



Figure 2.5: Adsorption isotherm of methyl segments of ethane in a slit-shaped pore at T = 250 K. Comparison between MC simulation (symbols) and DFT results: adsorption path (dotted curve), desorption path (dashed curve) and thermodynamic equilibrium (continuous curve).

## 2.4.3 Interfacial Tensions

In this section we compare interfacial tensions as calculated from DFT with experimental values. In the previous section we found the WDA1 variant of the dispersion contribution to the Helmholtz energy functional to be superior and thus use this variant for all calculations henceforth. The model parameter  $\psi$  was adjusted to n-alkanes and is subsequently treated as a universal model constant. Calculated surface tensions of most of the n-alkanes, that were considered in identifying the  $\psi$  value, are shown in Fig. 2.6. The calculated surface tensions correlate the experimental data very accurately over a wide temperature range. We summarize the pure component parameters in the Supporting Information.

It is expected that the n-alkanes are well described by the proposed Helmholtz energy functional, because a model parameter was adjusted to this class of substances. It is now interesting to assess how other substances are predicted. We consider one nonpolar and three polar components: 2,3-dimethyl pentane, dimethyl ether, diethyl ether, and benzene in Fig. 2.7. Dipole-dipole interactions are taken into account for the ether components and quadrupole-quadrupole interactions for benzene. The PCP-SAFT EoS overestimates the critical point somewhat. This leads to some deviations when approaching the critical



Figure 2.6: Surface tensions of several n-alkanes. Comparison between DFT calculations (full curve) and experimental data [92] (symbols).



Figure 2.7: Surface tensions of various pure components. Comparison between DFT calculations (full curve) and experimental data (symbols) of dimethyl ether [93, 94], diethyl ether [95–97], 2,3-dimethylpentane [92] and benzene [98].

temperature, as seen for dimethylether and benzene in Fig. 2.7. Overall, however, all four components are predicted in very good agreement to experimental data over the range of temperature, in particular considering that no parameters were adjusted to interfacial properties for these substances.

Further, we compare interfacial tensions of binary mixtures that were presented in earlier work [63, 64]. We first consider vapor-liquid systems and start with a mixture of small, almost spherical substances. The surface tension of a binary mixture of carbon monoxide (CO) and methane at vapor-liquid equilibrium conditions, at T = 90.67 K, is presented in Fig. 2.8. The binary interaction parameter  $k_{ij} = 0.018$  was adjusted



Figure 2.8: VLE surface tensions over the liquid-phase mole fraction  $x_{\rm CO}$  of the COmethane mixture at T = 90.67 K. Comparison between DFT calculations (full curve) and experimental data [99] (symbols).

to experimental VLE data [63]. Small deviations of calculated surface tensions from experimental data can be observed for both pure component boundaries and for the mixture. Nonetheless, we assess the agreement of the DFT-predictions with experimental data as good because no parameter is adjusted to interfacial properties. Corresponding density profiles of the CO-CH<sub>4</sub> system are provided as Supporting Information.

Carbon monoxide is a mildly dipolar substance. Tetrahydrofuran (THF) is significantly more polar and we consider the mixture of THF with n-hexane. Surface tensions of this binary mixture are shown Fig. 2.9, where the binary interaction parameter  $k_{ij} = 0.012$  was taken from ref. [63]. The surface tensions are in very good agreement over the entire range of THF composition. The results suggest the Helmholtz energy functional is suited for predicting the interfacial properties of polar mixtures.

The surface tension of n-hexane - n-dodecane, as a binary mixture of nonspherical, asymmetric species, is shown in Fig. 2.10. The binary interaction parameter between n-hexane and n-dodecane was set to zero. This predictive calculation leads to a good description of the experimental values.

Predicting the interfacial properties of liquid-liquid systems is particularly demanding. Analogous to Klink et al. [64], we apply the presented WDA dispersion functional to interfacial tensions of LLE for binary mixtures of ethylene glycol with various solvents at



Figure 2.9: VLE surface tensions over the liquid-phase mole fraction  $x_{\text{THF}}$  of the THFn-hexane mixture at T = 298.15 K. Comparison between DFT calculations (full curve) and experimental data [100] (symbols).



Figure 2.10: VLE surface tensions over the liquid-phase mole fraction  $x_{n-hexane}$  of the n-hexane-n-dodecane mixture at T = 298.15 K and T = 313.15 K. Comparison between DFT calculations (full curve) and experimental data [101] (symbols).

T = 293.15 K and p = 1.013 bar. Ethylene glycol is modeled as a dipolar and associating substance. We use the same binary interaction parameters  $k_{ij}$  and  $l_{ij}$  as proposed by Klink et al. [64] to describe the LLE systems. According to Tang and Gross [102], the  $l_{ij}$  parameter can be included via an expansion of the first order term of the dispersion contribution of the PCP-SAFT EoS. This expansion is used to calculate the LLE interfacial tensions shown in Fig. 2.11. The agreement of the predicted interfacial tensions to



Figure 2.11: LLE interfacial tensions of ethylene glycol binary mixtures at T = 293.15 K and p = 1.013 bar. Comparison between DFT calculations and experimental data [103].

experimental values is very satisfying considering that no parameter has been adjusted to interfacial properties. The results indicate that the suggested Helmholtz energy functional is able to predict rather complex binary mixtures, with significant associative and dipole-dipole interactions.

In Fig. 2.10 we have shown a comparison between DFT-results obtained with the here proposed Helmholtz energy functional and the functional proposed by members of our group earlier (1PT). The results are very similar. That similarity also holds for most other pure component and mixture interfacial tensions presented in this work. The corresponding surface tension to this density profiles are 19.19 mN/m and 19.03 mN/m for the DFT-1PT and the DFT-WDA1 approach, respectively. The suggested dispersion contribution  $F^{\text{disp}}$  performs comparable to the dispersion contribution  $F^{1PT}$  of the earlier works [62–64] in terms of interfacial tensions, however, with a much simpler Helmholtz energy functional. The simplicity of the Helmholtz energy functional is advantageous in three aspects: The functional is easier to implement and may facilitate the application of DFT approaches to various applications. Second, the calculation efficiency is much higher, with a typical calculation time of 4 seconds for the new functional, versus 300 seconds for the previous functional on a standard desktop computer. Lastly, the newly proposed functional is suitable for solid-fluid interfaces and the confined geometries that result from the solid structures.

## 2.5 Conclusion

Two variants of a dispersion contribution to the Helmholtz energy functional based on a WDA were presented. The resulting DFT model is applicable to confined systems and to fluid-liquid interfaces of mixtures. The two variants were compared and the superior variant was chosen. The local density of thin liquid adsorbed layer of a few molecular diameters thickness was particularly meaningful to discriminate between competing Helmholtz energy functionals. Calculated density profiles of fluids in slit-shaped pores show good agreement with density profiles obtained by MC simulations. Accurate results are found for the calculation of interfacial tensions. Pure components and mixtures with vapor-liquid and liquid-liquid interfaces were studied.

## **Appendix A: Functional Derivatives**

Eq. (2.4) requires the functional derivative of the residual Helmholtz energy for a multicomponent system. In this Appendix the derivatives of all considered Helmholtz energy contributions according to eq. (2.13) are presented for cylindrical coordinate systems where the density profiles vary only along the z-coordinate.

## 1. The Hard-Sphere Contribution

The derivative of the FMT functional [39, 40] is given by

$$\frac{\delta F^{\rm hs}\left[\rho_k\right]/kT}{\delta \rho_j(z^*)} = m_j \int_{-d_j/2}^{d_j/2} \left(\frac{1}{d_j} \frac{\partial \Phi}{\partial n_0} + \frac{1}{2} \frac{\partial \Phi}{\partial n_1} + \pi d_j \frac{\partial \Phi}{\partial n_2} + \pi \frac{\partial \Phi}{\partial n_3} \left[ \left(\frac{d_j}{2}\right)^2 - \hat{z}^2 \right] \right) d\hat{z}$$

$$+ \mathbf{e}_z m_j \int_{-d_j/2}^{d_j/2} \left(\frac{1}{d_j} \frac{\partial \Phi}{\partial \mathbf{n}_1} + 2\pi \frac{\partial \Phi}{\partial \mathbf{n}_2}\right) \hat{z} d\hat{z}$$

$$(2.37)$$

where  $d_j$  the temperature dependent segment diameter and  $\mathbf{e}_z$  the unit vector that points in z-direction.  $n_{\alpha}$  are the scalar and  $\mathbf{n}_{\alpha}$  are the vector weighted densities and calculate as

$$n_0(z) = \sum_{i}^{N_c} m_i \frac{1}{d_i} \int_{-d_i/2}^{d_i/2} \rho_i(z+\hat{z}) d\hat{z}$$
(2.38)

$$n_1(z) = \frac{1}{2} \sum_{i}^{N_c} m_i \int_{-d_i/2}^{d_i/2} \rho_i(z+\hat{z}) d\hat{z}$$
(2.39)

$$n_2(z) = \pi \sum_{i}^{N_c} m_i d_i \int_{-d_i/2}^{d_i/2} \rho_i(z+\hat{z}) \mathrm{d}\hat{z}$$
(2.40)

$$n_3(z) = \pi \sum_{i}^{N_c} m_i \int_{-d_i/2}^{d_i/2} \rho_i(z+\hat{z}) \left[ \left(\frac{d_i}{2}\right)^2 - \hat{z}^2 \right] d\hat{z}$$
(2.41)

$$\mathbf{n}_{1}(z) = -\mathbf{e}_{z} \sum_{i}^{N_{c}} m_{i} \frac{1}{d_{i}} \int_{-d_{i}/2}^{d_{i}/2} \rho_{i}(z+\hat{z})\hat{z}d\hat{z}$$
(2.42)

$$\mathbf{n}_{2}(z) = -2\pi \mathbf{e}_{z} \sum_{i}^{N_{c}} m_{i} \int_{-d_{i}/2}^{d_{i}/2} \rho_{i}(z+\hat{z})\hat{z}d\hat{z}$$
(2.43)

Note that the negative sign in eqs. (2.42) and (2.43) is required and that we erroneously omitted the sign in the corresponding equation in our previous work [62]. The partial derivation of the Helmholtz energy functional  $\Phi$  with respect to all  $n_{\alpha}$  and  $\mathbf{n}_{\alpha}$  provides

$$\frac{\partial \Phi}{\partial n_0} = -\ln\left(1 - n_3\right) \tag{2.44}$$

$$\frac{\partial \Phi}{\partial n_1} = \frac{n_2}{1 - n_3} \tag{2.45}$$

$$\frac{\partial \Phi}{\partial n_2} = \frac{n_1}{1 - n_3} + 3\left(n_2^2 - \mathbf{n}_2 \cdot \mathbf{n}_2\right) \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2}$$
(2.46)

$$\frac{\partial \Phi}{\partial n_3} = \frac{n_0}{1 - n_3} + \frac{n_1 n_2 - \mathbf{n}_1 \cdot \mathbf{n}_2}{(1 - n_3)^2} - \left(n_2^3 - 3n_2 \mathbf{n}_2 \cdot \mathbf{n}_2\right) \frac{n_3 \left(n_3^2 - 5n_3 + 2\right) + 2(1 - n_3)^3 \ln(1 - n_3)}{36\pi n_3^3 (1 - n_3)^3} \qquad (2.47)$$

$$\frac{\partial \Phi}{\partial \mathbf{n}_1} = -\frac{\mathbf{n}_2}{1 - n_3} \tag{2.48}$$

$$\frac{\partial \Phi}{\partial \mathbf{n}_2} = -\frac{\mathbf{n}_1}{1-n_3} - n_2 \mathbf{n}_2 \frac{n_3 + (1-n_3)^2 \ln(1-n_3)}{6\pi n_3^2 (1-n_3)^2}$$
(2.49)

## 2. The Chain Contribution

The functional derivative of the chain contribution is

$$\frac{\delta F^{\rm hc}\left[\rho_k\right]/kT}{\delta \rho_j(z^*)} = -\left(m_j - 1\right) \left( \ln \frac{y_{jj}^{\rm dd}(\bar{\rho}_k^{\rm hc}(z^*))\lambda_j(z^*)}{\rho_j(z^*)} - 1 \right)$$
(2.50)

$$-\frac{3}{4d_j^3} \sum_i (m_i - 1) \int_{-d_j}^{d_j} \rho_i(z^* + \hat{z}) \frac{\partial \ln y_{ii}^{\rm dd}}{\partial \bar{\rho}_j^{\rm hc}(z^* + \hat{z})} \left[ d_j^2 - \hat{z}^2 \right] d\hat{z} \qquad (2.51)$$

$$-\frac{1}{2d_j}(m_j - 1) \int_{-d_j}^{d_j} \frac{\rho_j(z^* + \hat{z})}{\lambda_j(z^* + \hat{z})} \mathrm{d}\hat{z}$$
(2.52)

where  $\lambda_i$  and  $\bar{\rho}_i^{\rm hc}$  are weighted densities of the chain contribution

$$\lambda_i(z) = \frac{1}{2d_i} \int_{-d_i}^{d_i} \rho_i(z+\hat{z}) \mathrm{d}\hat{z}$$
 (2.53)

$$\bar{\rho}_i^{\rm hc}(z) = \frac{3}{4d_i^3} \int_{-d_i}^{d_i} \rho_i(z+\hat{z}) \left[ d_i^2 - \hat{z}^2 \right] \mathrm{d}\hat{z}$$
(2.54)

## 3. The Contribution of Dispersive Attraction

The functional derivative of variant 1 reads

$$\frac{\delta F^{\text{disp},1}\left[\rho_{k}\right]/kT}{\delta\rho_{j}(z^{*})} = \frac{3}{4\psi_{1}^{3}d_{j}^{3}} \int_{-\psi_{1}d_{j}}^{\psi_{1}d_{j}} \left.\frac{\partial\bar{\rho}\tilde{a}^{\text{disp}}}{\partial\bar{\rho}_{j}}\right|_{z^{*}+\hat{z}} \left[\psi_{1}^{2}d_{j}^{2}-\hat{z}^{2}\right] \mathrm{d}\hat{z}$$
(2.55)

and variant 2

$$\frac{\delta F^{\text{disp},2}\left[\rho_{k}\right]/kT}{\delta\rho_{j}(z^{*})} = \tilde{a}^{\text{disp}}\left(\bar{\rho}_{k}(z^{*})\right) + \frac{3}{4\psi_{2}^{3}d_{j}^{3}}\int_{-\psi_{2}d_{j}}^{\psi_{2}d_{j}}\rho(z^{*}+\hat{z})\left.\frac{\partial\tilde{a}^{\text{disp}}}{\partial\bar{\rho}_{j}}\right|_{z^{*}+\hat{z}}\left[\psi_{2}^{2}d_{j}^{2}-\hat{z}^{2}\right]\mathrm{d}\hat{z}$$
(2.56)

Note that the weighted density depends on the value of the universal parameter  $\psi$ 

$$\bar{\rho}_i(z) = \frac{3}{4\psi^3 d_i^3} \int_{-\psi d_i}^{\psi d_i} \rho_i(z+\hat{z}) \left[\psi^2 d_i^2 - \hat{z}^2\right] d\hat{z}$$
(2.57)

## 4. The Multipolar Attraction

The functional derivative of the multipolar term uses the weighted density of eq. (2.57)

$$\frac{\delta F^{\rm mp}\left[\rho_k\right]/kT}{\delta\rho_j(z^*)} = \tilde{a}^{\rm mp}\left(\bar{\rho}_k(z^*)\right) + \frac{3}{4\psi^3 d_j^3} \int_{-\psi d_j}^{\psi d_j} \rho(z^* + \hat{z}) \left.\frac{\partial \tilde{a}^{\rm mp}}{\partial\bar{\rho}_j}\right|_{z^* + \hat{z}} \left[\psi^2 d_j^2 - \hat{z}^2\right] d\hat{z} \quad (2.58)$$

## Appendix B: Comparison with Shen et al.

The structure of the dispersion functional presented by Shen et al. [67] is similar to the WDA2 variant. Fore pure components, the functional of Shen et al. coincides with WDA2 for  $\psi_{WDA2} = 1.5$ . Fig. 2.12 compares the WDA1 and the Shen et al. functional applied to the adsorbed liquid-like film presented in Fig. 2.1 of the main text. The WDA1 functional proposed above is in better agreement to the results from molecular simulation data. We note, however, that both functionals showed rather small differences for many other systems.



Figure 2.12: Density profile of a Lennard-Jones fluid forming a liquid film on a planar wall at  $T^* = 0.9$  and  $\mu_i^* = -4.45$ .

## Appendix C: Derivation of the Weighted Density Formalism

We show a derivation of the weighted density formalism for the Helmholtz energy functional, similar to the work of Curtin and Ashcroft [83]. We recapitulate this derivation to show the formalism for multi component systems and to emphasize important assumptions required along the development. We start with an exact Helmholtz energy functional for an inhomogeneous system and assess what assumptions are required to bring a WDA functional into agreement with the exact functional.

We divide the intermolecular pair potential  $\phi_{ij}$  between molecule *i* and *j* into a reference part  $\phi_{ij}^{\text{ref}}$  and a perturbation contribution  $\phi_{ij}^{\text{PT}}$ , as

$$\phi_{\lambda,ij}(|\mathbf{r}_1 - \mathbf{r}_2|) = \phi_{ij}^{\text{ref}}(|\mathbf{r}_1 - \mathbf{r}_2|) + \lambda \phi_{ij}^{\text{PT}}(|\mathbf{r}_1 - \mathbf{r}_2|)$$
(2.59)

where the coupling parameter  $\lambda$  is introduced to allow a smooth transition between the reference fluid ( $\lambda = 0$ ) and the target fluid, with  $\phi_{ij} = \phi_{\lambda=1,ij}$  for  $\lambda = 1$ . Here, we regard  $\mathbf{r}_1$  as generalized coordinates for molecules of type *i*, detailing the position, orientation, and conformation. For simplicity and without considerable loss of detail, however, we can consider simple spherically symmetric substances such as argon or spherical segments of a chain molecule. An exact expression for the perturbation part of the Helmholtz

energy [71] (of a multi component inhomogeneous system) is

$$\frac{F^{\mathrm{PT}}\left[\rho_{k}\right]}{kT} = \frac{1}{2} \sum_{i} \sum_{j} \int \int \frac{\phi_{ij}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{2}|)}{kT} \int_{0}^{1} \rho_{\lambda,ij}^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{2}) \mathrm{d}\lambda \mathrm{d}\mathbf{r}_{2} \mathrm{d}\mathbf{r}_{1}$$
(2.60)

where  $\rho_{\lambda,ij}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$  is the two-body density of two molecules defined by the intermediate potential  $\phi_{\lambda,ij}(|\mathbf{r}_1 - \mathbf{r}_2|)$ . The intermolecular two-body density  $\rho_{\lambda,ij}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$  is related to the pair correlation function  $g_{\lambda,ij}(\mathbf{r}_1,\mathbf{r}_2)$  by

$$\rho_{\lambda,ij}^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \rho_i(\mathbf{r}_1)\rho_j(\mathbf{r}_2)g_{\lambda,ij}(\mathbf{r}_1,\mathbf{r}_2)$$
(2.61)

Inserting eq. (2.61) into eq. (2.60) and changing the sequence of summation and integration leads to

$$\frac{F^{\mathrm{PT}}\left[\rho_{k}\right]}{kT} = \frac{1}{2} \sum_{i} \int \rho_{i}(\mathbf{r}_{1}) \sum_{j} \int \rho_{j}(\mathbf{r}_{2}) \frac{\phi_{ij}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{2}|)}{kT} \int_{0}^{1} g_{\lambda,ij}(\mathbf{r}_{1}, \mathbf{r}_{2}) \mathrm{d}\lambda \mathrm{d}\mathbf{r}_{2} \mathrm{d}\mathbf{r}_{1} \qquad (2.62)$$

We realize, that  $F^{\rm PT}$  can be formulated compactly as

$$\frac{F^{\mathrm{PT}}\left[\rho_{k}\right]}{kT} = \sum_{i} \int \rho_{i}(\mathbf{r}_{1}) \tilde{a}_{i}^{\mathrm{PT}}\left[\rho_{k};\mathbf{r}_{1}\right] \mathrm{d}\mathbf{r}_{1}$$
(2.63)

by defining a reduced Helmholtz energy  $\tilde{a}_i^{\text{PT}}$ , which is itself a functional and is related to component *i* and position  $\mathbf{r}_1$ 

$$\tilde{a}_{i}^{\mathrm{PT}}\left[\rho_{k};\mathbf{r}_{1}\right] = \frac{1}{2}\sum_{j}\int\rho_{j}(\mathbf{r}_{2})\frac{\phi_{ij}^{\mathrm{PT}}(|\mathbf{r}_{1}-\mathbf{r}_{2}|)}{kT}\int_{0}^{1}g_{\lambda,ij}(\mathbf{r}_{1},\mathbf{r}_{2})\mathrm{d}\lambda\mathrm{d}\mathbf{r}_{2}$$
(2.64)

For bulk systems,  $\tilde{a}_i^{\rm PT}$  simplifies to a function

$$\tilde{a}_{i}^{\text{PT,b}}(\rho_{k}^{\text{b}}) = \frac{1}{2} \sum_{j} \rho_{j}^{\text{b}} \int \frac{\phi_{ij}^{\text{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{3}|)}{kT} \int_{0}^{1} g_{\lambda,ij}^{\text{b}}(|\mathbf{r}_{1} - \mathbf{r}_{3}|, \rho_{k}^{\text{b}}) d\lambda d\mathbf{r}_{3}$$
$$= \frac{1}{2} \sum_{j} \rho_{j}^{\text{b}} K_{ij}^{\text{b}}(\rho_{k}^{\text{b}}, T)$$
(2.65)

with the radial distribution function  $g_{\lambda,ij}^{\rm b}(r)$  as a function of the particle distance r, bulk partial densities  $\rho_k^{\rm b}$ , and temperature T. Of course, even for simple intermolecular potential functions, the radial distribution function  $g_{\lambda,ij}^{\rm b}(r)$  is not available for arbitrary values of  $\lambda$ . Note that position  $\mathbf{r}_1$  has no influence in eq. (2.65) due to the homogeneity of bulk phases. To keep the further derivation neat, we have introduced the abbreviation  $K_{ij}^{\rm b}$  and renamed the integration variable  $\mathbf{r}_2$  into  $\mathbf{r}_3$ . In what follows, we set the reduced Helmholtz energy  $\tilde{a}_i^{\text{PT,b}}$  to be equal to the full expression  $\tilde{a}_i^{\text{PT}} [\rho_k; \mathbf{r}_1]$  and deduce appropriate definitions of averaged densities, referred to as weighted densities, which capture the inhomogeneous density profile around a given position  $\mathbf{r}_1$  appropriately. For the weighted densities, we adopt the general formulation in eq. (2.15). Inserting the weighted densities into the bulk formulation of the reduced Helmholtz energy, eq. (2.65), leads to

$$\tilde{a}_{i}^{\text{PT,b}}(\bar{\rho}_{k}(\mathbf{r}_{1})) = \frac{1}{2} \sum_{j} \bar{\rho}_{j}(\mathbf{r}_{1}) K_{ij}^{\text{b}}(\bar{\rho}_{k}(\mathbf{r}_{1}), T)$$
(2.66)

where  $K_{ij}^{\rm b}$  as well as  $\bar{\rho}_j$  are related to position  $\mathbf{r}_1$ . We insert eq. (2.15), and obtain

$$\tilde{a}_{i}^{\text{PT,b}}(\bar{\rho}_{k}(\mathbf{r}_{1})) = \frac{1}{2} \sum_{j} \int \rho_{j}(\mathbf{r}_{2}) w_{j}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) d\mathbf{r}_{2} \cdot K_{ij}^{\text{b}}(\bar{\rho}_{k}(\mathbf{r}_{1}), T)$$

$$= \frac{1}{2} \sum_{j} \int \rho_{j}(\mathbf{r}_{2}) w_{j}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) K_{ij}^{\text{b}}(\bar{\rho}_{k}(\mathbf{r}_{1}), T) d\mathbf{r}_{2}$$
(2.67)

The correlation integral  $K_{ij}^{\rm b}$  is independent of  $\mathbf{r}_2$  and we moved it into the  $\mathbf{r}_2$  integral. An appropriate definition of  $w_i$  is found, when the weighted density version of the reduced Helmholtz energy, eq. (2.67), is brought to agreement with the exact form of the reduced Helmholtz energy of the inhomogeneous system, eq. (2.64), requiring  $\tilde{a}_i^{\rm PT}[\rho_k;\mathbf{r}_1] = \tilde{a}_i^{\rm PT,b}(\bar{\rho}_k(\mathbf{r}_1))$  for all considered components *i* and for the entire integration space of  $\mathbf{r}_1$ . We get

$$\frac{1}{2} \sum_{j} \int \rho_{j}(\mathbf{r}_{2}) \frac{\phi_{ij}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{2}|)}{kT} \int_{0}^{1} g_{\lambda,ij}(\mathbf{r}_{1}, \mathbf{r}_{2}) \mathrm{d}\lambda \mathrm{d}\mathbf{r}_{2}$$
$$= \frac{1}{2} \sum_{j} \int \rho_{j}(\mathbf{r}_{2}) w_{j}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) K_{ij}^{\mathrm{b}}(\bar{\rho}_{k}(\mathbf{r}_{1}), T) \mathrm{d}\mathbf{r}_{2}$$
(2.68)

and obtain the definition of  $w_i$  as

$$w_{j}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) = \frac{\phi_{ij}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) \int_{0}^{1} g_{\lambda,ij}(\mathbf{r}_{1}, \mathbf{r}_{2}) \mathrm{d}\lambda}{\int \phi_{ij}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{3}|) \int_{0}^{1} g_{\lambda,ij}^{\mathrm{b}}(|\mathbf{r}_{1} - \mathbf{r}_{3}|, \bar{\rho}_{k}(\mathbf{r}_{1})) \mathrm{d}\lambda \mathrm{d}\mathbf{r}_{3}}$$
(2.69)

We can see that the definition of a weight function is not unique for mixtures, because this equation needs to hold for every component-index *i*. Only if eq. (2.69) was satisfied for every (i, j)-pair and for all  $\mathbf{r}_1, \mathbf{r}_2$  combinations, would eq. (2.68) be exact. The assumption, that eq. (2.69) is fulfilled is known (although in a slightly different way of writing) as the one-fluid theory [104]. The equation nonetheless rationalizes the development of reasonable WDA models for the dispersion contribution of the Helmholtz energy functional. In order to have a uniquely defined starting point for developing an approximate model,

we only regard (j, j) correlations and interactions, as

$$w_{j}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) = \frac{\phi_{jj}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) \int_{0}^{1} g_{\lambda,jj}(\mathbf{r}_{1}, \mathbf{r}_{2}) \mathrm{d}\lambda}{\int \phi_{jj}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{3}|) \int_{0}^{1} g_{\lambda,jj}^{\mathrm{b}}(|\mathbf{r}_{1} - \mathbf{r}_{3}|, \bar{\rho}_{k}(\mathbf{r}_{1})) \mathrm{d}\lambda \mathrm{d}\mathbf{r}_{3}}$$
(2.70)

We further assume that the results of both integrals in eq. (2.70) are identical.

$$\int_{0}^{1} g_{\lambda,jj}^{\mathrm{b}}(|\mathbf{r}_{1} - \mathbf{r}_{3}|, \bar{\rho}_{k}(\mathbf{r}_{1})) \mathrm{d}\lambda \approx \int_{0}^{1} g_{\lambda,jj}(\mathbf{r}_{1}, \mathbf{r}_{2}) \mathrm{d}\lambda$$
(2.71)

We can make an attempt to justify this assumption. If the weight function is defined appropriately, then the Helmholtz energy as a functional of the single particle density is accurately described. The two-particle density (and thus the radial distribution function) is the functional derivative of the Helmholtz energy with respect to the pair potential. Therefore also the two-particle density is a functional of the same (appropriately defined) weighted density. If we construct a limiting case where a weight function leads to exact results, then also the two-particle density is accurately described (self-consistently) with the same appropriately defined weight function. As a consequence we conjecture: the better the weight function performs for the Helmholtz energy functional, the better the assumption, eq. (2.71), gets. Our arguments so far do not justify that a bulk phase expression for radial distribution function can be used. This aspect is discussed in more detail in the work of Schulte et al. [105].

With the two approximations given above, the weight function simplifies to

$$w_{j}(|\mathbf{r}_{1} - \mathbf{r}_{2}|) = \frac{\phi_{jj}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{2}|)}{\int \phi_{jj}^{\mathrm{PT}}(|\mathbf{r}_{1} - \mathbf{r}_{3}|)\mathrm{d}\mathbf{r}_{3}}$$
(2.72)

## Modeling of the Helmholtz Energy Using PC-SAFT EoS

In conclusion we obtain the perturbation part of the Helmholtz energy of an inhomogeneous system as

$$\frac{F^{\text{disp}}\left[\rho_{k}\right]}{kT} = \sum_{i} \int \rho_{i}(\mathbf{r}_{1})\tilde{a}_{i}^{\text{disp}}(\bar{\rho}_{k}(\mathbf{r}_{1}))\mathrm{d}\mathbf{r}_{1}$$
(2.73)

with  $\tilde{a}_i^{\text{disp}}(\bar{\rho}_k(\mathbf{r}_1))$  as the reduced Helmholtz energy of the corresponding bulk phase calculated with the weighted densities at position  $\mathbf{r}_1$ . The weighted densities  $\bar{\rho}_j(\mathbf{r}_1)$  are determined from eq. (2.15) using the weight  $w_j$  defined in eq. (2.72). At this point, we renamed  $\tilde{a}_i^{\text{PT,b}}$  into  $\tilde{a}_i^{\text{disp}}$  to illustrate, that we connect the dispersion functional to the PCP-SAFT EoS instead of performing eq. (2.66). To determine  $\tilde{a}_i^{\text{disp}}$ , we equate eq. (2.73) for bulk phases with the PCP-SAFT Helmholtz energy of the dispersion contribution  $F^{\text{disp}}/kT = N\tilde{a}^{\text{disp}}$ , where  $\tilde{a}^{\text{disp}}$  is the dispersion contribution of PCP-SAFT. This
leads to the desired relation between  $\tilde{a}_i^{\rm disp}$  and  $\tilde{a}^{\rm disp}$ 

$$\tilde{a}^{\text{disp}}(\rho_k^{\text{b}}) = \frac{V}{N} \sum_i \rho_i^{\text{b}} \tilde{a}_i^{\text{disp}}(\rho_k^{\text{b}}) = \sum_i x_i^{\text{b}} \tilde{a}_i^{\text{disp}}(\rho_k^{\text{b}})$$
(2.74)

with the bulk phase mole fraction  $x_i^{\rm b}$ . For  $\tilde{a}^{\rm disp}$  we introduce the equation described by Gross and Sadowski [23], and obtain for the component-wise additive reduced Helmholtz energy

$$\tilde{a}_{i}^{\text{disp}}(\rho_{k}^{\text{b}}) = -\pi m_{i} \sum_{j} \rho_{j}^{\text{b}} m_{j} \sigma_{ij}^{3} \frac{\varepsilon_{ij}}{kT} \left[ 2I_{1} + \frac{\varepsilon_{ij}}{kT} \bar{m} C_{1} I_{2} \right]$$
(2.75)

According to the WDA,  $\tilde{a}_i^{\text{disp}}$  must be evaluated as a function of locally defined weighted densities  $\bar{\rho}_k(\mathbf{r}_1)$  to provide a description of inhomogeneous systems

$$\tilde{a}_i^{\text{disp}}(\bar{\rho}_k(\mathbf{r}_1)) = -\pi m_i \sum_j \bar{\rho}_j(\mathbf{r}_1) m_j \sigma_{ij}^3 \frac{\varepsilon_{ij}}{kT} \left[ 2I_1(\bar{\eta}, \bar{m}) + \frac{\varepsilon_{ij}}{kT} \bar{m} C_1 I_2(\bar{\eta}, \bar{m}) \right]$$
(2.76)

The calculation of  $\bar{m}$ ,  $C_1$ , and  $\bar{\eta}$  proceeds as shown in eqs. (2.22), (2.24), and (2.25).

#### **Definition of Weight Functions**

To obtain a dispersion functional based on the PCP-SAFT EoS and the WDA, a definition of an appropriate weight  $w_j$  or, with eq. (2.72), of a perturbation part of the intermolecular potential  $\phi_{jj}^{\text{PT}}$  is required. The PCP-SAFT dispersion contribution  $\tilde{a}^{\text{disp}}$  is derived using the perturbation theory presented by Barker and Henderson [106, 107] with a hard-chain fluid as reference system. A Lennard-Jones perturbing potential has been used with model constants adjusted to pure component properties of n-alkanes [23] (with the soft repulsion only roughly approximated through a step potential [108]). Therefore, a Lennard-Jones perturbing potential  $\phi_{jj}^{\text{PT,LJ}}$  is the most obvious choice for eq. (2.72), leading to a Lennard-Jonesian weighted density  $\bar{\rho}_j^{\text{LJ}}$ . Because substantial approximations have gone into eq. (2.72), other choices are possible. A more short-ranged weight function is desirable for favorable computational efficiency. We tested the square-well (SW) potential,  $\phi_{jj}^{\text{PT,SW}}(r) = -\varepsilon_{jj}\Theta [\psi_{\text{SW}}d_{jj} - r] \Theta [r - d_{jj}]$ , with  $d_{jj}$  as the temperature-dependent effective repulsive (hard-sphere) diameter, and with  $\psi_{\text{SW}}$  as the well-width of the SWpotential. We have rewritten  $\phi_{jj}^{\text{PT,SW}}$  into a product of Heaviside functions  $\Theta$ , leading (with eq. (2.72) and (2.15)) to the SW weighted density, as

$$\bar{\rho}_{j}^{\text{SW}}(\mathbf{r}_{1}) = \frac{3}{4\pi d_{jj}^{3}(\psi_{\text{SW}}^{3} - 1)} \int \rho_{j}(\mathbf{r}_{2}) \Theta \left[\psi_{\text{SW}} d_{jj} - |\mathbf{r}_{1} - \mathbf{r}_{2}|\right] \Theta \left[|\mathbf{r}_{1} - \mathbf{r}_{2}| - d_{jj}\right] d\mathbf{r}_{2} \quad (2.77)$$

Eq. (2.77) states that  $\bar{\rho}_{j}^{\text{SW}}(\mathbf{r}_{1})$  is evaluated by an averaging of uniformly weighted local densities within a spherical shell, where the shell is defined by the radii  $d_{jj}$  and  $\psi_{\text{SW}} \cdot d_{jj}$ 

and its center is at position  $\mathbf{r}_1$ .

An even simpler definition of the weighted density, namely a density-averaging in a sphere of diameter  $\psi$  around a considered position is obtained with the Heaviside weight, eq. (2.16), was used in the main text of this work.

#### Remarks

The development in this Appendix led to two additional dispersion functionals, beyond the two variants that were compared in the main text, i.e. the Helmholtz energy according to eq. (2.73) evaluated with the weighted densities  $\bar{\rho}_k^{SW}$  and  $\bar{\rho}_k^{LJ}$ , respectively. We adjusted the universal parameter  $\psi_{SW}$  of the SW approach to the surface tension of pure n-alkane, just as described above for the WDA1 and WDA2 approaches. The LJ approach has no adjustable parameter. Applying all functionals to confined systems, however, showed that the variants WDA1 and WDA2 are clearly superior to the SW and the LJ approaches, so that no further examination of the LJ and SW approach was made.

## **Appendix D: Chain Contribution**

To discuss the origin of eq. (2.14), we look at the different definitions of the ideal gas reference state of the PCP-SAFT and the Tripathi and Chapman [45, 46] formalism, respectively. The PCP-SAFT EoS defines the ideal gas state for a mixture of chain molecules, eq. (2.5), as reference state.  $F^{id}$  of real molecules can either be estimated from quantum mechanical calculations [109] or it can be obtained from experimental data on ideal gas heat capacities. The native reference state according to Wertheim's theory, like in the work of Tripathi and Chapman, is defined by an ideal gas of nonbonded segments, with the Helmholtz energy functional

$$\frac{F^{\text{ID}}\left[\rho_{k}\right]}{kT} = \sum_{i} \sum_{\alpha_{i}}^{m_{i}} \int \rho_{\alpha_{i}}(\mathbf{r}) \{\ln\left(\rho_{\alpha_{i}}(\mathbf{r})\Lambda_{\alpha_{i}}^{3}\right) - 1\} \mathrm{d}\mathbf{r}$$
(2.78)

where the sum  $\alpha_i$  runs over all segments in molecule *i*. Capital-letter superscripts denote the Tripathi and Chapman formalism. The molecular density is defined as a local average of all segment densities

$$\rho_i(\mathbf{r}) = \frac{1}{m_i} \sum_{\alpha_i}^{m_i} \rho_{\alpha_i}(\mathbf{r})$$
(2.79)

For the case, where the segment density profiles are averaged, it follows that  $\rho_i(\mathbf{r}) = \rho_{\alpha_i}(\mathbf{r})$ and one gets

$$\frac{F^{\rm ID}\left[\rho_k\right]}{kT} = \sum_i m_i \int \rho_i(\mathbf{r}) \{\ln\left(\rho_i(\mathbf{r})\Lambda_{s,i}^3\right) - 1\} \mathrm{d}\mathbf{r}$$
(2.80)

where  $\Lambda_{s,i}$  is the de Broglie wavelength of any one nonbonded 'segment'. The choice of a particular ideal gas reference state defines a corresponding residual Helmholtz energy, as

$$F[\rho_k] \equiv F^{\text{id}}[\rho_k] + F^{\text{res}}[\rho_k]$$
(2.81)

$$\equiv F^{\rm ID}\left[\rho_k\right] + F^{\rm RES}\left[\rho_k\right] \tag{2.82}$$

We aim at a formulation, where the molecular fluid in the ideal gas is considered as a reference  $(F^{id}[\rho_k])$ , where the corresponding residual Helmholtz energy reads

$$F^{\rm res}[\rho_k] = F^{\rm RES}[\rho_k] + (F^{\rm ID}[\rho_k] - F^{\rm id}[\rho_k])$$
(2.83)

The difference between the ideal gas states is

$$\frac{F^{\text{ID}}\left[\rho_{k}\right] - F^{\text{id}}\left[\rho_{k}\right]}{kT} = \sum_{i} (m_{i} - 1) \int \rho_{i}(\mathbf{r}) \{\ln\left(\rho_{i}(\mathbf{r})\right) - 1\} d\mathbf{r} + \sum_{i} N_{i} \left[m_{i} \ln\Lambda_{s,i}^{3} - \ln\Lambda_{i}^{3}\right]$$
(2.84)

with  $N_i$  as the number of molecules *i* in the system. This difference quantifies the difference of ideal gas molecules to nonbonded ideal gas 'segments' for homonuclear chains. We consider the difference in the chain term

$$F^{\text{chain}}\left[\rho_{k}\right] = F^{\text{CHAIN}}\left[\rho_{k}\right] + \left(F^{\text{ID}}\left[\rho_{k}\right] - F^{\text{id}}\left[\rho_{k}\right]\right)$$
(2.85)

where  $F^{\text{CHAIN}}$  is the functional presented by Tripathi and Chapman [46] for homonuclear chains. There, Wertheim's theory accounts for the connectivity of segments to chain (even for ideal gas states). We omit the second term on the right hand side of eq. (2.84). This term eliminates for all applications, because only differences or gradients of the Helmholtz energy are required. Eq. (2.85), omitting the second term, leads to eq. (2.14).

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# Chapter 3

# Prediction of Adsorption Isotherms and Selectivities: Comparison between Classical Density Functional Theory Based on the PC-SAFT Equation of State and Ideal Adsorbed Solution Theory

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## 3.1 Introduction

Physical adsorption in porous systems plays an important role in many fields of research and technical applications. We refer to review by Gubbins et al. [1] for the role of molecular models and methods for correlating and predicting properties of confined systems. Classical density functional theory (DFT) is a powerful method for the predicting properties of inhomogeneous fluid systems and has successfully been applied to a variety of systems and applications [2–4]. For some theoretical and mathematical background of DFT we refer to refs 5 and 6. In this work, we apply a standard DFT implementation, but it is worth mentioning that insightful results were obtained from DFT methods based on lattice gas models [7].

Various physical phenomena related to adsorption in confined systems have been studied in the DFT framework. Adsorption isotherms obtained from DFT calculations can exhibit layering transitions [8–10] or capillary condensations [8, 11]. Gubbins and coworkers showed that DFT models are able to reproduce the different types of adsorptions isotherms [12] and adsorption selectivities [13] according to the 1985 IUPAC classification [14]. Solvation pressures [15, 16] and effects of trace components [17, 18] on adsorbed systems were examined. For various confined systems isosteric heats of adsorption were calculated using DFT [19–21]. Also, the analysis of pore size distributions of porous materials is of particular interest. DFT was applied to study carbon materials [22–30], siliceous materials [31–34], and organic rich shales [35, 36].

A solid is in most DFT applications, where solid-fluid interfaces occur, modeled by an external potential towards the fluid. The external potential reflects the interactions of molecules or atoms of the solid phase towards the considered fluid molecules. The most common confined system studied with DFT models is the slit-shaped pore defined by two opposing perfectly planar walls. But also other geometries were studied comprehensively, such as cylindrical pores [37–42] and spherical cavities [43, 44]. Phenomena of adsorption isotherms of ink-bottle type pores [45] were evaluated using results obtained from DFT. The introduction of a two-dimensional external potential enabled the investigation of slitshaped pores composed of chemically inhomogeneous walls [46]. Quenched solid DFT [33] (QSDFT) defines atoms or molecules of the solid phase as additional Lennard-Jones interaction sites in the system. Then a Helmholtz energy functional is used to define the solid-fluid interactions, instead of the external potential. By defining the density profile of the solid component, geometric heterogeneities can be introduced into the system.

Many models for Helmholtz energy functionals were applied in the DFT framework to calculate adsorption isotherms of confined systems. Models for Lennard-Jones fluids [47–54], homopolymer chains [55, 56], and associating particles [57–60] were validated with data obtained from molecular simulations. Also, Helmholtz energy functionals related to the Statistical Associating Fluid Theory (SAFT) equation of state (EoS) were developed and applied to adsorption isotherms and selectivities. The first-order thermodynamic perturbation theory (TPT1) [61–64] is the foundation of the SAFT model initially introduced by Chapman, Jackson and coworkers [65–68]. A review on the theoretical foundation of TPT1 was recently published [69] and we also refer to the literature for detailed reviews about SAFT models and their applications [70–73]. Mitchell et al. [74] examined pore size distributions of activated carbons using a Helmholtz energy functional [75] based on SAFT for potentials of variable range (SAFT-VR) [76, 77]. A different Helmholtz energy functional that also simplifies to the SAFT-VR model for homogeneous fluids, was proposed by Miqueu and coworkers and was applied to methane [78] and water [79] adsorption. Tripathi and Chapman [80, 81] proposed a SAFT variant for inhomogeneous systems referred to as iSAFT which has recently been applied to nanoslit graphite pores [82]. Helmholtz energy functionals based on perturbed-chain SAFT (PC-SAFT) [83, 84] were developed by Shen et al. [85–87] and by Sauer and Gross [88] and were applied to confined systems.

Adsorption isotherms and adsorption selectivities are popular quantities to evaluate developed models for the Helmholtz energy functional in the DFT context. Experimental results can be used for this purpose, but have the disadvantage that detailed knowledge of the actual chemical and geometrical structure of the solid substrate is unknown. Evaluations of DFT models using experimental data remain rather vague, because assumptions or parameter adjustments have to be introduced to address the lack of detailed chemical and topological details of the solid. Results obtained from Monte Carlo (MC) or molecular dynamics (MD) molecular simulations are meaningful for assessing Helmholtz energy functionals: all pore properties can be specified in detail, resulting in clearly defined systems and in unambiguity in comparing results from molecular simulations with DFT calculations.

In this work, we analyze a Helmholtz energy functional [88] consistent with the PC-SAFT model for DFT predictions of adsorption isotherms and adsorption selectivities. The results and the predictive capabilities are evaluated using MC simulation results of clearly defined confined systems in a slit-shaped and in cylindrical geometries. For the comparison, two basic types of systems are examined: a model system specified by Lennard-Jones interactions and a more realistic system using the TAMie [89] force field and a graphite-like solid surfaces. Predictions of mixture isotherms from DFT are also compared to correlation results from the Ideal Adsorbed Solution Theory [90] (IAST).

## 3.2 Methods

In this work we express adsorption isotherms as pore densities  $\rho^{\text{pore}} = \{\rho_1^{\text{pore}}, \rho_2^{\text{pore}}, ...\}$  defined as averaged densities in pore space

$$\boldsymbol{\rho}^{\text{pore}} = \frac{1}{V} \int \boldsymbol{\rho} \left( \mathbf{r} \right) \,\mathrm{d}\mathbf{r} \tag{3.1}$$

where V is the pore volume and  $\boldsymbol{\rho}(\mathbf{r}) = \{\rho_1(\mathbf{r}), \rho_2(\mathbf{r}), ...\}$  is vector of density profiles that describes the spatial distribution of molecules for all components of the system. Similar to experimental settings, we consider the porous system in contact with a (virtual) bulk liquid phase or bulk vapor phase reservoir. By assuming thermodynamic equilibrium between the bulk phase reservoir and the pore system,  $\rho^{\text{pore}}$  can be expressed as a function of the bulk mole fractions  $\boldsymbol{y} = \{y_1, y_2, ...\}$ , temperature T, the bulk pressure p, as well as variables representing properties of the solid material, such as chemical or geometrical inhomogeneity, and solid-fluid interactions. For the DFT approach and for molecular simulations, vector  $\rho^{\text{pore}}$  is calculated along somewhat different routes. Fig. 3.1 illustrates how pore adsorption  $\rho^{\text{pore}}$  is calculated for given T, p, and  $\boldsymbol{y}$ . The DFT approach consists of a Helmholtz energy functional [88] that simplifies to the PC-SAFT model [84] for the special case of homogeneous bulk phases. The properties of the bulk phase reservoir, such as chemical potentials  $\boldsymbol{\mu}$ , can thus simply be calculated from the PC-SAFT model. Equilibrium between the virtually connected bulk phase reservoir and the pore system



Figure 3.1: Illustration of the variables defined for calculations to obtain  $\rho^{\text{pore}}$  as a function of  $\boldsymbol{y}$  and p at constant T. Variables  $\boldsymbol{y}$ , p and T (left) are specified for an NpT-reservoir virtually connected, through the condition of equal chemical potentials, to the pore system (right) defined in the grand canonical ensemble, i.e. for defined  $\mu VT$ . The scheme holds for pure components and for mixtures.

requires equality in chemical potentials  $\mu$  of all species and equal temperature. The DFT approach is subsequently applied to calculate the density profile vector  $\rho$  (**r**) and eq. (3.1) is used to calculate  $\rho^{\text{pore}}$ . Along this route one has to ensure that the calculation for the bulk phase reservoir is conducted for the stable phase, instead of a metastable phase. Similarly, one has to be cautious to conduct the DFT calculation in a stable state, which depends on the initial density profiles.

For the MC approach, grand canonical MC (GCMC) simulations can be used in a straightforward way to calculate bulk or pore properties for given  $\boldsymbol{\mu}$ , V, and T. However, this means that a GCMC simulation only leads to a single equilibrium point. The transition matrix MC [91, 92] (TMMC) approach in combination with histogram reweighting techniques [93] is very useful, because it provides properties as continuous functions of  $\boldsymbol{\mu}$  at defined T and therefore alleviates the need to sample at every discrete point. As shown by Chen and Sholl [94, 95], this technique can also be applied to confined systems for pure component and binary mixtures. More specifically, a GCMC simulation with the TMMC method applied to a pore simulation provides the relation  $\boldsymbol{\rho}^{\text{pore}} = \boldsymbol{\rho}^{\text{pore}}(\boldsymbol{\mu}; T)$ . We further make use of the fact that a GCMC simulation for a bulk phase using the TMMC approach leads to the relations  $\boldsymbol{y} = \boldsymbol{y}(\boldsymbol{\mu}; T)$  and  $p = p(\boldsymbol{\mu}; T)$ . Combining a simulation for the pore

system and one for the bulk phase, thus gives the desired relation between  $\boldsymbol{y}$ , p, T and the adsorption loading  $\boldsymbol{\rho}^{\text{pore}}$ .

#### 3.2.1 Classical Density Functional Theory

Density functional theory, as a starting point [5], defines the grand potential functional  $\Omega_V$  for given T, V and  $\mu$ , as

$$\Omega_V[\boldsymbol{\rho}(\mathbf{r})] = F[\boldsymbol{\rho}(\mathbf{r})] + \sum_i \int \rho_i(\mathbf{r}) \{V_i^{\text{ext}}(\mathbf{r}) - \mu_i\} d\mathbf{r}$$
(3.2)

with  $V_i^{\text{ext}}$  as the external potential of component *i* and *F* as the Helmholtz energy functional that depends on the density profiles of all involved components. In thermodynamic equilibrium the grand potential functional  $\Omega_V$  is minimal with respect to internal degrees of freedom, more specifically with respect to the density profiles  $\rho(\mathbf{r})$ . In minimal state  $\Omega_V$  is equal to the grand potential  $\Omega$ . As the condition for thermodynamic equilibrium, thus, the first functional derivative of  $\Omega_V$  with respect to  $\rho_j(\mathbf{r})$  is zero for all *j*, leading to

$$0 = \frac{\delta F\left[\boldsymbol{\rho}(\mathbf{r})\right]}{\delta \rho_j(\mathbf{r})} + V_j^{\text{ext}}(\mathbf{r}) - \mu_j$$
(3.3)

Introducing residual quantities  $\mu_j^{\text{res}} = \mu_j - \mu_j^{\text{id}}$  and  $F^{\text{res}} = F - F^{\text{id}}$  gives

$$\rho_j(\mathbf{r}) = \rho_j^{\text{bulk}} \exp\left(\frac{1}{kT} \left[\mu_j^{\text{res}} - \frac{\delta F^{\text{res}}\left[\boldsymbol{\rho}(\mathbf{r})\right]}{\delta \rho_j(\mathbf{r})} - V_j^{\text{ext}}(\mathbf{r})\right]\right)$$
(3.4)

where the ideal gas contribution of the chemical potential evaluated at bulk phase conditions

$$\mu_j^{\rm id} = kT \ln \left( \rho_j^{\rm bulk} \Lambda_j^3 \right) \tag{3.5}$$

and the ideal gas contribution of the derivative

$$\frac{\delta F^{\rm id}\left[\boldsymbol{\rho}(\mathbf{r})\right]}{\delta \rho_j(\mathbf{r})} = kT \ln\left(\rho_j(\mathbf{r})\Lambda_j^3\right) \tag{3.6}$$

were used. Further, k is Boltzmann's constant and the de Broglie wavelength  $\Lambda_j$  from eq. (3.5) and (3.6) cancel in eq. (3.4). The density profiles are obtained by solving eq. (3.4) iteratively using a damped direct substitution scheme (Picard iteration). A study on convergence and computational speed of DFT problems showed that direct substitution is an inefficient solution procedure [96]. However, this study focuses on one-dimensional problems in cartesian coordinates and in cylindrical coordinates, where calculation efficiency was not of high concern.

The predictive quality of a DFT approach is determined through the chosen Helmholtz

energy model,  $F^{\text{res}}$ . Based on successive application of perturbation theories,  $F^{\text{res}}$  is composed of contributions related to types of intermolecular interactions. In accordance to the PC-SAFT equation of state these contributions are

$$F^{\text{res}}\left[\boldsymbol{\rho}(\mathbf{r})\right] = F^{\text{hs}}\left[\boldsymbol{\rho}(\mathbf{r})\right] + F^{\text{hc}}\left[\boldsymbol{\rho}(\mathbf{r})\right] + F^{\text{disp}}\left[\boldsymbol{\rho}(\mathbf{r})\right]$$
(3.7)

where the abbreviation hs, hc, and disp denote the hard-sphere, chain, and dispersion (i.e. van der Waals attraction) contribution, respectively. The molecular model of PC-SAFT describes molecules as chains of spherical segments that interact with spherical segments from other chains in various ways. Polar and hydrogen-bonding fluids are not examined in this study and we have here omitted the Helmholtz energy contributions, leaving only van der Waals type interactions. The pure component parameters are the number of segments per molecule  $m_i$ , the segment size parameter  $\sigma_{ii}$ , and the dispersive energy parameter  $\varepsilon_{ii}$ . For mixtures one can introduce a binary interaction parameter  $k_{ij}$ , correcting the Berthelot-estimate of the cross-energy parameter. The local value of the density profile of molecule *i* is determined as the local average of density profiles of the segments  $\alpha_i$ 

$$\rho_i(\mathbf{r}) = \frac{1}{m_i} \sum_{\alpha_i}^{m_i} \rho_{\alpha_i}(\mathbf{r})$$
(3.8)

which leads to  $\rho_i(\mathbf{r}) = \rho_{\alpha_i}(\mathbf{r})$ , when applying the homosegmented chain assumption. We refer to the original literature for more detailed information about the different Helmholtz energy functional contributions: see Roth et al. [97] and Yu and Wu [98] for  $F^{\text{hs}}$ , Tripathi and Chapman [80, 81] for  $F^{\text{hc}}$  and Sauer and Gross [88] for  $F^{\text{disp}}$  (the superior variant of the dispersion contribution denoted as  $F^{\text{disp},1}$  in the original work [88] was chosen).

In this work, we study slit-shaped and cylindrical pores. For slit-shaped pores, density profiles depend solely on the z coordinate perpendicular to both walls and therefore the complexity of the DFT formalism reduces significantly. See Appendix A of ref 88 for the explicit equations that need to be solved to calculate the functional derivative of eq. (3.4). The density profile of a fluid confined in a cylindrical pore depends only on the radial coordinate. We applied a Fast Hankel transform implementation [99] to solve convolutions that appear in the calculation of the functional derivative. See refs 100 and 101 for detailed information.

#### 3.2.2 Molecular Simulation

We use histogram reweighting techniques [93] to obtain continuous relations between  $\rho^{\text{pore}}$ ,  $\boldsymbol{y}$ , p, and  $\boldsymbol{\mu}$  for given T and V. This is achieved by shifting the particle-number

probability distribution  $\Pi$  according to [92]

$$\ln \Pi(\mathbf{N}; \boldsymbol{\mu}, V, T) = \ln \Pi(\mathbf{N}; \tilde{\boldsymbol{\mu}}, V, T) + \frac{\mathbf{N}}{kT} \cdot (\boldsymbol{\mu} - \tilde{\boldsymbol{\mu}})$$
(3.9)

with  $\mathbf{N} = \{N_1, N_2, ...\}$  as the vector of number of particles. To obtain the probability distributions  $\Pi^{\text{pore}}(\mathbf{N}; \tilde{\boldsymbol{\mu}}, V, T)$  and  $\Pi^{\text{bulk}}(\mathbf{N}; \tilde{\boldsymbol{\mu}}, V, T)$  we perform TMMC simulations at reference state  $\{\tilde{\boldsymbol{\mu}}, V, T\}$  for a pore system and a bulk system, respectively. With eq. (3.9) pore densities and bulk properties are available via

$$\rho_i^{\text{pore}}(\boldsymbol{\mu}, V, T) = \frac{1}{V} \sum_{N_1=0}^{N_1^{\text{max}}} \sum_{N_2=0}^{N_2^{\text{max}}} N_i \, \Pi_n^{\text{pore}}(\boldsymbol{N}; \boldsymbol{\mu}, V, T)$$
(3.10)

$$\rho_i^{\text{bulk}}(\boldsymbol{\mu}, V, T) = \frac{1}{V} \sum_{N_1=0}^{N_1^{\text{max}}} \sum_{N_2=0}^{N_2^{\text{max}}} N_i \Pi_n^{\text{bulk}}(\boldsymbol{N}; \boldsymbol{\mu}, V, T)$$
(3.11)

$$p(\boldsymbol{\mu}, V, T) = -\frac{kT}{V} \ln \Pi_n^{\text{bulk}}(\mathbf{0}; \boldsymbol{\mu}, V, T)$$
(3.12)

Subscript *n* indicates that the probability distributions were normalized after shifting. Bulk and pore mole fractions are calculated subsequently from  $\rho^{\text{bulk}}$  and  $\rho^{\text{pore}}$ , respectively.

We use an own MC implementation that contains transition matrix and bias techniques described by Errington [91] and by Hemmen et al. [89, 102]. The N space is divided into windows of width  $\Delta N$  for pure substances and windows of  $\Delta N_1 \times \Delta N_2$  for binary mixtures. Each window is simulated in a dedicated simulation that all run in parallel. The probability distribution  $\Pi(N; \tilde{\mu}, V, T)$  is stitched together in a post-processing step. Window sizes are defined as  $\Delta N = 12$  for pure substances and as  $\Delta N_1 = \Delta N_2 = 12$ for binary mixtures, with the exception of highly dense systems, where we used  $\Delta N = 3$ or  $\Delta N_2 = 3$ , respectively. As reference chemical potential for the TMMC simulation an excess value of  $\tilde{\mu}_i^{\text{ex}} = -8 kT$  was chosen for all components, with the excess chemical potential defined as  $\mu_i^{\text{ex}} = \mu_i - kT \ln \left(\Lambda_i^3/\text{Å}^3\right)$ .

We study four components in this work: argon, krypton, methane, and *n*-butane. For n-butane the TAMie [89] force field is used while the other components are modeled using Lennard-Jones potentials. All force field parameters are summarized in the supporting information. Translation, insertion and deletion MC moves [103] are performed during a simulation. For *n*-butane rotation and reconfiguration moves are applied additionally. A configurational bias scheme [104, 105] is used for insertion, deletion, and reconfiguration moves to improve the statistics.

Pore and bulk simulations differ according to the use of periodic boundary conditions and nearest image conventions. For slit-shaped pores both are deactivated in z-direction and for cylindrical pores both are disabled in x- and y-direction. For bulk simulations we use a cutoff radius of  $r_c^{\text{bulk}} = 14 \text{ Å}$  plus analytical long-range corrections (the same as in the original TAMie force field). In pore simulations, long-range corrections are rather complicated due to the inhomogeneity of the system. Therefore, a larger cutoff radius  $r_c^{\text{pore}} = 20 \text{ Å}$  is used and tail corrections are omitted. In general, the sizes of the simulation box  $L_x$ ,  $L_y$  and  $L_z$  are chosen to be twice the cutoff radius. For slit-shaped pores,  $L_z$  is defined by the given wall distance H, and for cylindrical pores,  $L_x$  and  $L_y$  are determined as twice the pore radius R.

Trial moves for molecular translation, rotation or reconfiguration can lead to penetration of molecular segments into solid walls. These trial moves have to be rejected. The external potential, representing the solid structure, is implemented as an energy contribution. The energy change from the external potential is used for assessing every MC trial move. For the equilibration phase we perform 25 million MC moves for bulk and 50 million trial MC moves for pore simulations. Relevant data for the calculation of the probability distribution is sampled in the production phase that consists of 250 million MC trial moves.

With these settings the calculated  $\Pi^{\text{pore}}$  of binary mixtures was of insufficient quality. The reduction of the window sizes led only to small improvements in the quality of  $\Pi^{\text{pore}}$ . We assume that the lack of an adequate maximum displacement value due to the strong inhomogeneity of the fluid structure is the reason for rather poor statistics and that therefore a significantly larger number of MC moves in the production phase would be required. Instead of performing GCMC simulations with TM sampling, for binary mixtures in pore simulations we conducted regular GCMC simulations and calculated  $\rho^{\text{pore}}$  from the average number of molecules sampled in a GCMC simulation at given { $\mu$ , V, T}. The number of equilibration and production MC moves of these simulations were the same as for the windowed TMMC simulations. Good statistics were found for TMMC simulations of pure components in pore systems and of binary mixtures and pure components in bulk systems.

#### **3.2.3** Solid-Fluid Interactions

External potentials are used to model the interaction between a solid phase and a molecular segment at position  $\mathbf{r}_{\alpha}$ . For the adsorption of methane and *n*-butane on a planar graphite-like surface, we use the Steele [106] potential

$$V_{\mathrm{s}\alpha}^{\mathrm{ext}}(z_{\alpha}) = 2\pi\rho_{\mathrm{s}}\varepsilon_{\mathrm{s}\alpha}\sigma_{\mathrm{s}\alpha}^{2}\Delta\left[\frac{2}{5}\left(\frac{\sigma_{\mathrm{s}\alpha}}{z_{\alpha}}\right)^{10} - \left(\frac{\sigma_{\mathrm{s}\alpha}}{z_{\alpha}}\right)^{4} - \frac{\sigma_{\mathrm{s}\alpha}^{4}}{3\Delta\left(z_{\alpha} + 0.61\Delta\right)^{3}}\right]$$
(3.13)

with  $z_{\alpha}$  as the perpendicular distance from the surface,  $\sigma_{s\alpha}$  as the solid-fluid segment diameter,  $\varepsilon_{s\alpha}$  as the dispersive energy parameter,  $\Delta$  as the distance between graphite lattice planes and  $\rho_s$  as the overall density of the solid phase. Berthelot-Lorentz combining rules are applied

$$\sigma_{\rm s\alpha} = \frac{1}{2} \left( \sigma_{\rm ss} + \sigma_{\alpha\alpha} \right) \tag{3.14}$$

$$\varepsilon_{\mathrm{s}\alpha} = \sqrt{\varepsilon_{\mathrm{ss}}\varepsilon_{\alpha\alpha}} \tag{3.15}$$

with  $\sigma_{\alpha\alpha}$  and  $\varepsilon_{\alpha\alpha}$  as Lennard-Jones parameters of methane or as the bead parameters of the TAMie force field for *n*-butane, respectively. The values of the Steele potential parameters are [48, 106]:  $\sigma_{ss} = 3.40$  Å,  $\varepsilon_{ss}/k = 28.0$  K,  $\Delta = 3.35$  Å, and  $\rho_s = 0.114$  Å<sup>-3</sup>. Eqs (3.13), (3.14), and (3.15) are directly applied in MC simulations.

To obtain the external potential for the DFT approach, we formulate the total solid-fluid interactions between the solid wall and molecule i is

$$V_i^{\text{ext}} = \sum_{\alpha=1}^{N_i^{\text{seg}}} V_{s\alpha}^{\text{ext}}(z_\alpha)$$
(3.16)

with  $N_i^{\text{seg}}$  as the number of segments in molecule *i*. The Helmholtz energy functional used in this work does not differentiate between density profiles of molecular segments, but locally averaged molecular density profiles [81, 88]. We therefore assume that if a molecule is located at distance  $z_i$ , all segments of this molecule are located at the same distance  $z_{\alpha} = z_i$ . The external potential towards any segment of a molecule *i* at position  $z_i$  is

$$V_i^{\text{ext}}(z_i) = N_i^{\text{seg}} V_{\text{s}\alpha}^{\text{ext}}(z_i)$$
(3.17)

In eq. (3.17), also homosegmented chains were assumed in accordance with the PC-SAFT model. We set  $N_i^{\text{seg}} = m_i$ , which is exact for molecular chains composed tangentially bonded segments, but is an approximation for fused chains. Eqs. (3.17) and (3.13) are used in the DFT approach in combination with Berthelot-Lorentz combining rules

$$\sigma_{\rm si} = \frac{1}{2}(\sigma_{\rm ss} + \sigma_{ii}) \tag{3.18}$$

$$\varepsilon_{\rm si} = \sqrt{\varepsilon_{\rm ss}\varepsilon_{ii}} \tag{3.19}$$

where  $\sigma_{si}$  and  $\varepsilon_{si}$  correspond to  $\sigma_{s\alpha}$  and  $\varepsilon_{s\alpha}$  in Eq. (3.13), respectively.

The second type of external potential used for the argon-krypton systems studied in this work is based on Lennard-Jones interactions between solid particles homogeneously distributed in a solid phase and a fluid particle  $\alpha$ , according to

$$V_{\mathrm{s}\alpha}^{\mathrm{ext}}(\mathbf{r}_{\alpha}) = \rho_{\mathrm{s}} \int_{\mathrm{solid}} 4\varepsilon_{\mathrm{s}\alpha} \left[ \left( \frac{\sigma_{\mathrm{s}\alpha}}{|\mathbf{r}_{s} - \mathbf{r}_{\alpha}|} \right)^{12} - \left( \frac{\sigma_{\mathrm{s}\alpha}}{|\mathbf{r}_{s} - \mathbf{r}_{\alpha}|} \right)^{6} \right] \mathrm{d}\mathbf{r}_{\mathrm{s}}$$
(3.20)

with  $\rho_s$  as solid density and  $\mathbf{r}_s$  and  $\mathbf{r}_{\alpha}$  as the position of solid and fluid particle, respectively. Assuming a solid phase in the domain  $-\infty < z \leq 0$  that is perfectly planar at z = 0 leads to the 9-3 external potential

$$V_{s\alpha}^{\text{ext}}(z_{\alpha}) = \frac{4}{3}\pi\rho_{s}\varepsilon_{s\alpha}\sigma_{s\alpha}^{3}\left[\frac{1}{15}\left(\frac{\sigma_{s\alpha}}{z_{\alpha}}\right)^{9} - \frac{1}{2}\left(\frac{\sigma_{s\alpha}}{z_{\alpha}}\right)^{3}\right]$$
(3.21)

Applying eq. (3.20) to an infinitely long cylindrical pore with perfectly smooth walls and a pore radius R results in [37]

$$V_{\mathrm{s}\alpha}^{\mathrm{ext}}(r_{\alpha}) = \pi \rho_{\mathrm{s}} \varepsilon_{\mathrm{s}\alpha} \sigma_{\mathrm{s}\alpha}^{3} \int_{\varphi_{\mathrm{d}}=0}^{\pi} \left[ \frac{7}{32} \left( \frac{\sigma_{\mathrm{s}\alpha}}{r_{\mathrm{d}}} \right)^{9} - \left( \frac{\sigma_{\mathrm{s}\alpha}}{r_{\mathrm{d}}} \right)^{3} \right] \mathrm{d}\varphi_{\mathrm{d}}$$
(3.22)

with the dependence of the external potential reduced to the radial coordinate of the fluid particle  $r_{\alpha}$ .  $\varphi_{\rm d}$  is the polar angle of the cylindrical coordinate system with the origin shifted to the position of the fluid particle. Further,  $r_{\rm d}$  is the distance between the fluid particle and the edge of the pore [37] and depends on  $\varphi_{\rm d}$  and the radial position of the fluid particle  $r_{\alpha}$  according to

$$r_{\rm d} = -r_{\alpha}\cos\varphi_{\rm d} + \sqrt{R^2 - r_{\alpha}^2\sin^2\varphi_{\rm d}}$$
(3.23)

Eq. (3.22) is solved numerically using the trapezoidal rule and results are stored in an array over a grid in  $r_{\alpha}$ . In MC simulations the required values of  $V_{s\alpha}^{\text{ext}}$  are linearly interpolated between grid points. The external potentials in eqs. (3.21) and (3.22) are applied in combination with eqs. (3.14) and (3.18) and  $\sigma_{ss} = 2.5$  Å. The solid-fluid interaction with argon and krypton are defined as  $\varepsilon_{s,\text{Ar}}/k = 220.0$  K and  $\varepsilon_{s,\text{Kr}}/k = 270.0$  K, respectively. The solid density is set to  $\rho_{s} = 0.09$  Å<sup>-3</sup>.

#### 3.2.4 Ideal Adsorbed Solution Theory

In order to assess and appreciate predictions of DFT we also apply the IAST [90] approach. We emphasize that IAST takes pure component adsorption isotherms as input, whereas DFT predicts pure component adsorption isotherms. For known pure component adsorption isotherms, however, IAST can be used to describe  $\rho^{\text{pore}}$  of mixture systems. The basic equation of IAST characterizing the chemical equilibrium between an adsorbed

phase and a bulk gas phase is

$$py_i = x_i p_i^o(\pi) \tag{3.24}$$

where  $x_i$  is the mole fraction in the adsorbed phase,  $\pi$  is the spreading pressure acting in the adsorbed phase, and superscript o indicates pure component properties. The pure component case of eq. (3.24) reveals the meaning of  $p_i^o(\pi)$ : it is the pressure in the gas phase of pure component i that is required to establish a certain spreading pressure  $\pi$ in the adsorbed phase. A relation between  $p_i^o$  and  $\pi$  is derived from the Gibbs-Duhem equation of the adsorbed phase and reads

$$\pi(p_i^o) = \frac{kT}{A} \int_{p=0}^{p_i^o} \frac{N_i^o(p)}{p} dp$$
(3.25)

where A is the surface area of the solid phase and  $N_i^o$  is the pure component adsorption isotherm. Rewriting eq. (3.25) in terms of the pure component pore density gives

$$\pi(p_i^o) = kT \frac{L}{2} \int_{p=0}^{p_i^o} \frac{\rho_i^{\text{pore},o}(p)}{p} dp$$
(3.26)

with L as a characteristic length equal to the wall distance L = H or to the pore radius L = R for slit-shaped or cylindrical pores, respectively. Adsorption isotherms  $\rho_i^{\text{pore},o}$  obtained from GCMC simulations were stored in a discretized form and provided as IAST input. The integral in eq. (3.26) is approximated using the trapezoidal rule and linear interpolations are used to approximate the upper boundary of the integral from the discretized data.

Eqs. (3.24) and (3.26) are solved iteratively for both components of the binary mixture in order to obtain the mole fractions in the adsorbed phase for given T, p, and y. The total adsorption isotherm  $\rho^{\text{pore}} = \rho_1^{\text{pore}} + \rho_2^{\text{pore}}$  is calculated from [90]

$$\frac{1}{\rho^{\text{pore}}} = \frac{x_1}{\rho_1^{\text{pore},o}(p_1^o)} + \frac{x_2}{\rho_2^{\text{pore},o}(p_2^o)}$$
(3.27)

### **3.3** Results and Discussion

In this work, we study two different types of systems. The argon-krypton mixture is described with Lennard-Jones potentials for the fluid-fluid as well as for the fluid-solid interactions. For PC-SAFT, the number of segments  $m_i$  is set to unity for argon and for krypton. This mixture allows an unambiguous comparison between MC and DFT simulations. We note, though, that PC-SAFT does not exactly reproduce Lennard-Jones properties: in ref 88 we estimated the deviation as 1.20% and 2.65% in vapor pressure and liquid density, respectively, which we consider sufficient for the comparing the DFT approach to results from MC simulations.

The second mixture is meant to resemble the adsorption behavior of real methane-nbutane in a graphite-like pore. For the MC approach, methane is defined as a Lennard-Jones fluid using parameters from Vrabec et al. [107] and *n*-butane is modeled by the TAMie [89] force field. As demonstrated in refs 89 and 107, *n*-butane and methane bulk phase densities and vapor pressures are in excellent agreement with experimental data and we assume that the behavior of the modeled methane and *n*-butane mixture is sufficiently close to the behavior of the real substances and their mixtures. Unlike real experimental data, results for such a mixture in confined media serve as an appropriate reference to analyze the predictive capabilities of the DFT approach, because the geometry of the solid phase and the solid-fluid interactions are clearly defined. Therefore, the comparability between the DFT and the MC approach is given, without adjustable parameters, although the molecular models for n-butane are different in both approaches. In the PC-SAFT model *n*-butane is represented as Lennard-Jones like segments freely arranged as a tangent chain, whereas in the TAMie force field *n*-butane is a chain molecule composed of overlapping spherical beads defined by Mie potentials that are constrained by angle and torsion potentials. PC-SAFT parameters from literature 84 are used for methane and *n*-butane for the DFT approach. All parameters used in this work are presented in the supporting information.

Instead of information about pore properties like the external potential, IAST requires the full pure component adsorption isotherms for the considered temperature and is therefore not predictive compared to the DFT approach. IAST only allows predictions of the mixture behavior. Comparisons of adsorption isotherms and selectivities obtained from Adsorbed Solution Theories (AST) and DFT were already presented by Sweatman and Quirke [108, 109]. Sweatman and Quirke adjusted DFT model parameters to pure component adsorption isotherms to establish a common ground for the DFT-AST comparison. That is avoided in our work, we don't use adjustable parameters in our study.

#### 3.3.1 Argon, Krypton and their Mixture

Argon and krypton are defined as Lennard-Jones interaction sites with parameters  $\sigma_{\text{ArAr}} = 3.405 \text{ Å}$  and  $\varepsilon_{\text{ArAr}}/k = 119.8 \text{ K}$  and  $\sigma_{\text{KrKr}} = 3.63 \text{ Å}$  and  $\varepsilon_{\text{KrKr}}/k = 163.1 \text{ K}$ , respectively. Mutual interactions are modeled using Berthelot-Lorentz combining rules. All argonkrypton calculations were performed at T = 290 K. At this temperature the PC-SAFT description of argon and krypton is in good agreement with bulk phase densities obtained from TMMC simulations. Comparisons for pure argon, pure krypton, and an argonkrypton mixture at  $y_{\text{Ar}} = 0.7$  are presented in the supporting information. We define a a slit-shaped pore according to

$$V_{\alpha}^{\text{ext}}(z_{\alpha}) = V_{\text{s}\alpha}^{\text{ext}}(z_{\alpha}) + V_{\text{s}\alpha}^{\text{ext}}(H - z_{\alpha})$$
(3.28)

where we use eq. (3.21) for  $V_{s\alpha}^{\text{ext}}$  and a wall distance of H = 20 Å. The considered cylindrical pore has a pore radius of R = 20 Å and the external potential is defined by eq. (3.22). Both pores exhibit the same ratio of solid surface area to pore volume: 2/H for the slit-shaped pore and 2/R for the cylindrical pore.

Adsorption isotherms for both pores are presented in Fig. 3.2 for pure argon and in Fig. 3.3 for pure krypton, respectively. A comparison between adsorption isotherms



Figure 3.2: Comparison between results obtained from DFT and from GCMC simulations with TM-sampling for pure argon: adsorption isotherms at T = 290 K for a slit-shaped pore with H = 20 Å and a cylindrical pore with R = 20 Å. For clarity, adsorption isotherms for the cylindrical pore are shifted by 0.002 Å<sup>-3</sup>.

of pure argon for a slit-pore and for a cylindrical pore shows only minor deviations of DFT predictions from MC results. A similarly good result is observed for krypton, noting that the adsorbed amount in the slit-shaped pore is higher for pressures between 50 - 200 bar. For both components and both type of pores, the adsorption isotherms predicted from DFT without adjustable parameters are in excellent agreement to results from MC simulations over a wide range of pressure.

The results for the adsorption of a binary mixture at  $y_{Ar} = 0.7$  are shown in Figs. 3.4. The adsorption behavior of the mixture is very well predicted from the DFT, as the comparison with results from MC simulations confirm. The adsorption isotherm in the cylindrical pore is similar to the isotherm in a slit pore, with somewhat higher pore densities in the slit-shaped pore for smaller and moderate pressures. For the same adsorption



Figure 3.3: Comparison between results obtained from DFT and from GCMC simulations with TM-sampling for pure krypton: adsorption isotherms at T = 290 K for a slit-shaped pore with H = 20 Å and a cylindrical pore with R = 20 Å. For clarity, adsorption isotherms for the cylindrical pore are shifted by 0.002 Å<sup>-3</sup>.



Figure 3.4: Comparison between results obtained from DFT, IAST, and GCMC for an argon-krypton mixture at  $y_{\rm Ar} = 0.7$ : adsorption isotherm at T = 290 K for a slit-shaped pore with H = 20 Å and a cylindrical pore with R = 20 Å. For clarity, adsorption isotherms for the cylindrical pore are shifted by 0.002 Å<sup>-3</sup>.

isotherm at  $y_{\rm Ar} = 0.7$ , Fig. 3.5 presents the adsorption selectivity of krypton defined



Figure 3.5: Comparison between results obtained from DFT, IAST, and GCMC for an argon-krypton mixture at  $y_{\rm Ar} = 0.7$ : selectivity of krypton in the pore at T = 290 K for a slit-shaped pore with H = 20 Å and a cylindrical pore with R = 20 Å

as [110]

$$S_{2,1} = \frac{x_{\rm Kr}/x_{\rm Ar}}{y_{\rm Kr}/y_{\rm Ar}}$$
(3.29)

The curved solid surface in the cylindrical pore leads to a more selective adsorption towards krypton. This can be illustrated using Henry's adsorption constants  $K_i$  as defined through  $\rho_i^{\text{pore,Henry}} = K_i p$  for the low-pressure limit  $p \to 0$ . Values for Henry's adsorption constants can be approximated from the presented pure component isotherms for  $p \to 0$ . While Henry's adsorption constant for krypton for the cylindrical pore is 49% higher than for the slit pore (from  $K_{\text{Kr}}^{\text{slit}} = 3.82 \cdot 10^{-9} \text{Å}^{-3}/\text{Pa}$  to  $K_{\text{Kr}}^{\text{cyl}} = 5.71 \cdot 10^{-9} \text{Å}^{-3}/\text{Pa}$ ), the increase in  $K_{\text{Ar}}$  for argon in the cylindrical pore compared to the slit pore is only 23% (from  $K_{\text{Ar}}^{\text{slit}} =$  $1.21 \cdot 10^{-9} \text{Å}^{-3}/\text{Pa}$  to  $K_{\text{Ar}}^{\text{cyl}} = 1.49 \cdot 10^{-9} \text{Å}^{-3}/\text{Pa}$ ). Krypton has a more pronounced preference for the cylindrical pore as compared to argon, which explains the large difference in selectivity for the cylindrical pore and for the slit-shaped pore in the low-pressure limit. The difference in selectivity disappears for high pressures. It was surprising for us to observe that the DFT is able to reproduce the subtle differences in adsorption behavior of that mixture in slit-pore and in cylindrical pores in such good quantitative agreement to MC data.

As opposed to DFT, IAST is not a predictive method because it requires pure component isotherms to be known. However, we find it interesting to compare results from IAST to DFT for mixtures. Because IAST uses the pure component adsorption isotherms obtained from GCMC simulations (Figs. 3.2 and 3.3) as input, the selectivities of the binary systems are necessarily in agreement for lower and moderate pressures. Due to the assumptions inherent in the IAST model, the accuracy decreases with increasing pressure. The selectivities obtained from the DFT approach overestimate the selectivities for moderate pressures somewhat. For lower and high pressures the selectivities are predicted very accurately by the DFT approach.

#### 3.3.2 Methane, *n*-Butane and their Mixture

The pure component adsorption behavior and the mixture adsorption of methane and n-butane were studied at T = 344.26 K, because experimental data for the vapor-liquid equilibrium is available at that temperature [111]. We first investigate bulk phase quantities to assess deviations of results obtained from PC-SAFT towards results from TAMie. The bulk phase densities for varying pressure for pure methane and for pure n-butane is shown in Fig. 3.6. Both model, PC-SAFT and the methane force-field [107] describe the



Figure 3.6: Comparison between results obtained from PC-SAFT and from GCMC simulations with TM-sampling for pure methane and pure *n*-butane: bulk phase isotherms at T = 344.26 K.

density of methane with small differences towards high pressures. Note that the segment size parameter  $\sigma_{ii}$  and the dispersive energy parameter  $\varepsilon_{ii}$  used in PC-SAFT are different from the force-field parameters for used in MC simulations. Both were independently adjusted to experimental data of pure methane. For *n*-butane one observes a vapor-liquid transition for the considered temperature at the vapor-pressure. Results obtained from PC-SAFT and GCMC calculations are in very good agreement concerning vapor pressures  $(p_{\text{EoS}}^{\text{sat}} = 8.327 \text{ bar and } p_{\text{MC}}^{\text{sat}} = 8.284 \text{ bar})$ , saturated liquid densities  $(\rho_{\text{EoS}}^{\text{L}} = 0.005313 \text{ Å}^{-3})$ 

and  $\rho_{\text{TMMC}}^{\text{L}} = 0.005277 \text{ Å}^{-3}$ ), and saturated vapor densities ( $\rho_{\text{EoS}}^{\text{V}} = 0.0002087 \text{ Å}^{-3}$  and  $\rho_{\text{TMMC}}^{\text{V}} = 0.0002076 \text{ Å}^{-3}$ ). Overall, the *n*-butane isotherm is accurately reproduced by PC-SAFT with some overestimations of  $\rho^{\text{bulk}}$  for high pressures. The vapor-liquid equilibrium of the mixture is analyzed in Fig. 3.7. For the DFT approach, we adjusted the



Figure 3.7: Comparison between PC-SAFT and experimental data [111] of a methane*n*-butane mixture at T = 344.26 K: Vapor-liquid equilibrium pressure over methane mole fraction  $x_{\text{Me}}$ .

 $k_{ij}$  parameter to the same experimental data at T = 344.26 K by correcting the Berthelot combining rule

$$\varepsilon_{ij} = (1 - k_{ij}) \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \tag{3.30}$$

leading to  $k_{ij} = 0.027744$ . Note that the chosen force fields for methane [107] and nbutane [89] also provide an excellent representation of experimental data [111] for this temperature, as reported in ref 89 (their Fig. 11).

Adsorption isotherms of methane and *n*-butane systems are studied in a graphite-like slit-shaped pore, defined by eq. (3.28) with H = 40 Å. Fig. 3.8 shows the results obtained from the DFT approach and from MC simulations for both pure components. Over the whole range of pressure the adsorption isotherm of methane as predicted from DFT very accurately matches results from molecular simulation. The adsorption isotherm of *n*butane shows a phase transition. Here, for the MC approach, the probability distribution of the pore simulation is bimodal and the phase transition corresponds to the chemical potential that leads to equal areas under both separated histograms. Similarly to Alvarez et al. [112] and Shi et al. [113], we applied histogram reweighting techniques and found  $\mu_i^{\text{ex}} = -9.391 \,\text{kT}$  for the state of capillary condensation. The corresponding pressure of the phase transition is obtained from the pure bulk phase GCMC simulations for *n*-butane



Figure 3.8: Comparison between results obtained from DFT and GCMC simulations with TM-sampling for pure methane and pure *n*-butane: adsorption isotherms at T = 344.26 K for a slit-shaped pore with H = 40 Å. The dotted lines represent the hysteresis loop of the DFT adsorption isotherm.

with a value of  $p_{\rm MC}^{\rm pt} = 4.273$  bar. This value should be compared to the vapor-liquid phase transition of bulk phases, occurring at vapor pressure of  $p_{MC}^{sat} = 8.284$  bar for this temperature. For the DFT approach, the phase transition can be calculated along a hysteresis loop (depicted by the dotted lines in Fig. 3.8): different isotherms are obtained when performing DFT calculations along an adsorption pathway and along a desorption pathway. The adsorption isotherm representing thermodynamic equilibria (continuous curve) is defined by the minimum values of the grand potential. The intersection of the grand potential curves obtained from the adsorption and desorption calculation approach define the actual, stable phase transition pressure  $p_{\text{EoS}}^{\text{pt}}$ . We refer to ref 37 for more detailed discussion. Following this procedure, we found  $p_{\text{EoS}}^{\text{pt}} = 4.268 \text{ bar}$ , which is in excellent agreement with the GCMC results. Also, the *n*-butane adsorption isotherm is very accurately predicted around the point of phase transition and for higher pressures. Larger relative deviations were found for smaller pressures and, thus, for Henry's adsorption constant. This is related to the applied external potentials and is due to different molecular models for PC-SAFT and for the TAMie force field, respectively. For the MC approach, the external potential distinguishes between the different interaction sites of n-butane. The external potential for the DFT approach, defined as interactions between the solid wall and the average site of a molecule is a simplified model of the more detailed external potential used in the MC approach. It should be possible to improve on the description of selectivities at low pressures if we would consider parameters defining the external potential, eqs. (3.21) and (3.22), as adjustable parameters. However in this study we strictly avoided any adjustable parameters in the DFT approach.

We calculate adsorption isotherms of binary methane-*n*-butane mixtures for two constant mole fractions of the connected fluid bulk phase:  $y_{\rm Me} = 0.4$  and 0.8. For  $y_{\rm Me} = 0.4$ the bulk phase is a stable vapor phase until the pressure exceeds  $p^{\rm dew} = 15.329$  bar (calculated from PC-SAFT). The total amount of adsorbed molecules and the selectivity of *n*-butane for  $y_{\rm Me} = 0.4$  are depicted in Fig. 3.9. The adsorption isotherm shows capillary



Figure 3.9: Comparison between results obtained from DFT, IAST, and GCMC for a methane-*n*-butane mixture at  $y_{\text{Me}} = 0.4$ : adsorption isotherm at T = 344.26 K for a slit-shaped pore with H = 40 Å. The dotted lines represent the hysteresis loop of the DFT adsorption isotherm.

condensation at approximately  $p^{\text{pt}} = 7.6$  bar. This phase transition leads to a discontinuity in the composition in the pore and therefore to a discontinuity in the selectivity, as seen in Fig. 3.10. A maximum in selectivity is observed at p = 0.105 bar (MC approach). Because IAST takes the MC results for pure substances as input, it is in good agreement at low pressures. In the limit of zero pressure it is exact. For increasing pressure the deviations in selectivity are increasing. A kink in  $S_{2,1}$  is found at  $p^{\text{pt}}$ , which is related to the integration in eq. (3.26) over the discontinuity of the *n*-butane adsorption isotherm. The capillary condensation, however, is qualitatively not described by IAST. For the DFT approach, the pressure-value of the  $S_{2,1}$  maximum is well predicted (p = 0.1158 bar), but the selectivity is significantly underestimated for the low pressure region. That is a result of deviations in the prediction of pure *n*-butane (Fig. 3.8). The deviations between DFT and GCMC results for low pressures are related to the different molecular models and thus somewhat different external potentials of *n*-butane in both approaches. For high



Figure 3.10: Comparison between results obtained from DFT, IAST, and GCMC for a methane-*n*-butane mixture at  $y_{\text{Me}} = 0.4$ : selectivity of *n*-butane at T = 344.26 K for a slit-shaped pore with H = 40 Å. The dotted lines represent the hysteresis loop of the DFT adsorption isotherm.

pressures, the adsorbed amount and selectivities obtained from DFT and GCMC are in very good agreement and  $p^{\text{pt}}$  is accurately predicted.

The adsorption isotherms for a bulk phase mole fraction  $y_{\rm Me} = 0.8$  are presented in Fig. 3.11. The adsorption selectivities for *n*-butane are visualized in Fig. 3.12. The mixture of the methane-n-butane is supercritical in the bulk fluid phase at these conditions, whereas the porous system undergoes a phase transition at approximately  $p^{\text{pt}} = 29$  bar. The observations above for another composition are also made for this system: The DFT results underestimate the adsorbed amount (Fig. 3.11) and underestimate the adsorption selectivity at low pressures (Fig. 3.12). For high pressures the DFT predictions provide quantitative agreement with results obtained from the MC approach. Also the phase transition is very satisfactorily described by the DFT model. IAST shows again good agreement at lower and moderate pressures, but deviates for higher pressures in  $\rho^{\text{pore}}$ and  $S_{2,1}$  from results of molecular simulations. IAST underestimates the position of the phase transition ( $p^{\text{pt}} = 18.6 \text{ bar}$ ) and is not qualitatively able to reproduce the discontinuous nature of the *n*-butane-selectivity at the phase transition. For the results shown in Figs. 3.11 and 3.12, IAST calculations are only possible for pressures lower than approximately 36 bar, because the adsorption isotherm of pure *n*-butane required in eq. (3.26) is limited up to  $p_{\rm MC}^{\rm sat} = 8.284$  bar.



Figure 3.11: Comparison between results obtained from DFT, IAST, and GCMC for a methane-*n*-butane mixture at  $y_{\text{Me}} = 0.8$ : adsorption isotherm at T = 344.26 K for a slit-shaped pore with H = 40 Å. The dotted lines represent the hysteresis loop of the DFT adsorption isotherm.



Figure 3.12: Comparison between results obtained from DFT, IAST, and GCMC for a methane-*n*-butane mixture at  $y_{\text{Me}} = 0.8$ : selectivity of *n*-butane at T = 344.26 K for a slit-shaped pore with H = 40 Å. The dotted lines represent the hysteresis loop of the DFT adsorption isotherm.

# 3.4 Conclusion

This study analyzes a density functional theory (DFT) approach for the prediction of adsorption processes of pure substances and mixtures of spherical and non-spherical molecular species. A recently published Helmholtz energy functional [88] was applied to multicomponent adsorption isotherms and selectivities in the framework of classical density functional theory (DFT). Results from grand canonical and transition matrix Monte Carlo molecular simulations were used to evaluate the DFT results. The results show the excellent predictive capabilities of the DFT model for pure component and mixture systems. Convincing agreement in terms of adsorbed amounts and selectivities was found for a Lennard-Jones model system, where results for a slit-shaped and a cylindrical pore geometry were compared. A more realistic methane-*n*-butane system showed capillary condensations that lead to discontinuities in the adsorption isotherms and selectivities. The position and the magnitude of capillary condensations are accurately predicted by the DFT model for pure *n*-butane and for mixture systems. Due to different molecular models of *n*-butane in the DFT and the MC approach, deviations for lower pressures were observed, but for higher pressures deviations vanish and good agreement was seen. For comparison, results obtained from the Ideal Adsorbed Solution Theory (IAST) were added for mixture systems, confirming good results for the entirely predictive DFT formalism.

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# Chapter 4

# Prediction of Contact Angles and Density Profiles of Sessile Droplets Using Classical Density Functional Theory Based on the PCP-SAFT Equation of State

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Copyright 2019 AMERICAN CHEMICAL SOCIETY. In comparison to the published work, the abstract is here omitted. Additions or deletions compared to the published work are marked with angular brackets. It should be noted that the first version of section "4.5. Experimental Method" was originally written by coauthor Dr.-Ing. Alexandros Terzis.

# 4.1 Introduction

A variety of technical applications require accurate predictions of wetting properties such as interfacial tensions or contact angles. Macroscopic approaches lose accuracy for small droplets or bubbles adhering to a solid surface. One reason is that the thickness of the vapor-liquid, solid-liquid, and solid-vapor interfaces increases relatively when the droplet size decreases. The assumption that the system is composed of solid, vapor, and liquid bulk phases separated by infinitely thin interfaces then loses validity. A proper description of small droplets requires detailed information about the shape of the interfaces as characterized by the the single-particle densities within the interface. Classical density functional theory (DFT) is a promising approach for this type of applications because it provides accurate single-particle densities for relatively small computational costs. We refer to the literature for mathematical background and recent developments of DFT [1–4].

DFT has been applied extensively to two typical cases: planar vapor-liquid interfaces (for example to calculate macroscopic surface tensions) and planar solid-fluid interfaces (e.g., to calculate adsorption isotherms or the thickness of liquid films). The study of sessile droplets is more demanding as it requires a Helmholtz energy functional that provides accurate descriptions of all occurring types of interfaces: vapor-liquid, solidliquid, solid-vapor and solid-liquid-vapor. The implementation of DFT also increases in complexity as the sessile droplet system cannot, like in the two planar cases, be simplified to a one-dimensional problem.

DFT is derived in the grand canonical ensemble [1], and equilibrium density profiles are calculated by minimizing the grand potential function  $\Omega$  for given temperature T, volume V, and chemical potential  $\mu$ . For open systems containing a droplet at a supersaturated state, the grand potential exhibits a maximum [5] for the critical radius  $R_0$  of the droplet. Therefore, a straightforward application of DFT to systems containing a droplet leads to a full evaporation if the droplet radius R is smaller than a critical radius  $R_0$ , whereas for R > 1 $R_0$  the droplet grows until the system is completely filled by the liquid phase. A droplet with  $R = R_0$  (critical nucleus) is associated with a metastable state. The application of DFT to a droplet system with  $R = R_0$  exhibits a saddle point of  $\Omega$  over iteration steps, which has been depicted graphically by Zeng and Oxtoby [6]. A closed system containing a droplet at given T, V and number of molecules N is thermodynamically stable for appropriate conditions. This state is defined by the canonical ensemble and can be found by minimizing the Helmholtz energy. For homogeneous nucleation, Lee et al. [5] calculated droplet systems with DFT by fixing the number of molecules using  $\mu$ as a Lagrange multiplier. Although this approach does not strictly lead to a canonical ensemble DFT [7–10], the obtained density profiles are in good agreement with results obtained from molecular dynamics [11].

The observation that a droplet in an open system is not thermodynamically stable holds for droplets completely surrounded by vapor as well as for droplets in contact with a planar solid substrate [12], that is, sessile droplets. To our knowledge, the first DFT study on sessile droplets was presented by Talanquer and Oxtoby [12]. Similar to Lee et al. [5], a Lagrange multiplier was introduced to fix the number of molecules in the system. The resulting system could be interpreted as enclosed by a cylindrical container with perfectly nonwetting-nondrying walls that do not lead to discontinuities in the density profile between the inner and the outer side of the wall [13]. In ref 12 a van der Waals fluid was studied, and the Helmholtz energy functional was modeled using a square-gradient approximation, analogously to Cahn [14]. The solid structure was assumed planar, and the solid-fluid interactions were defined by a density-dependent contribution [15]. The resulting model was used to investigate the rate of heterogeneous nucleation and the accuracy of classical nucleation theory. In subsequent works, Talanquer and co-workers studied nucleation phenomena in slit-shaped [16] and cylindrical pores [17], as well as on (and between) cylindrical plates [18].

Several working groups applied a lattice gas implementation of DFT (LDFT) to obtain equilibrium density profiles of sessile droplet systems. Doshi et al. [19] used LDFT [20] to interpret results for water droplets in contact with superhydrophobic surfaces obtained from neutron reflectivity experiments. Also, liquid droplets on superhydrophobic surfaces were studied by Porcheron and Monson [21]. The stability of surface nanobubbles was investigated by Liu and Zhang [22]. Guo et al. [23] and Malanoski et al. [24] studied the behavior of droplets on nanorough surfaces. Hughes et al. [25] used an LDFT model to calculate binding potentials for the effective interface Hamiltonian model and applied it to sessile droplet systems. In a subsequent work [26], a DFT based on the modified fundamental measure theory (FMT) [27, 28] and the mean-field approximation was applied to determine binding potentials.

Berim and Ruckenstein [29] used a residual Helmholtz energy functional separated into a repulsive contribution, modeled via a smoothed density approximation [30], and an attractive contribution in the mean-field approximation. The resulting density profiles are two-dimensional in Cartesian coordinates, which leads to infinitely elongated droplets (in a cylindrical shape). Density contours as obtained from the density profiles were used to calculate contact angles of the droplets. Comprehensive studies of the effects of geometrical [31–33] and chemical [33, 34] inhomogeneities of the solid substrate on the contact angle have also been presented. The effect of gravitational forces on the shape of the droplet was taken into account by Berim and Ruckenstein [35]. In subsequent works, specific substrate properties such as a hidden roughness [36] and a lubricant layer [37] were examined. Furthermore, the dependence of the contact angle on temperature and on parameters of the interaction potential was determined, and a general expression was proposed to describe this dependence for nanodroplets [38] and macroscopic droplets [39]. Also, bumplike droplets were regarded in a study of stable and metastable density profiles in slit-shaped pores for pure component [40] and mixture systems [41].

In addition to these two-dimensional implementations, heterogeneous nucleation of a droplet on a solid surface was studied in a three-dimensional implementation by Zhou et al. [42]. Applying DFT in the grand canonical ensemble, the evolution of the system during the DFT iteration process starting from an initial density profile was studied. The physical significance of the density profiles observed during the iteration process still needs to be shown. The residual Helmholtz energy functional was modeled using FMT [27, 28] for the repulsive contribution, whereas a weighted density approximation (WDA) has been used for the attractive contribution [43]. The resulting energy barriers and critical radii were presented. In a subsequent work, line tensions, contact angles and Tolman lengths were studied [44], and the effect of surface roughness on the wettability was investigated [45].

The effect of surface roughness was also examined by Malijevskỳ [46], who evaluated the prediction of Wenzel's law: that an increase of surface roughness leads to an increase in wettability of the fluid. The number of particles was constrained to a fixed value using a Lagrange multiplier, and the Helmholtz energy functional consists of a FMT [47, 48] and a mean-field approach for the repulsive and attractive contribution, respectively. A corrugated surface was modeled by introducing rectangular pillars, and the two-dimensional Cartesian implementation leads to cylindrical droplets. The results show that microscopic surface roughness always diminishes the wettability, which contradicts Wenzel's law. The phenomenological force-balance relation of the Cassie-Wenzel transition was studied by Tretyakov et al. [49] using a three-dimensional implementation of DFT and a squaregradient approximation. Droplets on chemically heterogeneous surfaces were targeted very recently by Malijevskỳ et al. [50].

In the DFT-related literature, droplet systems are often modeled using simplified models for the Helmholtz energy functional, such as a mean-field approach or a square-gradient approximation, since the focus is more directed to study the qualitative behavior of sessile droplet systems. The Helmholtz energy functional applied in this study is based on the perturbed-chain polar statistical associating fluid theory (PCP-SAFT) [51] Equation of State (EoS). Functionals based on the PCP-SAFT model were seen to predict the surface tension of pure components [52, 53] and of mixtures [54, 55] with good agreement to experimental data. More recently, two authors of this study proposed a simple weighted density form of a Helmholtz energy functional for dispersive interactions [56], where good agreement was found for liquid-fluid and for solid-fluid interfaces. Thermodynamic quantities of homogeneous systems are accurately described by PCP-SAFT, which makes the model an appropriate choice for a Helmholtz energy functional. SAFT models [57, 58] use the first-order thermodynamic perturbation theory (TPT1) developed by Wertheim [59–62]. We refer to reviews [63–67] and to a review of Wertheim's theory [68] for further details.

In this work, we assess how a Helmholtz energy functional based on the PCP-SAFT model [56] predicts single-particle density profiles and contact angles of droplet systems on solid surfaces. Monte Carlo (MC) molecular simulations for Lennard-Jones and ethane nanodroplets are conducted to serve as a quasi-exact reference whereby the DFT is applied without adjustable parameters. In contrast to many previous publications that

apply DFT to sessile droplet systems, this work studies droplets of spherical instead of elongated, cylindrical shape. Furthermore, the extrapolation to larger droplets is studied and compared to results obtained from Young's equation. For several organic components and water, we report experimental contact angles on Teflon solids and compare DFT calculations to this data set.

# 4.2 Simulation Details

Molecular simulations are here conducted to serve as an exact reference (within their statistical uncertainties) for DFT calculations. The solid surface is represented as a potential field toward the considered fluid. The DFT is applied with the same input so that no adjustable parameters are present that may lead to ambiguity in comparing between DFT results and molecular simulations. Monte Carlo (MC) simulations were carried out in the canonical ensemble with a fixed number of molecules  $N^{\rm MC}$ , volume V, and temperature T. The geometric shape of the system is depicted in Figure 4.1. The simulation box is



Figure 4.1: Schematics of the system sizes and geometric definitions.

cubic with the sizes  $L \equiv L_x = L_y = L_z$  and the origin of the coordinate system is at the center of the xy-plane at the bottom of the box. The semi-infinite solid wall is located at  $-\infty < z < 0$  and the solid-fluid interactions are modeled using an external potential  $V^{\text{ext}}$  that depends only on z due to the perfectly planar shape of the solid phase. Truncated Lennard-Jones and Mie potentials are used for molecular simulations in this work. Large values of cutoff radii are chosen to recover behavior of the full, nontruncated potentials. A study of appropriate cutoff radii is presented in the section 'Results and Discussion'.

At initialization, a cubic liquid phase is placed at the center of the empty box to shorten the duration of the equilibration phase. The inserted liquid phase is a product of a preceding NVT simulation at the same temperature. Translational and orientational (if the molecule is nonspherical) MC moves [69] are performed with equal probability. Penetration moves of molecules into the solid phase are not allowed and are rejected. Periodic boundary conditions are not reasonable in z-direction, and a move of a molecular interaction site out of the box at  $z = L_z$  is also rejected, which makes the region at  $z \ge L_z$  a perfectly planar hard-wall. Only in x- and y-direction periodic boundary conditions and the nearest image convention are applied. First trials showed that a high number of equilibration moves is required to find a sufficiently equilibrated configuration for the production phase. We have chosen 500 000 MC cycles for the equilibration phase, where 1 MC cycle consists of  $N^{\rm MC}$  MC moves for Lennard-Jones and 2  $N^{\rm MC}$  MC moves for ethane molecules.

The most important observables of the MC simulation are the density profile and the contact angle, which can be defined on the basis of the density profile. We assume that the averaged distribution of molecular interaction sites during the production phase is rotationally symmetric around a symmetry axis and that therefore the density profile depends only on z and r of a cylindrical coordinate system. Within an MC calculation, where no system momentum is preserved, like in molecular dynamics simulations, the location of the symmetry axis shifts randomly with progression of the simulation. The location of the symmetry axis is redetermined throughout the simulation by averaging the positions of all molecules in the volume  $0 < z < 0.5 L_z$ . The density profile is obtained by counting the positions of the molecular interaction sites in two-dimensional bins, where axial length  $L_z$  and radial length  $L_r = 0.5 L_x$  are separated in 300 and into 75 bins, respectively. Centering of the droplet axis and sampling of the positions of all molecular interaction sites are done every MC cycle.

The sampling of an accurate droplet density profile from molecular simulations is tedious because the droplets are often asymmetrical and their shape can change substantially during the simulation [70]. We have chosen 500 000 MC cycles for the production phase to average different droplet shapes and to generate reliable density profiles. We furthermore found a significant effect of the maximum displacement  $\Delta x_{\max}$  value on the results. Setting a 50 % acceptance ratio for displacement moves, a small  $\Delta x_{\max}$  value is gained during the equilibration phase because most molecules are densely packed in the liquid phase or next to the solid surface. For simulations using this small value for  $\Delta x_{\max}$ an accumulation of molecules in the vapor phase next to the hard surface at  $z = L_z$  was observed. We assume that the unphysical accumulation of particles results from insufficient number of MC steps during the equilibration phase. Setting the maximum displacement to a fixed value  $\Delta x_{\max} = 0.01 L_x$  for the equilibration and production phases solved the problem. The value 0.01  $L_x$  lies between maximum displacement values of homogeneous vapor and homogeneous liquid phases. This problem could also be addressed following the propositions made by Han [71].

# 4.3 Classical Density Functional Theory

### 4.3.1 Helmholtz Energy Functional

In this work, we use the model presented in ref 56 and refer to the original work for detailed information. The residual part of the Helmholtz energy  $F^{\text{res}} = F - F^{\text{id}}$ , with  $F^{\text{id}}$  as the ideal gas contribution, is separated into contributions analogously to the PCP-SAFT [51] EoS

$$F^{\text{res}}\left[\rho(\mathbf{r})\right] = F^{\text{hs}}\left[\rho(\mathbf{r})\right] + F^{\text{hc}}\left[\rho(\mathbf{r})\right] + F^{\text{disp}}\left[\rho(\mathbf{r})\right] + F^{\text{assoc}}\left[\rho(\mathbf{r})\right] + F^{\text{dp}}\left[\rho(\mathbf{r})\right]$$
(4.1)

where the abbreviations hs, hc, disp, assoc, and dp denote the hard-sphere, chain, dispersion, association, and dipolar contribution, respectively. The density profile  $\rho(\mathbf{r})$  within the square brackets indicate that F is a functional of  $\rho(\mathbf{r})$  with  $\mathbf{r}$  as spatial vector. The comparison of DFT results to molecular simulations is done for pure components with only van der Waals attraction, i.e. without dipolar and association contributions. For comparing DFT contact angles with experimental values, however, components that exhibit hydrogen bonds (association) or dipolar interactions are considered. For more information about the Helmholtz energy contributions, we refer to the original literature: see Roth et al. [27] and Yu and Wu [28] for  $F^{\rm hs}$ , Tripathi and Chapman [72, 73] for  $F^{\rm hc}$ , Sauer and Gross [56] for  $F^{\rm disp}$ , Yu and Wu [74] for  $F^{\rm assoc}$ , and Gross and Vrabec [75] with the weighted density approximation as described in ref 56 for  $F^{\rm dp}$ .

## 4.3.2 DFT Implementation

DFT is an efficient approach to quantify the inhomogeneity of a fluid by calculating singleparticle density profiles for given T, V, and chemical potential  $\mu$ . The density profiles are obtained by minimizing the functional  $\Omega_V$ 

$$\Omega_V[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int \rho(\mathbf{r}) \{ V^{\text{ext}}(\mathbf{r}) - \mu \} \mathrm{d}\mathbf{r}$$
(4.2)

The external potential  $V^{\text{ext}}(\mathbf{r})$  describes the interactions between the solid phase and an interaction site at location  $\mathbf{r}$  of a fluid molecule. In the equilibrium state,  $\Omega_V$  is minimal with respect to the density profile  $\rho(\mathbf{r})$ , and at the minimum,  $\Omega_V$  is the grand potential  $\Omega$ . Setting the first functional derivative of  $\Omega_V$  to zero leads to the Euler-Lagrange equation for the equilibrium single-particle density of the grand canonical case

$$\rho(\mathbf{r}) = \frac{1}{\Lambda^3} \exp\left(\beta\mu - \frac{\delta\beta F^{\text{res}}}{\delta\rho(\mathbf{r})} - \beta V^{\text{ext}}(\mathbf{r})\right)$$
(4.3)

where we introduced the first derivative of the ideal gas contribution

$$\frac{\delta\beta F^{\rm rd}}{\delta\rho(\mathbf{r})} = \ln\left(\rho(\mathbf{r})\Lambda^3\right) \tag{4.4}$$

where  $\beta = (kT)^{-1}$ , k is Boltzmann's constant, and  $\Lambda$  is the de Broglie wavelength.

We follow the idea of constraining the number of molecules by introducing a Lagrange multiplier [5, 12], knowing that this approach does not exactly lead to a canonical ensemble [7–10]. Differences between this constrained DFT and a (hypothetically existing) true canonical DFT appear for small confined systems, but should be negligible for large systems containing thousands of molecules. The number of molecules in the system is calculated as

$$N = \int \rho(\mathbf{r}) \mathrm{d}\mathbf{r} \tag{4.5}$$

and eq. (4.3) needs to be solved subject to the constraint in eq. (4.5). Inserting eq. (4.3) in eq. (4.5) gives

$$N = \frac{1}{\Lambda^3} \exp\left(\beta\mu\right) \int \exp\left(-\frac{\delta\beta F^{\rm res}}{\delta\rho(\mathbf{r})} - \beta V^{\rm ext}(\mathbf{r})\right) d\mathbf{r}$$
(4.6)

Reorganizing eq. (4.6) to eliminate  $\mu$  in eq. (4.3) leads to the Euler-Lagrange equation of the constrained grand canonical ensemble [46]

$$\rho(\mathbf{r}) = \frac{N \exp\left(-\frac{\delta\beta F^{\text{res}}}{\delta\rho(\mathbf{r})} - \beta V^{\text{ext}}(\mathbf{r})\right)}{\int \exp\left(-\frac{\delta\beta F^{\text{res}}}{\delta\rho(\mathbf{r})} - \beta V^{\text{ext}}(\mathbf{r})\right) d\mathbf{r}}$$
(4.7)

We solve this equation iteratively, using a damped direct substitution scheme (Picard iteration) for given T, V, and N.

The DFT simulation corresponds to the cylindrical system shown within the cube in Figure 4.1 with the sizes  $L_r$  and  $L_z$ . The density profile for negative z values is set to zero. Neumann boundary conditions are applied at the boundary  $z = L_z$  and at both r-boundaries r = 0 and  $r = L_r$ . The starting profile is defined by a liquid density within a hemisphere of an appropriate radius around the origin and a vapor density elsewhere, where both densities correspond to the vapor-liquid equilibrium densities for given T, calculated with PCP-SAFT.

To produce comparable MC and DFT results, we have to ensure that the number of molecules in both systems is identical. Obviously, the number of molecules in the cylinder N has to be smaller than the number of molecules in the cube  $N^{\text{MC}}$ . In the DFT calculation, we subtract the excess of molecules from  $N^{\text{MC}}$  by assuming that the density profile at  $r = L_r$  is homogeneous along the r-direction, which is a good assumption if the system is sufficiently large. For a given density profile, the number of molecules in the cylinder is then

$$N = N^{\rm MC} - (4 - \pi)L_r^2 \int_{z=0}^{L_z} \rho(z, r = L_r) \mathrm{d}z$$
(4.8)

This equation is solved simultaneously with eq. (4.7) to calculate the equilibrium density profile. Similar to Boţan et al. [76], Fourier and Hankel transforms are used to solve the set of equations efficiently. More details are provided in the Supporting Information.

# 4.4 Determination of Contact Angles from MC and DFT

The following method for the contact angle calculation is mostly similar to the methods presented by Peng et al. [77]. DFT and MC simulations provide density profiles as density values over a discretized z and r space. In a first step, a density contour curve  $r_{\rm iso}$  as a function of z is determined. It describes the isodensity line over space where  $\rho(z, r_{\rm iso}) =$  $\rho_{\rm div}$  holds, with  $\rho_{\rm div}$  as the dividing density defined as the arithmetic mean of the bulklike liquid density and the density of the surrounding supersaturated vapor.  $r_{\rm iso}$  is determined for every z discretization point by interpolating the r coordinate for the given density profile.

In a second step, a circular function is defined

$$r(z) = \sqrt{R^2 - (z - z_0)^2} \tag{4.9}$$

The parameters  $z_0$  and R are adjusted so that eq. (4.9) matches  $r_{\rm iso}$ . The contact angle is then defined over the slope of the circular function at position z = 0. In some cases, the droplet shape is rather nonspherical and the parameter adjustment does not lead to a satisfying representation of  $r_{\rm iso}$ . We therefore follow the argumentation of Ruckenstein and Berim [29] and their definition of an upper  $\theta_u$  and a lower contact angle  $\theta_l$ . Both contact angles are distinguished by the fitting data of the circular function:  $\theta_u$  is obtained by using  $r_{\rm iso}(z)$  in the region  $z > 5 \sigma_{\rm ff}$  and  $\theta_l$  by using  $r_{\rm iso}(z)$  in the interval  $5 \sigma_{\rm ff} > z > 2.5 \sigma_{\rm ff}$ for the adjustment procedure.

Different from macroscopic droplets (in continuum approximation), contact angles of nanodroplets are not clearly defined. Due to the diffuse interfaces, the sharp kink approximation cannot be applied [29]. Furthermore, the value of the contact angle depends to some extent on the calculation method because these methods contain some ambiguity. For example, elliptic or polynomial functions instead of eq. (4.9) lead to deviating values [77]. Also, the choice of the dividing density  $\rho_{iso}$  and the fitting region for  $\theta_u$  or  $\theta_l$ affect contact angle values. Santiso et al. [70] reported a deviation of 5° or more depending on the choice of the contact line. Therefore, a comparison between contact angles calculated from different methods should be conducted carefully. In our work, contact angles obtained from MC and DFT density profiles are determined using the same method and are therefore comparable.

# 4.5 Experimental Method

Contact angles of various polar and nonpolar liquids on a polytetrafluoroethylene (PTFE, Teflon) substrate were experimentally determined in this work. The solid was selected to effectively exhibit only van der Waals type attractive interactions with the fluid substances. That is advantageous in assessing the DFT formalism (in particular the Helmholtz energy functional) used in this work because the solid material can then be only characterized by a single dispersive energy parameter (assuming Berthelot-Lorentz combining rules). The possible ambiguity in characterizing the solid material with other attractive interaction parameters that determine local dipole moments or hydrogen bonds (association) is thus avoided, and the comparison of results from the DFT to experimental data allows for a meaningful assessment of the DFT functional.

A circular Teflon piece of 10 mm thickness and 25 mm diameter was ultrasonically cleaned in absolute ethanol and water for 3 min., removing oil residuals from the surface. Then, the Teflon substrate was completely wetted with isopropanol, which was directly evaporated at ambient conditions by applying smoothly oil-free compressed air. Therefore, any contact of the PTFE substrate with cleaning fibers or other chemicals was avoided. The repeatability of the cleaning process was evaluated using distilled water as a probe liquid, providing an average contact angle of  $115.3^{\circ}(\pm 2.4\%)$ .

The wettability of the liquids on the PTFE substrate was evaluated with an OCA-15EC measuring device from DataPhysics Instruments. Sessile drops of approximately  $4 \,\mu\text{L}$  were deposited on a solid surface using a 1 mL Hamiltin syringe with a flat needle of 0.25 mm inner diameter. The sessile drops were generated by placing the needle, initially, very close to the solid. Then, the dispense process was initiated at a rate of  $0.5 \,\mu\text{L}/\text{s}$ . During the dispense process of the liquid, the syringe was vertically traversed upward ensuring rather symmetric droplets. The geometric postprocessing of the images was performed with various polynomial fitting approaches [78, 79], depending on the wettability of the droplet. We refer to an earlier work [80] for more detailed information regarding the experimental methodology.

## 4.6 **Results and Discussion**

This section starts with an analysis of the required cutoff radius. Then, a comparison between DFT and MC results for Lennard-Jones and ethane nanodroplets is presented. Subsequently, the extrapolation of DFT results to macroscopic sessile droplets is analyzed. We emphasize that all DFT results are predictively produced. PCP-SAFT parameters of real substances were adjusted to bulk phase properties such as liquid densities and vapor pressures and are taken from the literature [51, 75]. The only adjustable parameter in this work appears in the last part of this section, where we compare DFT results to experiments. Here, the external potential, characterizing Teflon, was adjusted to the contact angle of an *n*-octane droplet. The same external potential was subsequently used to predict contact angles of various other components. PCP-SAFT and force field parameters are summarized in the Supporting Information.

### 4.6.1 Cutoff Radii in MC Simulations

We here determine the effect of the cutoff  $r_c$  on sessile droplet systems for a Lennard-Jones potential

$$\phi_{\rm ff}(r) = \begin{cases} 4\varepsilon_{\rm ff} \left[ \left( \frac{\sigma_{\rm ff}}{r} \right)^{12} - \left( \frac{\sigma_{\rm ff}}{r} \right)^6 \right] & \text{if} \quad r < r_c \\ 0 & \text{if} \quad r \ge r_c \end{cases}$$
(4.10)

We assume argon as a representative example and set the interaction parameters to  $\sigma_{\rm ff} = 3.405$  Å and  $\varepsilon_{\rm ff}/k = 119.86$  K [81]. We define the external potential between the solid phase and an argon atom as

$$V^{\text{ext}}(z) = \frac{\varepsilon_{\text{sf}} \sigma_{\text{sf}}^3 \rho_{\text{s}}}{45} \left[ 2 \left( \frac{\sigma_{\text{sf}}}{z} \right)^9 - 15 \left( \frac{\sigma_{\text{sf}}}{z} \right)^3 \right]$$
(4.11)

with the solid density  $\rho_{\rm s} = 0.1137 \,\text{\AA}^{-3}$ . For simplicity, we set  $\sigma_{\rm sf} = \sigma_{\rm ff}$  and  $\varepsilon_{\rm sf} = \xi \varepsilon_{\rm ff}$ , with  $\xi$  as a measure for the solid-fluid attraction. No cutoff for the external potential was defined; hence, the solid surface acts in the entire system. We further defined the edge length as  $L = 210 \,\text{\AA}$ , number of argon molecules as  $N^{\rm MC} = 5000$ , and the temperature  $T = 0.7 \varepsilon_{\rm ff}/\text{k}$ . Density profiles were determined for different dimensionless cutoff radii  $r_c^* = r_c/\sigma_{\rm ff}$  with  $\xi = 1.3$ . Contour curves obtained from these profiles are depicted in Figure 4.2. All contour curves are smooth where the influence of the solid surface is small and show a wavy behavior next to the surface due to undulations in the density profiles. Contact angles obtained from the contour curves are shown in Figure 4.3. The results show that  $r_c^*$  has a significant effect on the droplet shape and on the contact angle. Especially the contact angles of the  $r_c^* = 2.5$  and 5 droplets deviate strongly from each other (about 17°). Furthermore, the comparison with the  $r_c^* = 20$  droplet in Figures 4.2



Figure 4.2: Contour curves of an argon droplet at  $T = 0.7 \varepsilon_{\rm ff}/{\rm k}$  obtained from MC simulations for different cutoff radii:  $r_c^* = 20$  (continuous curve), 5 (dashed), and 2.5 (dashed-dotted) for  $\xi = 1.3$ .



Figure 4.3: Upper and lower contact angles for varying cutoff radii for  $\xi = 1.3$ . The dashed lines serve as a guide for the eye.

and 4.3 shows that the  $r_c^* = 5$  droplet is not an accurate representation of a nontruncated Lennard-Jones droplet. The differences between the contact angles of the  $r_c^* = 10$ , 15 or 20 droplets are within the typical standard deviation of the molecular simulation data. The error that occurs due to truncation at a certain  $r_c^*$  value is not exactly available, and therefore some ambiguity lies in the choice of an appropriate  $r_c^*$ . Nevertheless, the results indicate that  $r_c^* = 20$  is an accurate approximation for a sessile droplet system of a nontruncated Lennard-Jones fluid. Hence, we chose  $r_c^* = 20$  for all MC simulations in this work.

#### 4.6.2 Comparison between DFT and MC

#### 4.6.2.1 Lennard-Jones Droplets

For the comparison with MC simulation data, the same Lennard-Jones parameters are chosen for the DFT calculation, that is, we define  $m_i = 1$ ,  $\sigma_i = \sigma_{\rm ff}$ , and  $\varepsilon_i = \varepsilon_{\rm ff}$  as the appropriate PCP-SAFT parameters for a Lennard-Jones argon. One should note that PCP-SAFT does not exactly reproduce Lennard-Jones properties and therefore some inaccuracies are introduced by using PCP-SAFT with  $m_i = 1$ . However, the deviations are relatively small and can be quantified [56] as 1.20 and 2.65% in vapor pressure and liquid density, respectively.

The input variables of the DFT calculation are defined analogously to the MC input variables:  $T = 0.7 \varepsilon_i/k$ , the number of argon molecules is  $N^{\rm MC} = 5000$ , the system sizes are L = 210 Å and  $L_r = 105$  Å, and the external potential from eq. (4.11) is used with  $\rho_{\rm s} = 0.1137$  Å<sup>-3</sup>,  $\sigma_{\rm sf} = \sigma_i$ , and  $\varepsilon_{\rm sf} = \xi \varepsilon_i$ . Eq. (4.7) is solved iteratively for  $\xi = 1.3$ and provides the equilibrium density profile as well as, according to eq. (4.8), the actual number of molecules in the cylindrical system: N = 4854.6.

In Figure 4.4 we compare the contour curves obtained from DFT and MC results. As



Figure 4.4: Comparison between results obtained from DFT and MC for an argon droplet for  $\xi = 1.3$ : contour curves.

for the MC result, the DFT contour is smooth at the vapor-liquid interface region and is wavy in the vicinity of the solid surface, although less wavy compared to the MC contour. The slope of the DFT contour in the three-phase contact region is slightly lower, which leads to a smaller lower contact angle ( $\theta_l^{\text{DFT}} = 89.0^{\circ}$  compared to  $\theta_l^{\text{MC}} = 94.6^{\circ}$ ) and a smaller upper contact angle ( $\theta_u^{\text{DFT}} = 86.6^{\circ}$  compared to  $\theta_u^{\text{MC}} = 91.6^{\circ}$ ). A closer look at the vapor-liquid interface is depicted in Figure 4.5, for normal coordinate z = 34 Å. We have chosen z = 34 Å, where the contour curves obtained from DFT and MC results



Figure 4.5: Comparison between results obtained from DFT and MC for an argon droplet for  $\xi = 1.3$ : density profiles in *r*-direction at z = 34 Å.

are in good agreement, to allow a comparison of the shape of the profiles. Note that the size of cylindrical bins depends on r and therefore the MC density profile shows a poor statistical quality for small r values. Neglecting this region, the density profiles are in good agreement. Because of the nonlocal character of the proposed DFT, a slightly oscillatory behavior [82] is visible in the liquid phase. Figure 4.6 presents density profiles in z-direction at r = 17.5 Å, where the density profile go through the liquid phase and where the statistical quality of the MC profile is acceptable. The profile exhibits typical undulations observed for a liquid phase on a planar solid surface, and the vaporliquid interface looks similar to Figure 4.5. At r = 17.5 Å the droplet size is slightly underestimated, but overall the DFT prediction is in very good agreement with MC data. The density profiles through the vapor phase in z-direction at r = 55 Å are shown in Figure 4.7. Both are in good agreement, in particular, because through constraining the number of particles, the density of the supersaturated vapor is not known a priori but is a result of the calculation.

Furthermore, we compare DFT and MC contact angles in Figure 4.8. The presented results were calculated under the same conditions as defined above but with varying attractive interaction parameter  $\xi$  (which scales the solid-to-fluid interactions). Upper



Figure 4.6: Comparison between results obtained from DFT and MC for an argon droplet for  $\xi = 1.3$ : density profiles in z-direction at r = 17.5 Å.



Figure 4.7: Comparison between results obtained from DFT and MC for an argon droplet for  $\xi = 1.3$ : density profiles in z-direction at r = 55.3 Å.

and lower contact angles show the physically correct behavior. For low values of  $\xi$ , the droplet is completely nonwetting, and for high  $\xi$  the fluid is completely wetting the surface. In between, the contact angle decreases monotonously with  $\xi$  and can be approximated by a linear function [33, 38]. The DFT predictions are in very good agreement with the results from MC simulations. Figure 4.8 shows also results obtained from Young's equation in combination with DFT calculations (see eqs. (4.18) and (4.19)) that represent contact



Figure 4.8: Upper and lower contact angles of argon droplets as functions of  $\xi$  at  $T = 0.7 \varepsilon_{\rm ff}/\rm k$ , where  $\xi$  scales the solid-fluid interactions: comparison between DFT and MC. Contact angles from Young's equation according to eqs. (4.18) and (4.19).

angles of macroscopic droplets. The results show that contact angles of nanodroplets differ mostly from contact angles of macroscopic droplets in the limits  $\theta \to 0^{\circ}$  and  $\theta \to 180^{\circ}$ . For high  $\xi$  values, the contour of the nanodroplet adopts a more flat and pancakelike shape and therefore the determination of the contact angle via a circular function loses validity and leads to increased deviations between  $\theta_u^{\text{DFT}}$  and  $\theta_l^{\text{DFT}}$ .

#### 4.6.2.2 Ethane

In this section, we study the predictive capabilities of the Helmholtz energy functional for a more realistic fluid. We regard an ethane droplet on a graphite-like surface. PCP-SAFT parameters for ethane were taken from ref 51. Different from the Lennard-Jones system studied in previous sections, the chain contribution in the Helmholtz energy functional does not vanish for ethane as the segment number parameter  $m_i$  is greater than unity. MC simulations were performed using the transferable anisotropic Mie (TAMie) [83] force field. As shown in ref 83, the TAMie force field parametrization for ethane provides very accurate descriptions of experimental densities and vapor pressures. Ethane is modeled as two Mie-interaction sites connected with a bond of constant length. Considering the results in Figure 4.3 on varying cutoff lengths, we decided to truncate the Mie potential at  $r_c^* = 20$ .

We apply the 10,4,3 potential proposed by Steele [84] to model the interactions between the planar graphite-like surface and the fluid. The external potential is defined between the solid surface s and a segment  $\alpha$  of the fluid molecule

$$V_{\mathrm{s}\alpha}^{\mathrm{ext}}(z_{\alpha}) = 2\pi\rho_{\mathrm{s}}\varepsilon_{\mathrm{s}\alpha}\sigma_{\mathrm{s}\alpha}^{2}\Delta\left[\frac{2}{5}\left(\frac{\sigma_{\mathrm{s}\alpha}}{z_{\alpha}}\right)^{10} - \left(\frac{\sigma_{\mathrm{s}\alpha}}{z_{\alpha}}\right)^{4} - \frac{\sigma_{\mathrm{s}\alpha}^{4}}{3\Delta\left(z_{\alpha} + 0.61\Delta\right)^{3}}\right]$$
(4.12)

with  $z_{\alpha}$  as the position of segment  $\alpha$  on the z coordinate. As solid parameters, we use [84, 85]:  $\sigma_{ss} = 3.40 \text{ Å}$ ,  $\varepsilon_{ss} = 28.0 \text{ K}$ ,  $\Delta = 3.35 \text{ Å}$ , and  $\rho_s = 0.114 \text{ Å}^{-3}$ . Adding the potentials of all segments in a molecule gives the external potential between the surface and the entire molecule

$$V^{\text{ext}} = \sum_{\alpha}^{N_i} V_{\text{s}\alpha}^{\text{ext}}(z_{\alpha})$$
(4.13)

with  $N_i$  as the number of segments in molecule *i*.

Eq. (4.13) applied to the presented DFT simplifies to  $V^{\text{ext}} = N_i V_{\text{si}}^{\text{ext}}(z_i)$ , because the underlying Helmholtz energy functional model does not distinguish between segments of a molecule, that is, between segment density profiles. This is an assumption introduced in the chain contribution [52, 56]. Furthermore, PCP-SAFT defines the segment number as  $m_i$ , which leads intuitively to  $V^{\text{ext}} = m_i V_{\text{si}}^{\text{ext}}(z)$ . The interaction parameters for  $V_{\text{si}}^{\text{ext}}$  are defined using Lorentz-Berthelot combining rules

$$\sigma_{\rm si} = \frac{1}{2} \left( \sigma_{\rm ss} + \sigma_{ii} \right) \tag{4.14}$$

$$\varepsilon_{\rm si} = \xi \sqrt{\varepsilon_{\rm ss} \varepsilon_{ii}} \tag{4.15}$$

with  $m_i$ ,  $\sigma_{ii}$ , and  $\varepsilon_{ii}$  as PCP-SAFT pure component parameters for ethane [51] and  $\xi$  as a measure for the solid-fluid attraction.

Eq. (4.13) applied to MC simulations lead to  $V^{\text{ext}} = V^{\text{ext}}_{\text{s,CH}_3}(z_{\alpha}) + V^{\text{ext}}_{\text{s,CH}_3}(z_{\beta})$ , where the distinction between the two methyl interaction sites  $\alpha$  and  $\beta$  is taken into account. For the potential  $V^{\text{ext}}_{\text{s,CH}_3}$ , again, Lorentz-Berthelot combining rules are used

$$\sigma_{\rm s,CH_3} = \frac{1}{2} \left( \sigma_{\rm ss} + \sigma_{\rm ff}^{\rm TAMie} \right) \tag{4.16}$$

$$\varepsilon_{\rm s,CH_3} = \xi \sqrt{\varepsilon_{\rm ss} \varepsilon_{\rm ff}^{\rm TAMie}}$$
(4.17)

with parameters of a methyl interaction site,  $\sigma_{\rm ff}^{\rm TAMie}$  and  $\varepsilon_{\rm ff}^{\rm TAMie}$ , from ref 83.

DFT and MC density profiles are calculated for  $N^{\rm MC} = 3000$ , T = 200 K, and L = 200 Å as the edge length of the cubic system. Since the MC simulation with the TAMie force field provides naturally the density distribution of methyl interaction sites and the DFT calculation leads to the distribution of ethane molecules, the MC density profile is divided by two to make DFT and MC profiles comparable. The contour curves for sessile droplets calculated from MC and from DFT are shown in Figure 4.9 for varying  $\xi$  values,

that is, for varying solid-fluid interactions. Good agreement of results from DFT with contour curves from MC is observed, especially for larger contact angles. Figure 4.10 shows contact angles of ethane droplets from DFT and MC simulations for the full range of contact angles. Predictions of contact angles from DFT are thereby in very good agreement with the values from MC simulations. In accordance with MC results, DFT determines a sessile droplet in the state of complete drying for  $\xi = 0.05$ . With increasing values of the solid-fluid interaction parameter  $\xi$  the droplets become increasingly flat and the presented calculation method of contact angles loses accuracy (for DFT and MC) because a decreasing circular segment ( $z > 5 \sigma_{\rm ff}$  for  $\theta_u$  and  $z > 2.5 \sigma_{\rm ff}$  for  $\theta_l$ ) can be used for the parameter adjustment of eq.(4.9). Furthermore, the increasing atomic layering inside the liquid phase due to undulations limits a reliable determination of contact angles. Weijs et al. [86] suggested a lower limit for contact angles at approximately 70°.

The good agreement of the DFT results for the Lennard-Jones fluid and for ethane with the results from molecular simulations supports on the one hand that the presented Helmholtz energy functional has a very strong predictive capability for solid-fluid interfaces and for vapor-liquid interfaces. On the other hand, the results indicate that DFT applied with a Lagrange multiplier is an suitable approach for studying these kinds of systems in the canonical ensemble, that is, with a fixed molecule number, temperature, and volume.

#### 4.6.3 Size Dependence of Contact Angles for Sessile Droplets

In this section, we examine whether the DFT results for contact angles extrapolate correctly to macroscopic droplet sizes. For macroscopic sessile droplets, the size of the vapor-liquid, solid-liquid, and solid-vapor interfaces is very small compared to the droplet size, and interfaces can therefore be approximated as infinitely thin (sharp interface approximation). Then, Young's equation is valid for planar solid surfaces

$$\gamma_{\rm sv} = \gamma_{\rm sl} + \gamma_{\rm vl} \cos \theta^{\rm macro} \tag{4.18}$$

with  $\gamma_{\rm sv}$ ,  $\gamma_{\rm sl}$ , and  $\gamma_{\rm vl}$  as the solid-vapor, solid-liquid, and vapor-liquid surface tensions, respectively. Similarly to van Giessen et al. [87] and Ancilotto et al. [88], we obtain all three surface tensions from the presented DFT for planar interfaces, that is, for a onedimensional DFT implementation: the equilibrium density profile of the planar interface that separates the corresponding bulk phases a and b is determined by solving eq. (4.3). With the resulting density profile, the grand potential per unit area  $\Omega_{\rm ab}/A$  is calculated from eq. (4.2). The thermodynamic relation between the grand potential and the surface



Figure 4.9: Contour curves obtained from DFT (continuous curve) and MC (symbols) for ethane droplets at T = 200 K and varying solid-fluid interaction strengths  $\xi$ : 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4.



Figure 4.10: Upper and lower contact angles of ethane droplets as functions of  $\xi$  at T = 200 K: comparison between DFT and MC. Contact angles from Young's equation according to eqs. (4.18) and (4.19).

tension for planar interfacial systems is

$$\gamma_{\rm ab} = \frac{\Omega_{\rm ab}}{A} + L_z p \tag{4.19}$$

where p is the pressure of both bulk phases and  $L_z$  is the system length of the onedimensional DFT calculation. The surface tensions of the planar interface can be used in eq. (4.18) by introducing the capillarity approximation [89], which is accurate for macroscopic droplets. For highly curved interfaces of small droplets, the surface tension is known to deviate from the value of planar, macroscopic systems. The curvature-dependent surface tension is usually expressed in terms of the Tolman length. A study on the the Tolman length for the Helmholtz energy functional considered in this study was recently presented by Rehner and Gross [90].

We calculate  $\theta^{\text{macro}}$ , for argon and the external potential from eq. (4.11) based on the corresponding parameters listed in Section 4.6.1. The solid-fluid prefactor is  $\xi =$ 1.3, and the temperature is  $T = 0.7 \varepsilon_{i}/k$ . Using PCP-SAFT, the related macroscopic vapor-liquid equilibrium defines the vapor pressure  $p^{\text{sat}} = 0.5815$  bar, the liquid density  $\rho_{l}^{\text{sat}} = 0.02085 \text{ Å}^{-3}$ , and the vapor density  $\rho_{v}^{\text{sat}} = 5.131 \cdot 10^{-5} \text{ Å}^{-3}$ . With this information, all three planar interface surface tensions are calculated from DFT and eq. (4.19) for a system with  $L_z = 150 \text{ Å}$  and  $p = p^{\text{sat}}$ , leading to  $\gamma_{vl} = 14.28 \text{ mN/m}$ ,  $\gamma_{sl} = -0.8152 \text{ mN/m}$ , and  $\gamma_{sv} = -0.1136 \text{ mN/m}$ , respectively. Negative parameters for the solid-fluid surface tensions have also been reported by other groups [39, 87, 88]. With Young's equation, the upper contact angle  $\theta^{\text{macro}}$  is determined as 87.18°.

Several sessile droplet DFT calculations were performed for different system sizes L and numbers of molecules  $N^{\text{MC}}$ . The resulting contact angles are presented in Figure 4.11. The



Figure 4.11: Upper and lower contact angles of argon droplets as functions of the reciprocal droplet radius at  $T = 0.7 \varepsilon_{\rm ff}/\rm k$ : DFT results (symbols) and linear correlations (continuous curves).

conditions of the various DFT results are specified in detail in the Supporting Information. We obtained the droplet radii R from the parameter adjustment of the circular function in eq. (4.9). The results indicate a linear trend; therefore, a linear correlation was adjusted to the  $\theta_u$  and  $\theta_l$  DFT data, respectively. The calculated results from DFT, although analytic, show some nonsmooth behavior in Figure 4.11, which is not caused by numerical noise in the results, but is caused by the undulations in the density profiles. The extrapolation of the inverse droplet radius to droplets of infinite size  $(R^{-1} \rightarrow 0)$  leads to  $\theta_u^{\text{macro}} = 83.93^{\circ}$  and  $\theta_l^{\text{macro}} = 87.24^{\circ}$ , where especially  $\theta_l^{\text{macro}}$  is very close to the upper contact angle obtained from Young's equation ( $\theta_l^{\text{macro}} = 87.18^{\circ}$ ). We therefore conclude that the calculation of contact angles using a two-dimensional DFT density profile and the contour curve adjustment is consistent with the Young's equation approach.

One should note that the largest droplet calculated with the presented DFT implementation exhibits a radius of about 100 Å. The main restriction to compute larger droplets is, besides limited RAM, the logarithmical version of the Hankel transform: for higher rvalues, the resolution decreases drastically and therefore a proper representation of the vapor-liquid interface is limited to smaller r values. An equidistant version of the Hankel transform would minimize this problem, and significantly larger droplets would be available for DFT calculations.

### 4.6.4 Comparison between DFT and Experimental Data

We proceed by comparing results from DFT with experimental data for various substances. The experimentally deposited droplet consists of a pure substance and, in the state of a sessile droplet, is surrounded by air at ambient pressure and  $T \approx 298.15$  K. For all studied liquids, contact angles and the corresponding standard deviations are presented in a tabular format in the Supporting Information.

For the DFT calculation we use Young's equation, as described in Section 4.6.3: the surface tensions  $\gamma_{\rm sv}$ ,  $\gamma_{\rm sl}$ , and  $\gamma_{\rm vl}$  are calculated using a one-dimensional DFT implementation and eq. (4.19). Subsequently, the contact angle is calculated using eq. (4.18). To accurately model the experimental setting, we define a three-component system consisting of nitrogen, oxygen, and the considered substance. Nitrogen and oxygen PCP-SAFT pure component parameters as well as the nitrogen-oxygen binary parameter were taken from Stoll et al. [91]. We used PCP-SAFT pure component parameters of *n*-hexane, *n*-heptane, *n*-nonane, *n*-dodecane, and toluene from Gross and Sadowski [51]. Pure component parameters of diiodomethane were adjusted to vapor pressure and liquid density data compiled in the DIPPR database [92] for a fixed dipole moment also from ref 92. The parameters of ethylene glycol and water (parameter set W4C<sub>-</sub>1) were obtained from Klink et al. [93] and Liang et al. [94], respectively. No binary parameter except for the  $k_{ij}$  parameter between nitrogen-oxygen was used. PCP-SAFT was used to calculate the vapor-liquid phase equilibrium conditions at T = 298.15 K, p = 1.013 bar, and at a ratio of nitrogen-oxygen mole fraction of 78:21 in the vapor phase to model the typical composition of air. Calculated properties are given in the Supporting Information. We assume that the PTFE (Teflon) substrate is perfectly planar. The effective (planar) PTFE-fluid interactions are not known a priori, and therefore the solid-fluid interactions are modeled using  $V^{\text{ext}}(z) = 2\pi m_i V_{\text{s}i}^{\text{ext}}(z)$  and eq. (4.11) for  $V_{\text{s}i}^{\text{ext}}$  with the fixed parameters  $\rho_{\text{s}} = 0.08 \text{ Å}^{-3}$ and  $\sigma_{\rm ss} = 3.0$  Å. We use Lorentz-Berthelot combining rules  $\sigma_{\rm sf} = 0.5 (\sigma_{\rm ss} + \sigma_{ii})$  and  $\varepsilon_{\rm sf} = \sqrt{\varepsilon_{\rm ss}\varepsilon_{ii}}$  with  $\sigma_{ii}$  and  $\varepsilon_{ii}$  as PCP-SAFT pure component parameters and with  $\varepsilon_{\rm ss}$  as an adjustable parameter for the effective planar PTFE-fluid interactions. Because the experimental contact angle of *n*-octane on Teflon has the smallest standard deviation, we adjusted  $\varepsilon_{\rm ss}$  to this contact angle, leading to  $\varepsilon_{\rm ss}/k = 72.39$  K. We used this value to predict the contact angles of a macroscopic sessile droplet for eight other solvents.

Figure 4.12 compares contact angles of all solvents on PTFE (Teflon) predicted from the DFT with experimental data determined in this work. We regard nonpolar fluids (alkanes from *n*-hexane to *n*-dodecane and toluene), an aprotic polar solvent (diiodomethane), as well as ethylene glycol and water as strongly hydrogen-bonding solvents. Figure 4.12 shows a surprisingly good agreement of predicted contact angles with experimental values even for the most polar and hydrogen-bonding fluids. That is an important finding because it suggests that the distribution of van der Waals attraction to polar and hydrogen-bonding Helmholtz energy functionals (in Eq. (4.1)) is meaningful because simple Berthelot-Lorentz combining rules can otherwise not be expected to lead to reasonable contact angles with a nonpolar solid substrate, which offers only van der Waals attraction. For the hydrogen-bonding substances, ethylene glycol and water, the Helmholtz energy functional of Yu and Wu [74] was taken into account to model associative interactions. Dipolar interactions were considered in the Helmholtz energy functional for diiodomethane and ethylene glycol using the weighted density approximation described in ref 56. The DFT applied to the *n*-hexane droplet predicts a state of complete wetting on the PTFE surface, which is in agreement with the experiment.



Figure 4.12: Comparison between contact angles as obtained from DFT and experiments at ambient pressure and  $T = 25 \,^{\circ}\text{C}$  and for various components.

Moreover, the good agreement of predicted contact angles with experimental values suggests that, first, a real solid substrate can be modeled as a perfectly planar surface with effective interactions toward the solvent and, second, that the concept of characterizing these effective interactions through an interaction potential (eq. (4.11)) with an effective solid-to-solid interaction parameter  $\varepsilon_{ss}$  in combination with Berthelot-Lorentz combining rules is a suitable concept for predicting the behavior of real solid-to-fluid systems.

The DFT results demonstrate that the proposed Helmholtz energy functional is able to predict the contact angle of complex inhomogeneous systems with good quantitative agreement with experimental data.

## 4.7 Conclusion

Density functional theory (DFT) with a recently developed Helmholtz energy functional [56] was applied to sessile droplets. The DFT problem is formulated in a cylindrical coordinate system. Molecular simulations of Lennard-Jones and of ethane nanodroplets on planar solid substrates with varying solid-fluid interaction potentials were performed in order to assess the DFT formalism and the Helmholtz energy functional. For both systems, Lennard-Jones and ethane nanodroplets, we find excellent agreement of DFT calculations with results from molecular simulations. We conclude that using Lagrange multipliers to constrain the number of molecules within DFT, thus mimicking a canonical ensemble, is a successful concept. We show that contact angles for nanodroplets of different sizes as calculated from DFT extrapolate to the contact angle of macroscopic droplets. Predicted upper contact angles of an argon model system were shown to compare accurately to those obtained from Young's equation using surface energies obtained from one-dimensional DFT calculations as input.

DFT calculations were compared to experimental results obtained in this work for the contact angle of various liquids in ambient air on a solid Teflon surface. We observe excellent agreement with experimental data, even for polar and hydrogen-bonding fluids. Our work suggests that the Teflon surface can be regarded as a perfectly planar solid with an effective solid-fluid interaction potential. We find that simple Berthelot-Lorentz combining rules can be applied between various solvents and the solid substrate, whereby an effective solid-to-solid interaction potential is assigned to the solid substrate. A single parameter of this effective solid-to-solid interaction potential was adjusted (here to the contact angle of n-octane on Teflon), which was then applied to all other solvents.

This study demonstrates the capability of the DFT formalism (and the here applied Helmholtz energy functional) to predict contact angles and density profiles of rather complex molecular fluids in good quantitative agreement with experimental data.

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### Chapter 5

### Conclusion

In this thesis, a Helmholtz energy functional based on the PCP-SAFT equation of state for use in Classical Density Functional Theory (DFT) is proposed. Two variants of a dispersion contribution to the Helmholtz energy functional were developed using the weighted density approximation. A model parameter, characterizing the effective range of the van der Waals attractions, was adjusted to experimental data of pure n-alkane surface tensions with equivalent accuracy. The superior variant showed excellent parameter transferability when applied to solid-fluid interface systems.

The Helmholtz energy functional earlier presented by Gross [Gross, J. J. Chem. Phys. **2009**, 131(20), 204705] for pure components and extended by Klink and Gross [Klink, C.; Gross, J. Ind. Eng. Chem. Res. **2014**, 53(14), 6169–6178] for mixtures uses a dispersion functional based on a perturbation approach for inhomogeneous systems and predicts interfacial tensions of various systems accurately. However, the application of the functional to solid-fluid interfaces is limited, due to the locally defined correction term in the dispersion contribution that ensures consistency with PCP-SAFT. The substitution of the dispersion contribution with the model based on the weighted density approximation proposed in this thesis removed this limitation. Despite of the rather strong assumptions introduced via the weighted density approximation, the model shows excellent predictive capabilities.

For various applications and systems the accuracy and predictive capability of the model was examined. Interfacial tensions of non-polar-non-associating and polar-associating components were studied and compared to experimental data. The application of the model to adsorption isotherms and adsorption selectivities of fluids in slit-shaped and cylindrical pores showed good agreement when compared with results obtained from Monte Carlo simulations. Nanodroplets and macroscopic droplets on planar solid surfaces were studied with respect to contact angles and confirmed the excellent predictive capability of the proposed model. In order to mimic systems with defined number of molecules (canonical ensemble), Lagrange multipliers within DFT were used to constraint the number of molecules. Results obtained for argon and ethane nanodroplets showed very good agreement to results from molecular simulations in canonical ensemble (i.e. with fixed number of molecules). Furthermore, the application of Fourier transforms lead to efficient solving of the model equations.

Comparisons were performed on three different levels: clearly defined but rather artificial systems, more realistic systems and real systems characterized by experimental data. Since precise results were obtained at all levels, the proposed functional is not only an appropriate model for clearly defined systems, such as Lennard-Jones mixtures, but also for realistic systems, like ethane in graphite-like pores or alkane droplets on PTFE surfaces. Therefore, DFT in combination with the proposed functional can be a powerful tool for engineering applications, especially when experimental data are scarce and predictiveness is required. Appendices

### Appendix A

### Supporting Information to Chapter 2

#### **PCP-SAFT** Pure Component Parameters

The pure component parameters of all components used in this work are presented in Table A.1. Also references are specified.

species $i$	$m_i$	$\sigma_i/[\text{Å}]$	$\varepsilon_i/k/[{ m K}]$	$\mu_i/[D]^a$	$ Q_i /[DÅ]^b$	$\varepsilon^{A_i B_i}/k/[{ m K}]$	$\kappa^{A_i B_i}$	$\operatorname{ref}$
methane	1.0000	3.7039	150.03					1
ethane	1.6069	3.5206	191.42					1
propane	2.0020	3.6184	208.11					1
butane	2.3316	3.7086	222.88					1
hexane	3.0576	3.7983	236.77					1
heptane	3.4831	3.8049	238.40					1
octane	3.8176	3.8373	242.78					1
dodecane	5.3060	3.8959	249.21					1
tridecane	5.6877	3.9143	249.78					1
pentadecane	6.2855	3.9531	254.14					1
hexadecane	6.6485	3.9552	254.70					1
octadecane	7.3271	3.9668	256.20					1
2,3-dimethylpentane <sup>c</sup>	3.0256	3.9452	251.63					-
dimethylether	2.2634	3.2723	210.29	1.30				2
diethylether	2.9726	3.5127	219.53	1.15				2
benzene	2.291	3.756	294.1		5.591			3
carbon monoxide (CO)	1.4358	3.1356	87.719	0.1098				4
tetrahydrofuran (THF)	2.4740	3.5137	274.182	1.6310				4
ethylene glycol	3.575	2.806	255.6	2.410		2476.9	0.126	3

Table A.1: Pure Component Parameters.  ${}^{a}D = 3.3356 \cdot 10^{-30} \text{ Cm}, {}^{b}D\text{\AA} = 3.3356 \cdot 10^{-40} \text{ Cm}^{2},$ c: Parameters adjusted to vapor pressure and liquid density data compiled in the DIPPR database [5]

We found an error in our earlier parametrization [3] for the binary system ethylene glycol - benzene. For this system, we now obtained:  $k_{ij} = 0.08207$ ,  $l_{ij} = -0.00395$ .

### Absolute Average Deviations of Pure Component Surface Tensions

The deviation from experimental data of the four components presented in Fig. (4) are listed in Table A.2.

$$AAD = \frac{1}{N_{\gamma}} \sum_{i=1}^{N_{\gamma}} \left| \gamma_i^{exp} - \gamma_i^{calc} \right|$$
(A.1)

species $i$	$N_{\gamma}$	AAD/mN/m
dimethylether	49	0.288
diethylether	49	0.303
2,3-dimethylpentane	13	0.105
benzene	27	0.155

Table A.2: Results from DFT predictions of pure component surface tensions.

#### **Density Profiles of Binary Vapor-Liquid Interfaces**

Fig. A.1, A.2 and A.3 show density profiles of the CO-methane system at T = 90.67 K. DFT calculation using the WDA1 variant.



Figure A.1: Density profiles of the vapor-liquid interface at  $x_{\rm CO}^{\rm liq} = 0.0202$  and p = 0.6 bar.



Figure A.2: Density profiles of the vapor-liquid interface at  $x_{\rm CO}^{\rm liq} = 0.4104$  and p = 1.2 bar.



Figure A.3: Density profiles of the vapor-liquid interface at  $x_{CO}^{liq} = 0.770$  and p = 1.9 bar.

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### Appendix B

### Supporting Information to Chapter 3

#### **PCP-SAFT** Parameters

The pure component parameters of all components used in this work are presented in Table B.1. Also references are specified. Used PC-SAFT binary parameter: methane-*n*-butane  $k_{ij} = 0.027777$  (adjusted to experimental data [1] at T = 344.26 K).

species $i$	$m_i$	$\sigma_{ii}/[\text{\AA}]$	$\varepsilon_{ii}/k/[{\rm K}]$	$\operatorname{ref}$
argon	1.0000	3.4050	119.80	2
krypton	1.0000	3.6300	163.10	3
methane	1.0000	3.7039	150.03	4
n-butane	2.3316	3.7086	222.88	4

Table B.1: Pure Component Parameters.

#### Force Field Parameters used in Monte Carlo Simulations

No binary parameters were used in Monte Carlo simulations. Lennard-Jones parameters for argon [2] :  $\sigma_{\rm ff} = 3.405 \,\text{\AA}, \, \varepsilon_{\rm ff}/k = 119.80 \,\text{K}$ Lennard-Jones parameters for krypton [3] :  $\sigma_{\rm ff} = 3.630 \,\text{\AA}, \, \varepsilon_{\rm ff}/k = 163.10 \,\text{K}$ Lennard-Jones parameters for methane [5] :  $\sigma_{\rm ff} = 3.7281 \,\text{\AA}, \, \varepsilon_{\rm ff}/k = 148.55 \,\text{K}$ TAMie parameters for *n*-butane [6] with individualization parameter [7]: • Mie potential CH<sub>3</sub>:  $\sigma_{\rm ff}^{\rm CH_3} = 3.6034 \,\text{\AA}, \, \varepsilon_{\rm ff}^{\rm CH_3}/k = 136.644 \,\text{K}, \, n = 14$ 

- Mie potential CH<sub>2</sub>:  $\sigma_{\rm ff}^{\rm CH_2}=4.0400\,{\rm \AA},\,\varepsilon_{\rm ff}^{\rm CH_2}/k=53.0403\,{\rm K},\,n=14$
- Bond lengths:  $r_0 = 1.74$  Å for CH<sub>3</sub>-CH<sub>2</sub> and  $r_0 = 1.54$  Å for CH<sub>2</sub>-CH<sub>2</sub>
- Bond angles:  $\Theta_0 = 114.0^{\circ}$  and  $k_{\Theta}/k = 62500 \text{ K}$  for  $\text{CH}_x\text{-CH}_2\text{-CH}_y$

• Torsional potential for  $CH_x$ - $CH_2$ - $CH_2$ - $CH_y$ :  $c_0/k = 0 \text{ K}, c_1/k = 355.03 \text{ K}, c_2/k = -68.19 \text{ K}, \text{ and } c_3/k = 791.32 \text{ K}$ 

#### Argon-Krypton Bulk Phase Isotherm

Deviations between the PC-SAFT and the Lennard-Jones model are studied at T = 290 K to increase the meaningfulness of comparisons between results obtained from DFT and MC for pore systems. Fig. B.1 compare the bulk phase densities obtained from TMMC simulations and PC-SAFT calculations for pure argon, pure krypton, and an argon-krypton mixture at mole fraction  $y_{\text{Ar}} = 0.7$ . The bulk densities are in very good



Figure B.1: Comparison between bulk densities obtained from PC-SAFT and TMMC for argon-krypton systems at T = 290 K. Left: pure argon and pure krypton isotherm. Right: argon-krypton mixture isotherm at  $y_{\rm Ar} = 0.7$ .

agreement for a wide pressure range. A small deviation of the PC-SAFT results for krypton is presumably observed due to the closer vicinity to the critical region: the critical temperatures and pressures are  $T_{\rm Ar}^c = 157.2 \,\mathrm{K}, T_{\rm Kr}^c = 214.0 \,\mathrm{K}, p_{\rm Ar}^c = 53.56 \,\mathrm{bar},$  and  $p_{\rm Kr}^c = 470.6 \,\mathrm{bar}$  (using the dimensionless critical temperature and pressure presented by Potoff and Panagiotopoulos [8]).

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### Appendix C

### Supporting Information to Chapter 4

#### **PCP-SAFT** Pure Component Parameters

The pure component parameters of all components used in this work are presented in Table C.1. Also references are specified. The PC-SAFT binary parameter used for nitrogenoxygen mixtures is  $k_{ij} = -0.0016$  [1].

species $i$	$m_i$	$\sigma_i/[\text{\AA}]$	$\varepsilon_i/k/[{ m K}]$	$\mu_i/[D]^a$	$\varepsilon^{A_i B_i}/k/[{ m K}]$	$\kappa^{A_i B_i}$	$\operatorname{ref}$
nitrogen	1.2365	3.2975	89.492				1
oxygen	1.1457	3.1711	113.98				1
argon	1.0000	3.4050	119.86				2
ethane	1.6069	3.5206	191.42				2
<i>n</i> -hexane	3.0576	3.7983	236.77				2
<i>n</i> -heptane	3.4831	3.8049	238.40				2
n-octane	3.8176	3.8373	242.78				2
<i>n</i> -nonane	4.2080	3.8448	244.51				2
n-dodecane	5.3060	3.8959	249.21				2
toluene	2.8149	3.7169	285.69				2
$diiodomethane^b$	2.371	3.6565	388.64	1.220			-
ethylene glycol	3.575	2.8060	255.60	2.410	2476.90	0.126	3
water $(W4C_1)$	1.500	2.6273	180.30		1804.22	0.180	4

Table C.1: Pure Component Parameters.  ${}^{a}D = 3.3356 \cdot 10^{-30}$  Cm,  ${}^{b}Parameters m_{i}$ ,  $\sigma_{i}$ , and  $\varepsilon_{i}$  adjusted to vapor pressure and liquid density data compiled in the DIPPR database [5] (dipole moment also from ref. [5]) that resulted in absolute average deviations of 0.19 % for liquid density and 1.59 % for vapor pressure data.

#### Force Field Parameters used in Monte Carlo Simulations

Lennard-Jones parameters for argon:  $\sigma_{\rm ff} = 3.405 \,\text{\AA}, \, \varepsilon_{\rm ff}/k = 119.86 \,\text{K}$ TAMie parameters for ethane methyl beads:  $\sigma_{\rm ff}^{\rm TAMie} = 3.6463 \,\text{\AA}, \, \varepsilon_{\rm ff}^{\rm TAMie}/k = 130.78 \,\text{K}, \, \text{repulsive exponent Mie potential } n = 14$ TAMie bond length between ethane methyl beads:  $r_0^{\rm TAMie} = 1.94 \,\text{\AA}$ 

#### **Experimental Contact Angles and Standard Deviations**

species $i$	contact angle / $^\circ$	standard deviation / $^{\circ}$
<i>n</i> -hexane	complete wetting	-
n-heptane	15.2	0.360
n-octane	23.2	0.224
<i>n</i> -nonane	27.3	0.570
n-dodecane	34.0	0.584
toluene	40.6	0.644
diiodomethane	86.9	1.022
ethylene glycol	96.5	0.200
water	115.3	0.885

Table C.2: Measured contact angles and standard deviations.

# PC-SAFT and DFT Results for Comparison with Experimental Data

species $i$	$x_{\mathrm{l},i}$	$x_{1,N_2}$	$x_{\mathrm{v},i}$	$x_{v,N_2}$	$\gamma_{\rm sv}/{\rm mN/m}$	$\gamma_{\rm sl}/{\rm mN/m}$	$\gamma_{\rm lv}/{\rm mN/m}$	$ heta_{ m macro}$ / °
<i>n</i> -hexane	0.99833	0.0009085	0.2028263	0.62913	-1.93510	-20.372	17.729	-
n-heptane	0.99720	0.0018953	0.0613779	0.73950	-0.74870	-19.813	19.470	11.716
n-octane	0.99705	0.0019839	0.0190079	0.77292	-0.34890	-19.649	20.999	23.200
<i>n</i> -nonane	0.99701	0.0020051	0.0059086	0.78328	-0.19410	-19.264	22.223	30.896
n-dodecane	0.99678	0.0021411	0.0001940	0.78779	-0.06990	-18.791	24.563	40.343
toluene	0.99847	0.0009829	0.0381912	0.75782	-0.20170	-18.454	24.563	42.006
diiodomethane	0.99953	0.0002652	0.0017800	0.78651	-0.04980	-12.158	53.352	76.883
ethylene glycol	0.99993	0.0000328	0.0001083	0.78778	-0.04210	10.868	62.777	100.01
water	0.99999	0.000066	0.0099586	0.78003	-0.04210	29.387	73.868	113.48

Table C.3: Composition of the liquid phase l and the vapor phase v of the three component system (O<sub>2</sub>, N<sub>2</sub>, and *i*) at T = 25 °C, p = 1.013 bar, and defined nitrogen-oxygen mole fraction ratio  $x_{N_2}/x_{O_2} = 78/21$ . Surface tensions of the planar solid-vapor, solid-liquid, and liquid-vapor interface and contact angle from Young's equation.

Size Depend	lency of	Sessile	Droplet	Systems
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$N^{\mathrm{MC}}$	$L_z/\text{\AA}$	$L_r/\text{\AA}$	$ ho^{ m V}/{ m \AA}^{-3}$	$ ho^{ m L}/{ m \AA}^{-3}$	S	$ heta_l/^\circ$	$ heta_u/^\circ$	$R_l/ m \AA$	$R_u/\text{\AA}$
40000	334	167	0.00005841	0.020966	1.138	87.975	85.142	99.858	101.146
20000	334	167	0.00006054	0.020754	1.180	88.087	85.386	77.518	78.646
10000	334	167	0.00006382	0.021183	1.244	88.319	85.778	58.247	59.212
10000	265	133	0.00006323	0.021166	1.232	88.608	86.069	61.115	62.081
5000	265	133	0.00006756	0.021751	1.317	88.974	86.642	45.590	46.399
5000	210	105	0.00006700	0.021946	1.306	88.967	86.52	48.220	49.078
2500	210	105	0.00007326	0.021287	1.428	89.382	87.311	35.783	36.450
5000	166	83	0.00006652	0.021922	1.297	88.899	86.455	49.458	50.324
2500	166	83	0.00007164	0.021590	1.396	89.253	87.111	38.136	38.839
1250	166	83	0.00008067	0.020860	1.572	89.826	88.174	27.980	28.474

Table C.4: Details of the DFT calculations performed to study the droplet size dependency on number of particles and system size. The vapor and liquid densities  $\rho^{\rm V}$  and  $\rho^{\rm L}$  are averaged values from the two-dimensional density profile. The supersaturation of the vapor phase is approximated as  $S = \rho^{\rm V}/\rho^{\rm V,sat}$  using the vapor density of a planar vapor-liquid interface at equilibrium  $\rho^{\rm V,sat} = 5.1309 \cdot 10^{-5} \text{ Å}^{-3}$  (PC-SAFT). Contact angle  $\theta$  and droplet radius R are results of the parameter adjustment of the circular function.

#### Fourier and Hankel Transforms

The costliest part in terms of calculation time in eq. (7) are the functional derivatives of  $F^{\text{res}}$ . Here, the most expensive calculations are convolutions of the type

$$h(\mathbf{r}_1) = \int g(\mathbf{r}_2) w_\alpha(|\mathbf{r}_1 - \mathbf{r}_2|) \mathrm{d}\mathbf{r}_2$$
(C.1)

with h as the convolution of a certain function g (e.g. the density profile) with a weighting function  $w_{\alpha}$  of type  $\alpha$ . In this work, it is advantageous to describe the three-dimensional space using a rotationally symmetric cylindrical coordinate system. Therefore, twodimensional convolutions are required (in z- and r-direction). To achieve an efficient implementation, the convolutions are calculated using the Fourier convolution theorem and the Fourier transform  $\mathscr{F}$  along the z-direction

$$\mathscr{F}{g}(k_z) = \int_{-\infty}^{\infty} g(z)e^{-izk_z} \mathrm{d}z \tag{C.2}$$

and the Hankel transform  $\mathscr{H}_{\nu}$  along the r-direction

$$\mathscr{H}_{\nu}\{g\}(k_r) = \int_0^\infty g(r) J_{\nu}(rk_r) r \mathrm{d}r \tag{C.3}$$

with *i* as the imaginary number,  $\nu$  as the order of the Hankel transform and  $J_{\nu}$  as Bessel function of the first kind. Using the Fourier convolution theorem, the convolution *h* is

$$h = \mathscr{F}^{-1}\{\mathscr{H}^{-1}_{\nu}\{\hat{g}\cdot\hat{w}_{\alpha}\}\}$$
(C.4)

where the hat symbolizes two-dimensionally transformed functions

$$\hat{g} = \mathscr{F}\{\mathscr{H}_{\nu}\{g\}\}$$
(C.5)

All required  $\hat{w}_{\alpha}$  are known analytically and are listed below. The Hankel transform of first order is required in eqs. (C.4) or (C.5), if a vector weighting function in *r*-direction  $(\hat{w}_{1r} \text{ or } \hat{w}_{2r}, \text{ see FMT [6]})$  is used. All other convolutions are calculated with the Hankel transform of zeroth order  $\mathscr{H}_0^{-1}$ . See Boţan et al. [7] for further information.

In our work, we use published codes of a Fast Fourier implementation [8] and a logarithmically discretized Fast Hankel implementation [9]. As pointed out by Hamilton [10], an improved application of the Fast Hankel implementation in terms of aliasing effects requires functions and transformed functions that go sensibly to zero at the boundaries. Similarly to Boţan et al. [7], we define auxiliary functions  $g^0$  using

$$g(z,r) = g^{0}(z,r) - g^{\text{end}}(z)$$
 (C.6)

where  $g^{\text{end}}$  is the background function at the largest value of r in the defined system. For the droplet system,  $g^0(z,r)$  tends properly to zero for all z discretization points (if the system is large enough) and is therefore suitable for the Fast Hankel implementation. With eq. (C.6) the transformation of function g separates into two terms

$$\hat{g}(k_z, k_r) = \mathscr{F}\{\mathscr{H}_0\{g^0(z, r) - g^{\text{end}}(z)\}\} = \hat{g}^0(k_z, k_r) - \frac{\delta(k_r)}{k_r}\mathscr{F}\{g^{\text{end}}(z)\}$$
(C.7)

where  $\delta$  is the Dirac delta function.

#### Weighting Functions

Transformed weighting functions  $\hat{w}_{\alpha}$  exist in analytical form. Knepley et al. [11] derived all  $\hat{w}_{\alpha}$  from FMT [6] and presented the correct evaluation of these. We recite the FMT weighting functions and add the analytic transforms of the chain and the dispersion contribution.

$$\hat{w}_2^{\rm hs}(k_z, k_r) = \frac{4\pi R}{|\mathbf{k}|} \sin(R |\mathbf{k}|) \tag{C.8}$$

$$\hat{w}_{3}^{\text{hs}}(k_{z},k_{r}) = \frac{4\pi}{|\mathbf{k}|^{3}} \left( \sin(R|\mathbf{k}|) - R|\mathbf{k}|\cos(R|\mathbf{k}|) \right)$$
(C.9)

with R = 0.5 d and d as the PCP-SAFT temperature-dependent segment diameter. In the cylindrical coordinate system the absolute value of the **k** vector is

$$\mathbf{k}| = \sqrt{k_z^2 + k_r^2} \tag{C.10}$$

The vector weighting functions in z- and r-direction of the FMT contribution are

$$\hat{w}_{2z}^{\rm hs}(k_z, k_r) = -ik_z \hat{w}_3^{\rm hs}(k_z, k_r) \tag{C.11}$$

$$\hat{w}_{2r}^{\rm hs}(k_z, k_r) = -ik_r \hat{w}_3^{\rm hs}(k_z, k_r) \tag{C.12}$$

respectively. Further FMT weighting functions result from other weighting functions multiplied by a prefactor, according to

$$\hat{w}_1^{\rm hs}(k_z, k_r) = \frac{\hat{w}_2^{\rm hs}(k_z, k_r)}{4\pi R} \tag{C.13}$$

$$\hat{w}_0^{\rm hs}(k_z, k_r) = \frac{\hat{w}_2^{\rm hs}(k_z, k_r)}{4\pi R^2} \tag{C.14}$$

$$\hat{w}_{1z}^{\rm hs}(k_z,k_r) = \frac{\hat{w}_{2z}^{\rm hs}(k_z,k_r)}{4\pi R} \tag{C.15}$$

$$\hat{w}_{1r}^{\rm hs}(k_z, k_r) = \frac{\hat{w}_{2r}^{\rm hs}(k_z, k_r)}{4\pi R} \tag{C.16}$$

The weighting functions of the chain and the dispersion contribution look qualitatively the same, but vary in the range of the weighting.

$$\hat{w}_2^{\rm ch}(k_z, k_r) = \frac{1}{d |\mathbf{k}|} \sin(d |\mathbf{k}|) \tag{C.17}$$

$$\hat{w}_{3}^{ch}(k_{z},k_{r}) = \frac{3}{d^{3} |\mathbf{k}|^{3}} \left( \sin(d |\mathbf{k}|) - d |\mathbf{k}| \cos(d |\mathbf{k}|) \right)$$
(C.18)

where  $\hat{w}_2^{\text{ch}}$  and  $\hat{w}_3^{\text{ch}}$  is the weighting function of the chain weighted density [12, 13]  $\lambda$  and  $\bar{\rho}^{\text{hc}}$ , respectively. The weighting function of the dispersion contribution is

$$\hat{w}_{3}^{\text{disp}}(k_{z},k_{r}) = \frac{3}{\psi^{3}d^{3}\left|\mathbf{k}\right|^{3}}\left(\sin(\psi d\left|\mathbf{k}\right|) - \psi d\left|\mathbf{k}\right|\cos(\psi d\left|\mathbf{k}\right|)\right) \tag{C.19}$$

with the universal parameter  $\psi = 1.3862$ .

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