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

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PCP-SAFT Parameters

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

Also references are specified.

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

species i	m_i	$\sigma_i/[\mathrm{\AA}]$	$\varepsilon_i/k/[\mathrm{K}]$	$\mu_i/[\mathrm{D}]^a$	$\lvert Q_i\rvert/[\mathrm{D\AA}]^b$	$\varepsilon^{A_iB_i}/k/[\mathrm{K}]$	$\kappa^{A_iB_i}$	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^c	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

We found an error in our earlier parameterization[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 2.

$$\mathrm{AAD} = \frac{1}{N_\gamma} \sum_{i=1}^{N_\gamma} \left| \gamma_i^{exp} - \gamma_i^{calc} \right| \tag{1}$$

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

species i	N_γ	AAD/mN/m
dimethylether	49	0.288
diethylether	49	0.303
2,3-dimethylpentane	13	0.105
benzene	27	0.155

Density Profiles of Binary Vapor-Liquid Interfaces

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

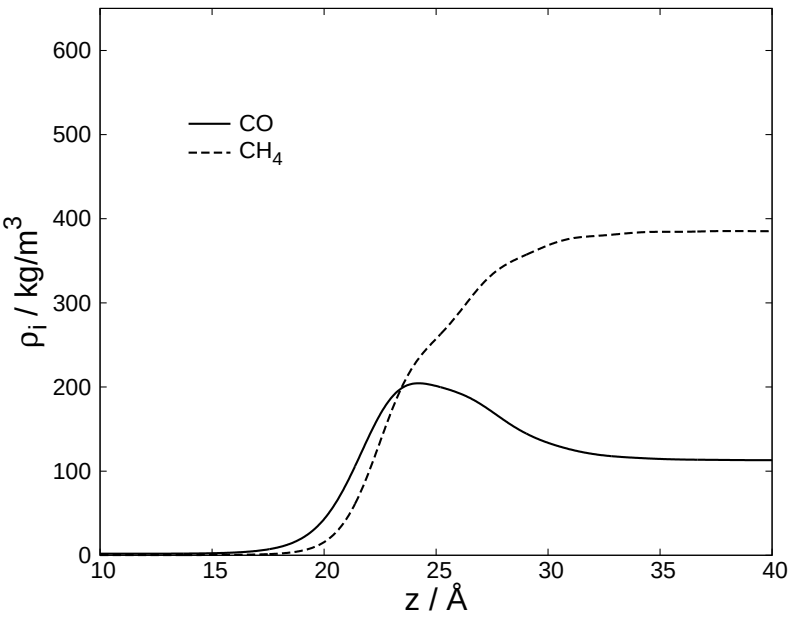

Figure 1: Density profiles of the vapor-liquid interface at $x_{\mathrm{CO}}^{\mathrm{liq}} = 0.0202$ and $p = 0.6\,\mathrm{bar}$.

References

(1) Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260.

(2) Gross, J.; Vrabec, J. An Equation-of-State Contribution for Polar Components: Dipolar Molecules. *AIChE J.* **2006**, *52*, 1194–1204.

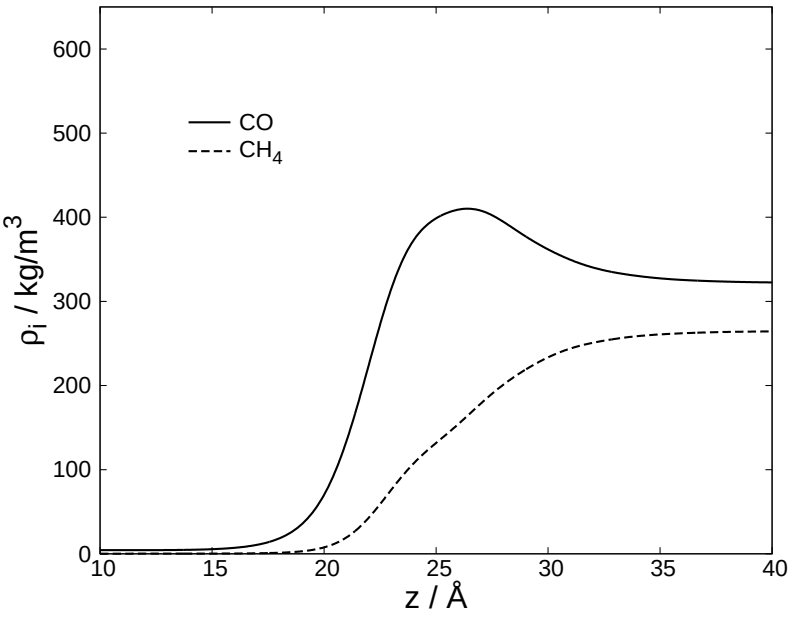

Figure 2: Density profiles of the vapor-liquid interface at $x_{\mathrm{CO}}^{\mathrm{liq}} = 0.4104$ and $p = 1.2\,\mathrm{bar}$.

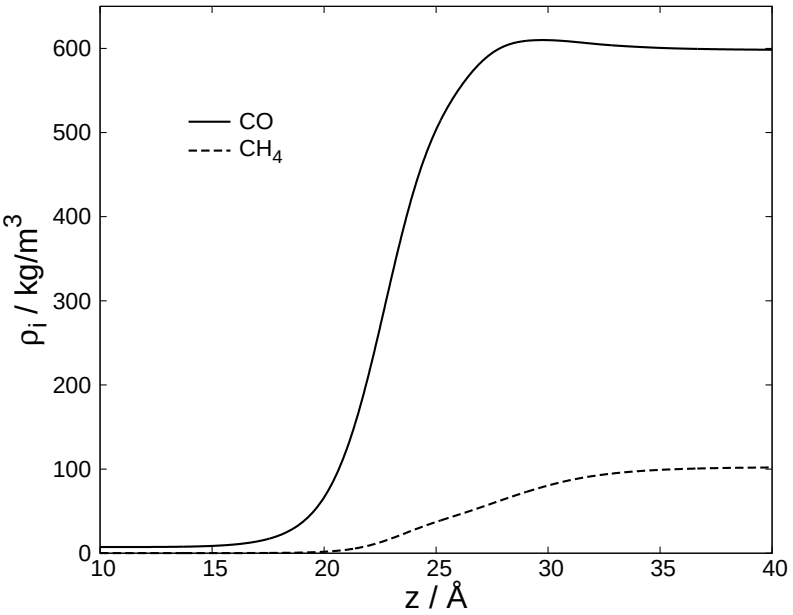

Figure 3: Density profiles of the vapor-liquid interface at $x_{\mathrm{CO}}^{\mathrm{liq}} = 0.770$ and $p = 1.9\,\mathrm{bar}$.

(3) Klink, C.; Planková, B.; Gross, J. Density Functional Theory for Liquid–Liquid Interfaces of Mixtures Using the Perturbed-Chain Polar Statistical Associating Fluid Theory Equation of State. *Ind. Eng. Chem. Res.* **2015**, *54*, 4633–4642.

(4) Klink, C.; Gross, J. A density functional theory for vapor–liquid interfaces of mixtures using the perturbed-chain polar statistical associating fluid theory equation of state. *Ind. Eng. Chem. Res.* **2014**, *53*, 6169–6178.

(5) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Yang, Y.; Zundel, N. A.; Daubert, T. E.; Danner, R. P. *DIPPR Data Compilation of Pure Chemical Properties* Design Institute for Physical Properties, AIChE: New York, NY, 2009.