Mathematical modeling of planar and spherical vapor-liquid phase interfaces for multicomponent fluids

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Introduction

Methods for accurate modeling of phase interfaces are important for understanding of natural processes and applications in technology such as carbon capture and storage (CCS). In particular, the prediction of non-equilibrium phase transitions requires a detailed knowledge of the structure of the phase interfaces. We focus on planar and spherical vapor-liquid phase interfaces for binary mixtures relevant to CCS.

Phase interface

Usually, the phase interface is modeled as infinitesimally thin, merely a mathematical surface dividing homogeneous bulk phases. However, for prediction of the phase interface properties, it is necessary to consider the detailed structure of the phase interface and the continuous transition of local properties between phases, occurring over a finite thickness of the phase interface. The phase interfaces are described by the density profiles of the individual system components. By the term "density profile" we understand density (or concentrations of individual components) depending on the spatial coordinate perpendicular to the phase interface (axial coordinate z or radius r).

Figure 1 shows planar and spherical phase interfaces from molecular dynamic simulations. The illustration is supplemented with the density profiles and data fits using hyperbolic tangent, which represents reasonable estimate for the density profile.
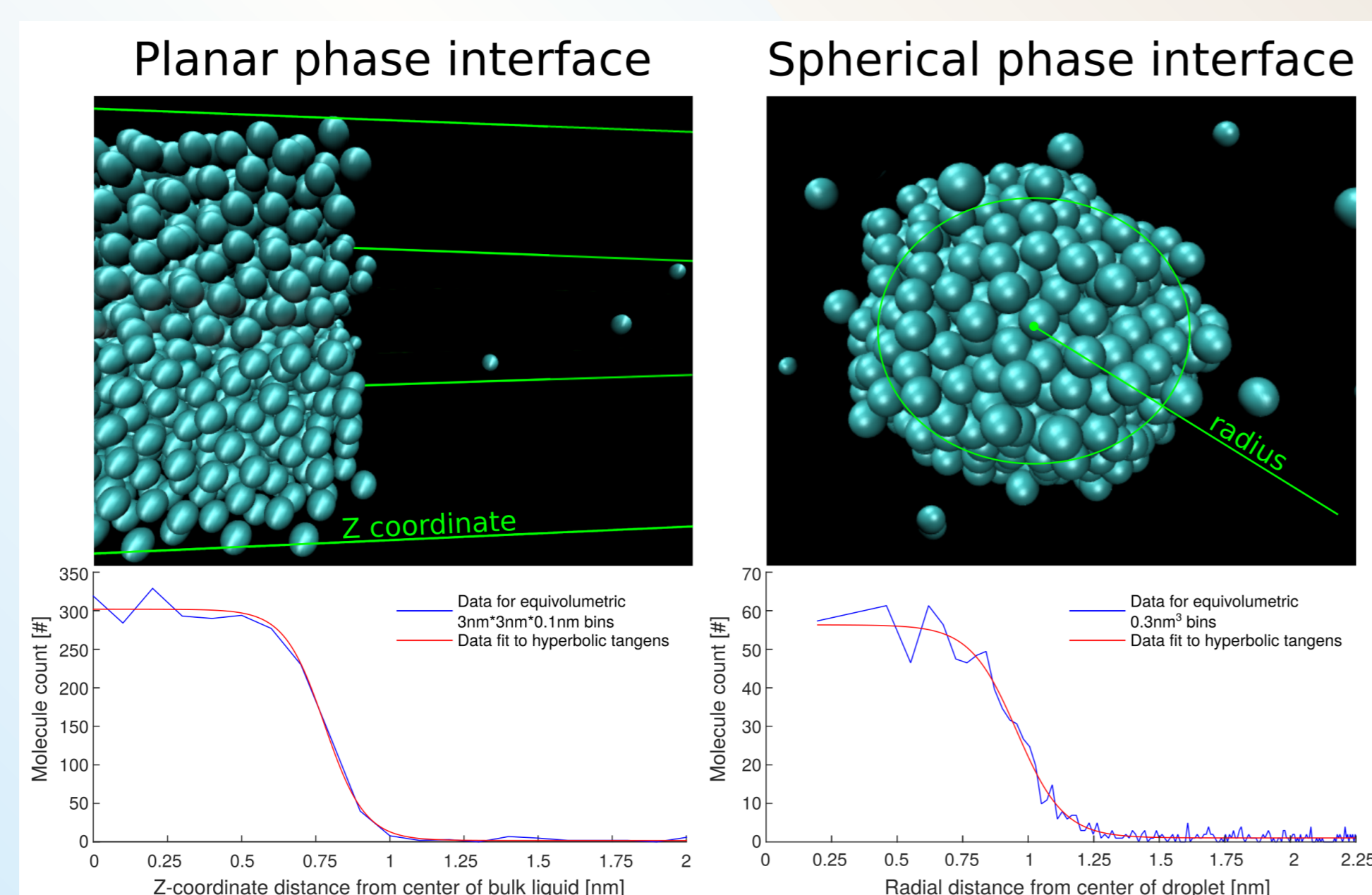

Figure 1: Illustration of two basic phase interface geometries and their corresponding density profiles with hyperbolic tangent data fits.

Modeled system

We have selected a system relevant for CCS is as a binary mixture of carbon dioxide CO_2 and n-butane C_4H_{10}. This choice reflects the effort of filtering carbon dioxide during natural gas processing. The second component (butane) was chosen for comparative purposes due to the lack of experimental data for the surface tension of binary mixtures of CO_2 and lighter alkanes.

The following table summarizes properties of selected substances. Thermophysical properties of the selected binary mixtures required in the computational method described below need to be modeled with the convenient equation of state (EOS). In our case, PC-SAFT EOS developed by Gross and Sadowski [3] was employed.

Component	$T_c[K]$	$P_c[MPa]$	$\rho_c[mol/m^3]$	$M[g/mol]$	Influence parameter $[J m^5/mol^2]$
CO_2	304.1282	7.3773	10624.9	44.0095	1.608E-19
C_4H_{10}	425.125	3.796	3922.769614	58.1222	2.398E-20

The surface tension of the CO_2 and C_4H_{10} mixture was investigated by Hsu et al. [5] at temperatures of 319 K, 344 K and 377 K. Brauer and Hough [1] have studied this system in the temperature range from 310 K to 352 K.

Computational method

The fundamentals of our method lie in the gradient theory (GT), which was proposed by Cahn and Hilliard [2] in 1958 as a tool to obtain the Helmholtz energy of an inhomogeneous system. The density profile is obtained by finding a stationary point of the grand potential for the inhomogeneous system. This theoretical formulation results in following system of Euler-Lagrange second order differential equations:

$$\sum_{i=1}^{n} c_{i,i}\left(\frac{2}{r}\rho_i' + \rho_i''\right) = \Delta\mu_k\left(\rho_1, \rho_2, \ldots, \rho_n\right), \; k \in \hat{n}. \tag{1}$$

Here $c_{i,j}$ is an element of influence parameter matrix, r is the radius, ρ_i stands for concentrations and $\Delta\mu_k$ is the chemical potential difference.

$$c_{i,j} = \sqrt{c_{i,i} \cdot c_{j,j}} \tag{2}$$

$$X = -\frac{\Delta\mu_1}{\sqrt{c_{1,1}}} \tag{3}$$

$$\tilde{\rho} = \frac{\sum_{i=1}^{n}\sqrt{c_{i,i}}\rho_i}{\sum_{i=1}^{n}\sqrt{c_{i,i}}} \tag{4}$$

Our method uses structure of Euler-Lagrange equations (1) and assumption of nondiagonal influence parameters (2) to perform special substitutions (3,4) that simplify the general differential system into single differential equation (5a) and nonlinear algebraic system (5b).

$$\left(\sum_{i=1}^{n}\sqrt{c_{i,i}}\right)\left(\frac{2}{r}\tilde{\rho}' + \tilde{\rho}''\right) = -X\left(\tilde{\rho}\right) \tag{5a}$$

$$\frac{\Delta\mu_{j+1}}{\sqrt{c_{j+1,j+1}}} = -X\left(\tilde{\rho}\right), j \in \{1, 2, \ldots n-1\} \tag{5b}$$

The system of equation (5) can be solved substantially quicker then system of differential equations (1). Problem in this form can be divided into two separate sections. In the first section (5b), we solve a system of non-linear algebraic equations. The results are used in the second section to solve single differential equation (5a). The complete overview of this computational method is given in Figure 2.
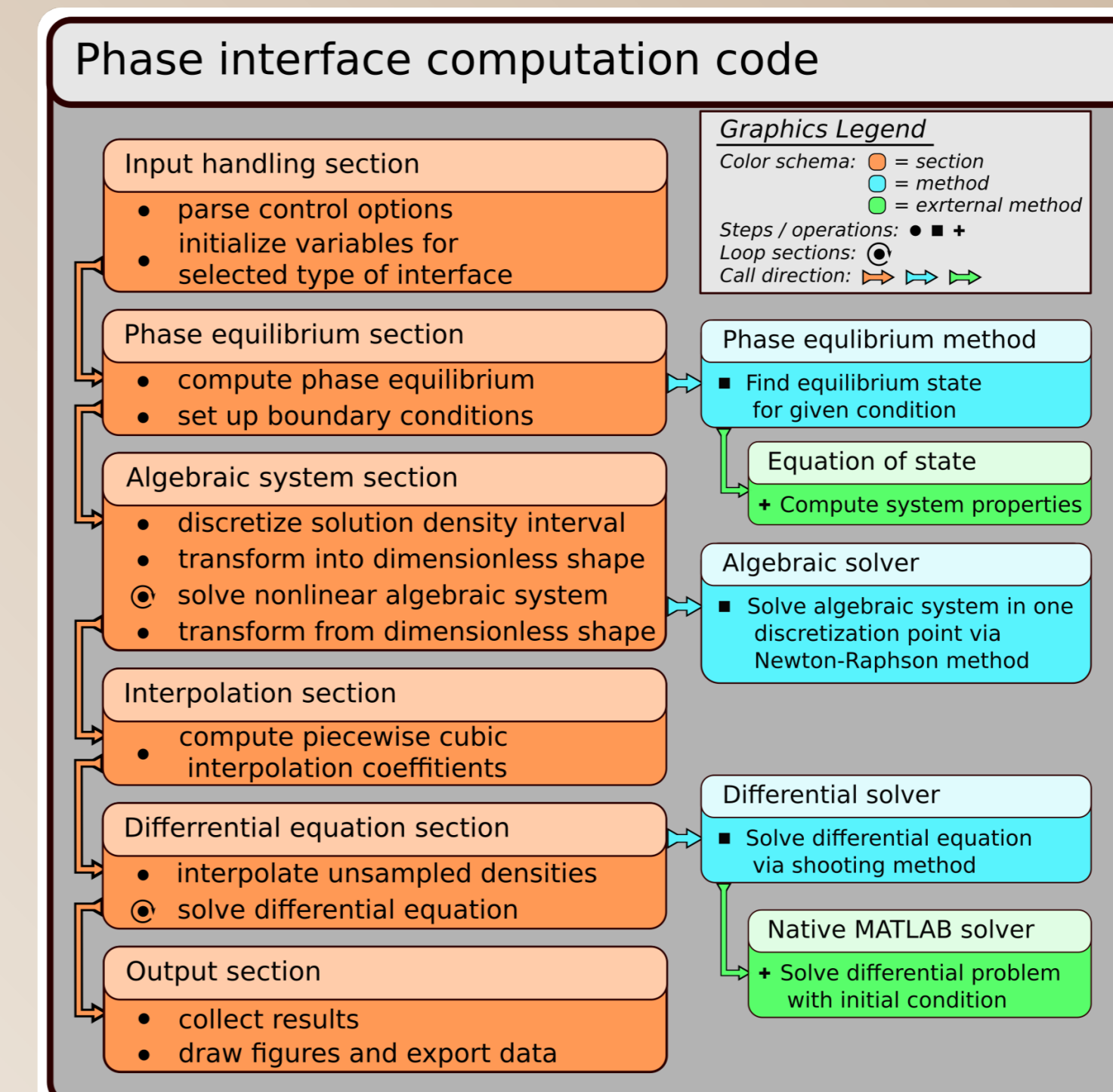

Figure 2: Call diagram of computational code generalized for both types of interface geometries.

Results

For chosen system of CO_2 and C_4H_{10}, the density profiles for various system states were successfully computed. Although the developed computing code can provide spherical phase interface density profiles we present here only the planar results, which can be compared to the available experimental data.

The following Figures 3 and 4 show the resulting density profiles. The black lines represent computational density $\tilde{\rho}$. Boundary conditions obtained from vapor liquid equilibria are denoted with blue dashed lines and red dash-dotted lines. The partial density profiles for individual components are shown as magenta and green lines.
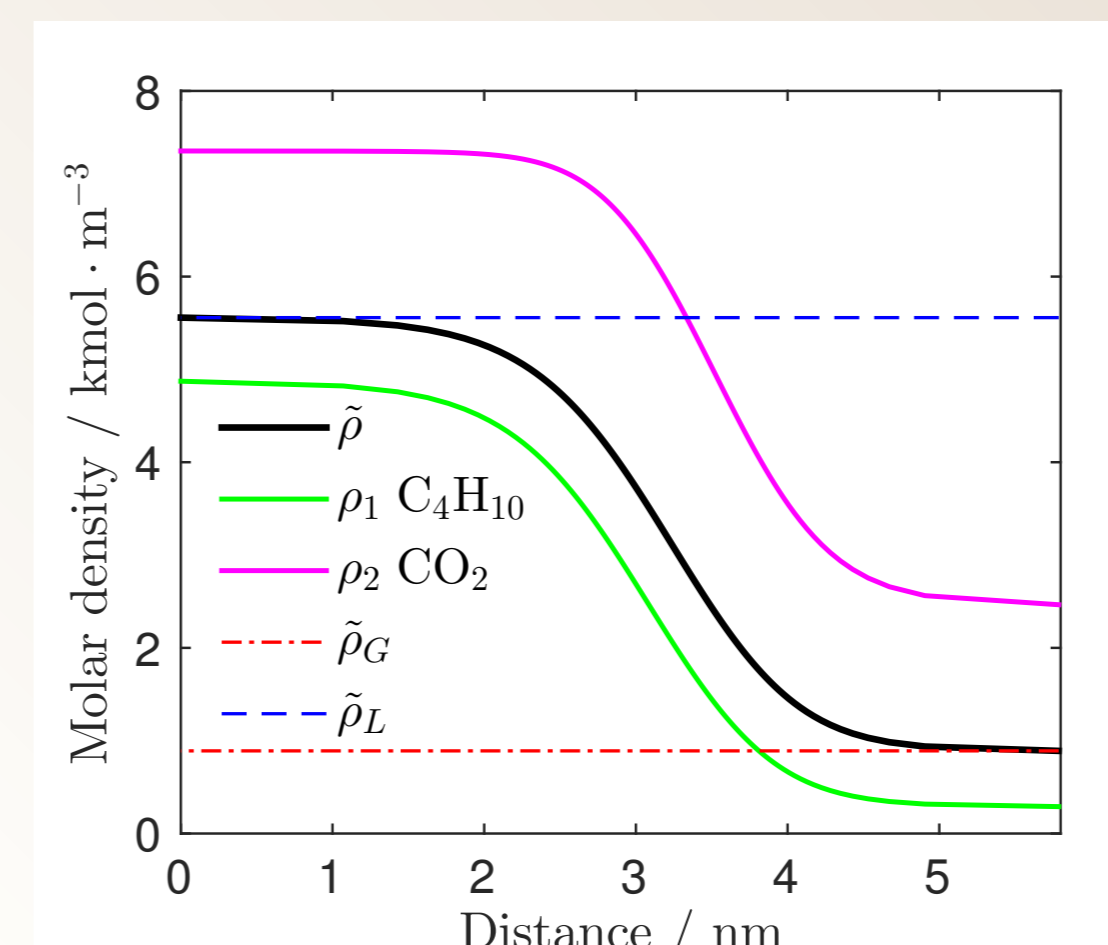

Figure 3: Dnsity profile for CO_2 and C_4H_{10} system at 319.26 K and 5 MPa.
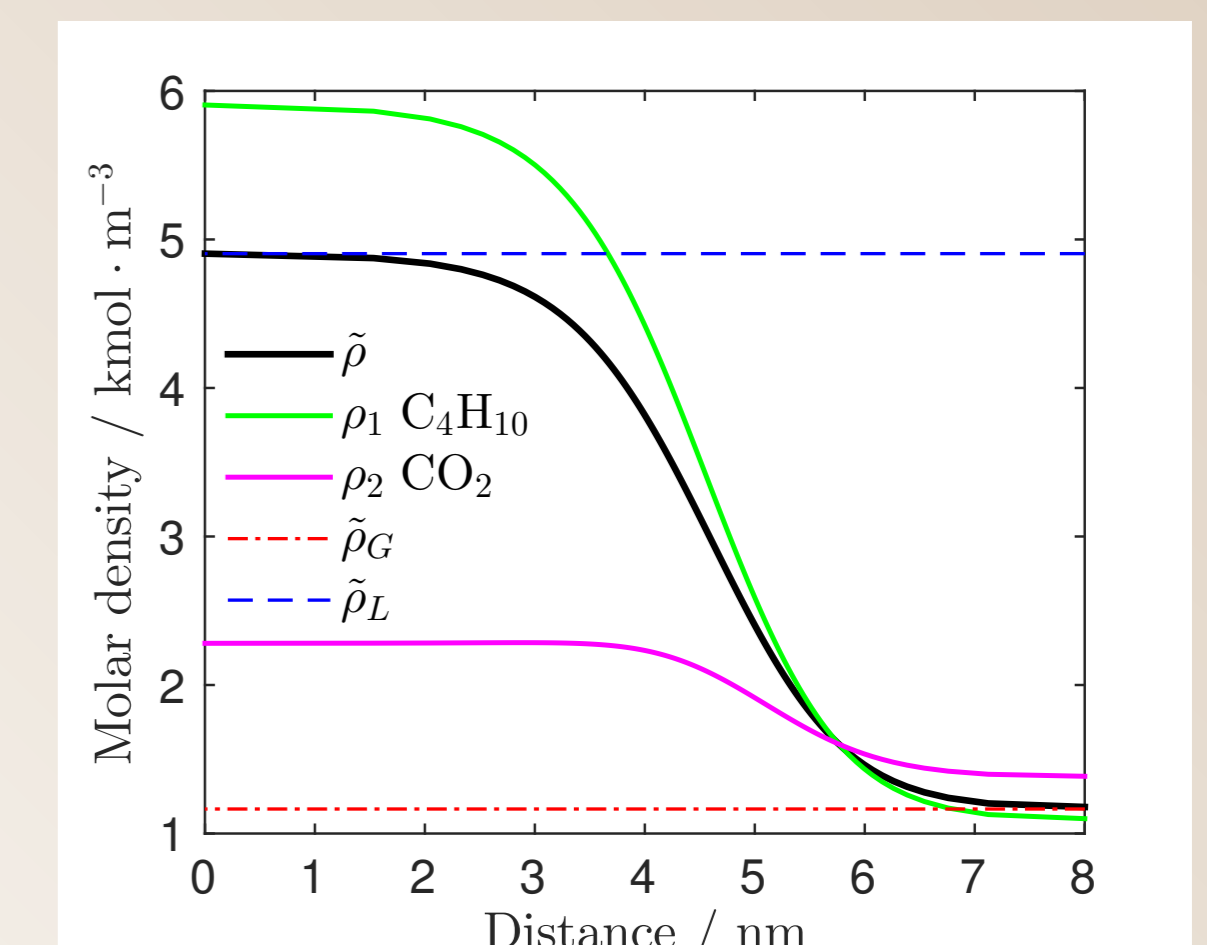

Figure 4: Dnsity profile for CO_2 and C_4H_{10} system at 377.59 K and 5 MPa.

The density profiles were used afterwards to compute the surface tension for the given system. Obtainedsurface tension was compared to the experimental data from Hsu et al. [5] and Brauer and Hough [1] in Figure 5. The introduced model is in quite good agreement with the experimental data for higher temperatures and the pure butane data taken from NIST [6].

In addition, comparative calculation with an extended PCP-SAFT EOS [4] incorporating the quadrupolar nature of CO_2 were performed. Figure 6 shows dependency of surface tension on pressure at single temperature for both non-polar and quadrupolar CO_2. The effect of quadrupolar interactions was found to be negligible for the investigated binary system as n-butane is purely nonpolar compound. Consequently, CO_2 and C_4H_{10} can be modeled as nonpolar system without any significant error.
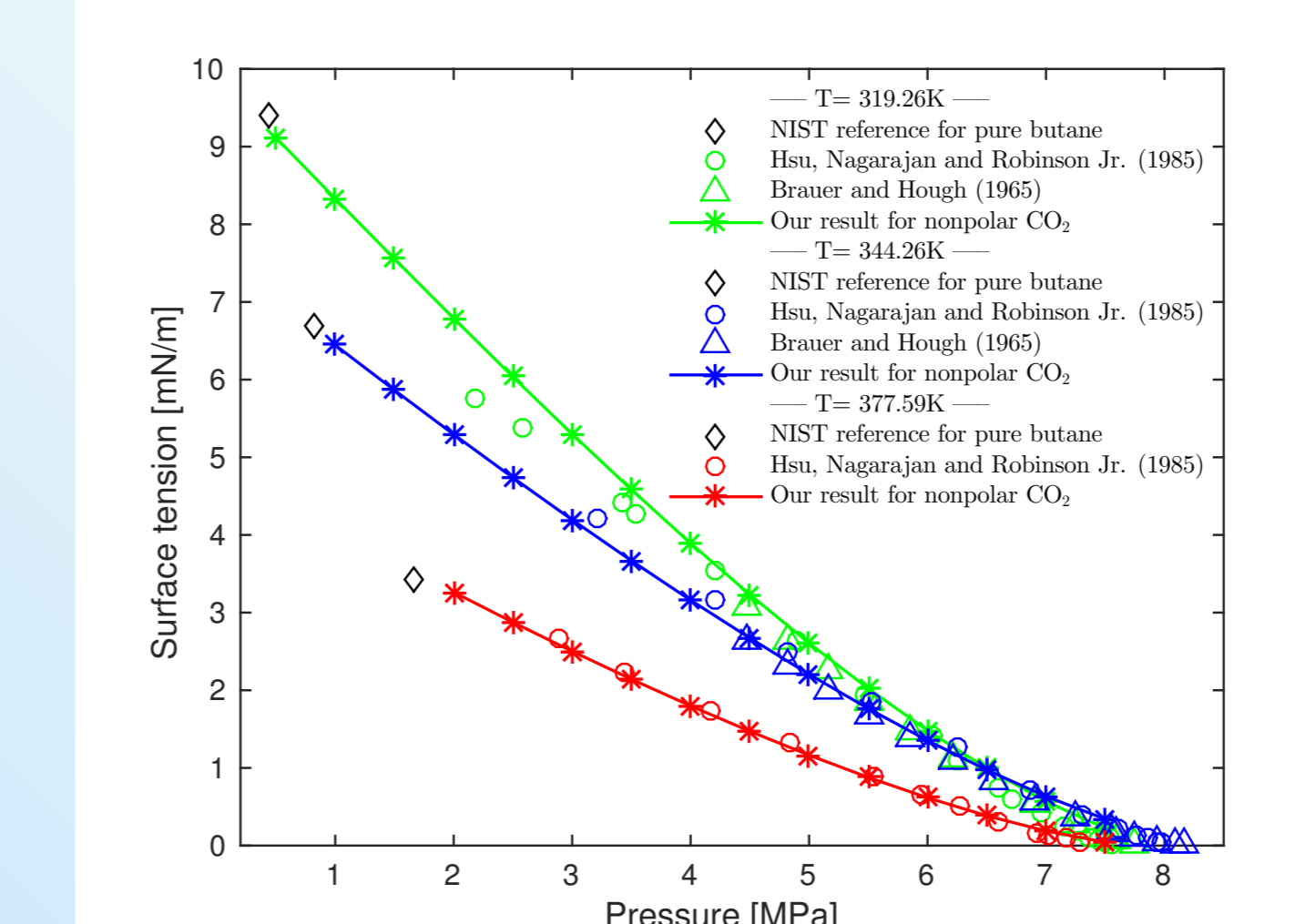

Figure 5: Comparison of experimental data with surface tensions computed for system of CO_2 and C_4H_{10}
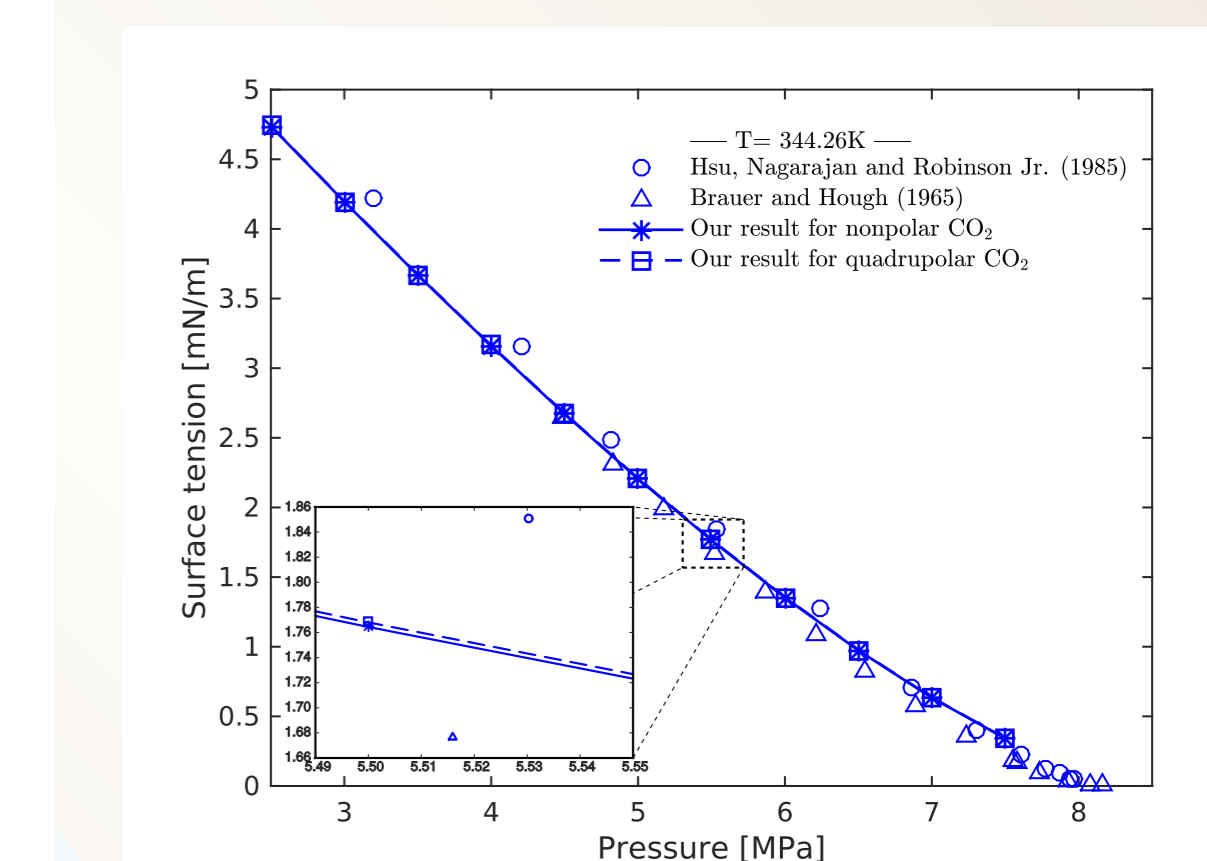

Figure 6: Comparison of experimental data with surface tensions computed for system of CO_2 and C_4H_{10} where CO_2 is computed as nonpolar and quadrupolar substance

Acknowledgement

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