Description of doctoral project and research results achieved to date

Introduction
This doctoral project is focused on porous media at a molecular scale instead of a pore network scale or a REV scale. At this molecular scale, a quantity of interest is the density profile of a fluid component. A density profile describes the distribution of molecules of the same kind in space and can be considered as a probability of finding a molecule dependent on spatial coordinates.

An example of a density profile is depicted in Fig. 1. On the left side is a conceived illustration of a two-phase pure component fluid confined in a cylindrical pore. The system is assumed to be rotationally symmetric and thus depends only on a radial ($r$) and an axial ($z$) coordinate. The blue phase is supposed to be a liquid phase whereas the colorless phase above and under the liquid phase is a vapor phase. Note that the interfacial areas between the phases show menisci and that the liquid phase is the wetting phase. The simulation of this system using Monte Carlo molecular simulations and sampling the positions of the particles leads to the density profile plotted on the right side of Fig. 1. The oscillatory curvature in the middle of the pore ($z$-range $\approx 20 - 35 \sigma$) describes the structure of the liquid phase. The density profile on the boundaries (vapor phase) shows no oscillation but only one mono-layer peak next to the solid wall. Furthermore, the two-dimensional plot illustrates menisci-like interfacial areas between the phases.

The aim of this work is to develop and enhance approaches that give information on density profiles. Molecular simulations can provide density profiles but are very costly and therefore not the first choice. A different and significantly more efficient approach to obtain density profiles is the classical density functional theory (DFT). A reliable DFT gives the possibility to study various fluid behaviors in porous systems.

Theoretical Background
The DFT is based on a thermodynamic relation between the grand potential $\Omega$ and the Helmholtz...
energy $F$

$$\Omega [\rho_k] = F[\rho_k] + \sum_i \int dr \rho_i(r) \left( V_i^{ext}(r) - \mu_i \right) \tag{11}$$

where $\rho_i$ is the density profile and $\mu_i$ the chemical potential of component $i$. The function $V_i^{ext}$ is used to include an external potential into the system and for confined systems, $V_i^{ext}$ is used to introduce interactions between solid and fluid particles into the description. After some reorganization and for the introduction of the condition of thermodynamic equilibrium for given temperature, volume and chemical potentials, Eq. 11 can be solved and the results are density profiles for every fluid component considered in the system.

The quality of the obtained density profiles depends on the quality of the model of the Helmholtz energy functional $F[\rho_k]$. In the work of our group\cite{1,2,3}, $F[\rho_k]$ is modeled as

$$F[\rho_k] = F^{ig} [\rho_k] + F^{hc} [\rho_k] + F^{disp} [\rho_k] \tag{12}$$

Here $F^{ig}$, $F^{hc}$ and $F^{disp}$ denote the Helmholtz energy functional contributions of ideal gases, hard-chains and dispersion (van-der-Waals-like attractive interactions), respectively. The separation of $F$ into contributions follows the logic of the perturbed-chain statistical associating fluid theory\cite{4} (PC-SAFT) equation of state (EoS). Whereas the PC-SAFT EoS is valid for bulk systems, Eq. 12 can be seen as an extension to inhomogeneous fluid systems.

In order to apply the DFT to porous systems a new model for the dispersive contribution $F^{disp} [\rho_k]$ was required. For this reason, we applied the so-called weighted density approximation (WDA): an averaging of the density profile in combination with a bulk EoS (PC-SAFT in our case) leads to an efficient and reliable model of $F^{disp} [\rho_k]$. The introduction of the WDA leads to some ambiguity and therefore we introduced one parameter and adjusted it to experimental surface tension data of C1 to C20 n-alkanes for a wide temperature range. It should be mentioned, that this parameter is an universal parameter and thus all created results are purely predictive (except for n-alkane surface tensions).

**Results: Interfacial Tensions and Porous Systems**

Applying the DFT with the new developed functional to vapor-liquid-equilibria (VLE) and liquid-liquid-equilibria (LLE) leads to good agreement with experimental data. The results are of the same quality as the results obtained with the functional proposed in earlier works for pure component VLEs\cite{1}, mixture VLEs\cite{2} and LLEs\cite{3}.

The advantage of the new functional is, that it also can be applied to porous systems.

Fig. 2 shows two examples of a fluid mixture within two planar walls (slit-shaped pore). The systems differ in the properties of the corresponding bulk phase, i.e. in packing fraction $\eta$ and mole fraction $x_i$. The solid-fluid interactions consist of an attractive and a repulsive contribution. We compared the density profiles of the DFT calculation with molecular dynamics (MD) molecular simulations\cite{5} to evaluate the developed Helmholtz energy functional. A very good agreement is found.

A further result of this work is that the DFT is able to calculate the thickness of liquid films for given solid-fluid interactions. Fig. 3 shows the resulting liquid film in the thermodynamic equilibrium condition that is present for given solid-fluid interactions and a vapor methane bulk phase at $p = 10$ bar and $T = 150$ K. The calculated liquid film is about 3 nm thick.

Another development in this doctoral project is an implementation of the DFT that enables calculations of two-dimensional density profiles. The solving of the DFT-equations for two-dimensional systems is in general not trivial and can require a large computational effort. For this reason, fast Fourier and fast Hankel algorithms were implemented. With the recently developed codes, density profiles of two-dimensional rotationally symmetric systems can be calculated very efficiently.
Figure 2: Density profiles of binary Lennard-Jones mixtures within a slit-shaped pore. Comparison between molecular dynamics (MD) molecular simulation\(^5\) and DFT with the new Helmholtz energy functional. Left: \(\eta = 0.2545, x_i = 0.262\). Right: \(\eta = 0.0511, x_i = 0.891\).

Figure 3: Density profile of a liquid film that converges to a vaporous bulk phase (methane at \(p = 10\text{ bar}\) and \(T = 150\text{ K}\)) next to a planar wall.

References


