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Modelling of Interfacial Tension and Adsorption of Inhomogeneous Systems with Classical Density Functional Theory

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Classical Density Functional Theory (DFT) has shown to be a consistent framework for the study of surface thermodynamics, being used for the calculation of interfacial tensions and adsorption, to the calculation of properties of colloidal systems and self-assembly [1,2]. Classical DFT finds the local density profile of an inhomogeneous fluid system in the presence of fluid-fluid interfaces or fluid-solid surfaces, that later can be used for the calculation of interfacial tensions between fluid phases, or adsorption of fluids on the walls of an adsorbent.

Classical DFT is based on statistical mechanics concepts used in molecular simulations, and with the definition of a Helmholtz free energy functional of the particle density, it allows the implementation of the already well-known knowledge of bulk equations of state into the study of inhomogeneous fluids. This locates classical DFT in an advantageous position, as it allows the determination of density profiles and surface properties with accuracy similar to molecular simulations, but with only requiring a modest amount of time characteristic of the conventional models, such as Multicomponent Potential Adsorption Theory [3] (MPTA) and Density Gradient Theory [4] (DGT), for adsorption and surface tension respectively. The Helmholtz free energy functional is defined using a perturbation approach over the Helmholtz free energy of the inhomogeneous hard sphere as the reference state. The free energy functional contains the information of the particle interactions of the inhomogeneous fluid, such as dispersion, chain formation, association, polar and electrostatic interactions, which in the bulk limit reduces to the Helmholtz free energy of the homogeneous fluid.

In this work, the Perturbed Chain Statistical Association Fluid Theory [5] (PC-SAFT) equation of state is used to define the Helmholtz free energy functional within the classical DFT framework. Which enables the important feature that it is not required to fit new pure component parameters and only those from bulk fluids are used. The PC-SAFT DFT implementation is used for the calculation of adsorption and surface tension of pure components and multicomponent systems of non-associating and associating fluids of interest for the chemical and petroleum industries. The objective is to test the performance, accuracy and limits of the results obtained with classical DFT with the already implemented models by our research group for interfacial tensions and adsorption, DGT and MPTA, respectively.

Examples of the results obtained with classical DFT and PC-SAFT for the calculation of adsorption isotherms of methane, nitrogen and carbon dioxide on an activated carbon in a slit-like pore are shown in Figure 1. This calculation uses the pure component parameters of methane, nitrogen and carbon dioxide used in the bulk PC-SAFT equation of state [5]. In Figure 2 are shown the particle density profiles at different temperatures for the vapor-liquid interface of methane. As it can be seen, as the temperature reaches the critical temperature the interface begins to vanish.

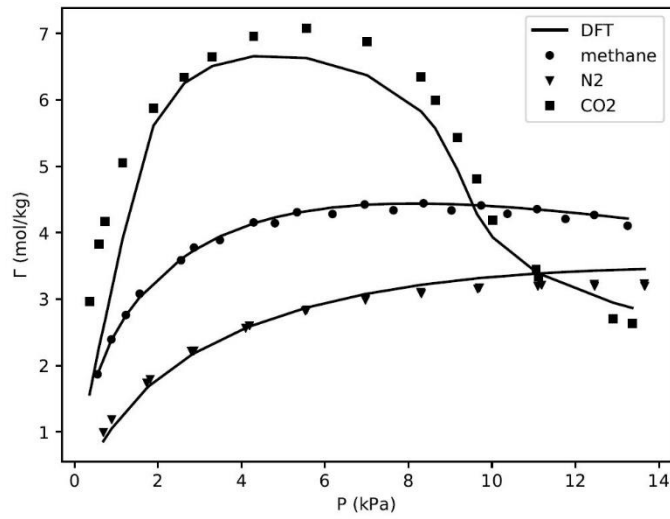


Figure 1. Adsorption of methane, nitrogen and carbon dioxide on activated carbon [6] calculated with classic DFT with the PC-SAFT equation of state at 318 K.

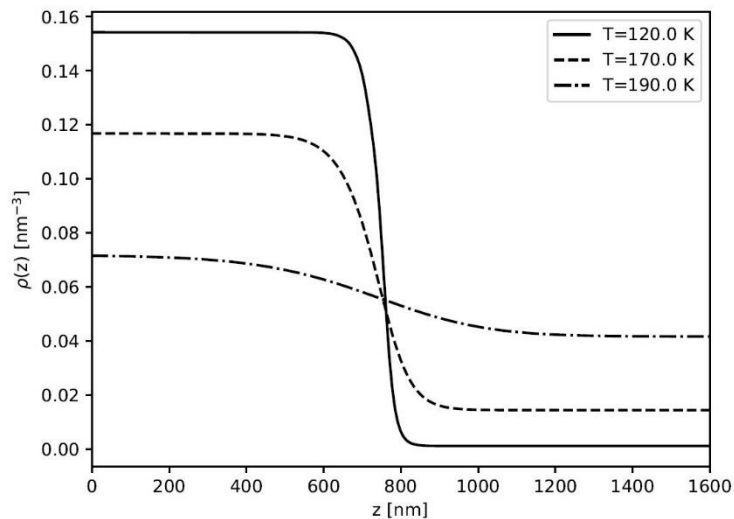


Figure 2. Particle density profiles of the vapor-liquid interface of methane at different temperatures calculated with classical DFT and PC-SAFT.

- [1] J. Wu, "Density Functional Theory for Chemical Engineering: From Capillarity to Soft Materials," *AICHE Journal*, vol. 52, no. 3, pp. 1169-1193, 2005.
- [2] C. P. Emborsky, Z. Feng, K. R. Cox, W. G. Chapman, "Recent Advances in Classical Density Functional Theory for Associating and Polyatomic Molecules," *Fluid Phase Equilibria*, vol. 306, pp. 15-30, 2011.
- [3] M. A. Monsalvo, A. A. Shapiro, "Study of high-pressure adsorption from supercritical fluids by the potential theory," *Fluid Phase Equilibria*, vol. 283, pp. 56-64, 2009
- [4] X. Liang, M. L. Michelsen, G. M. Kontogeorgis, "A Density Gradient Based Method for Surface Tension Calculations," *Fluid Phase Equilibria*, vol. 428, pp. 153-163, 2016.

- [5] J. Gross and G. Sadowski, "Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules," *Industrial & Engineering Chemistry Research*, vol. 40, no. 4, pp. 1244-1260, 2001.
- [6] M. Sudibandriyo, Z. Pan, J. E. Fitzgerald, R. L. Robinson, and K. A. Gasem, "Adsorption of methane, nitrogen, carbon dioxide, and their binary mixtures on dry activated carbon at 318.2 K and pressures up to 13.6 MPa," *Langmuir*, vol. 19, no. 13, pp. 5323-5331, 2003.