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Classical Density Functional Theroy for Liquid-Fluid Interfaces using modified iSAFT and the heterosegmented GC-PC-SAFT Equation of State

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Objective

- determine density profiles on a segment level to study the molecular structure at interfaces in detail
- good agreement with experimental data including associating components
- consistency with bulk equation of state (here: heterosegment GC-PC-SAFT[1])

Classical Density Functional Theory (DFT)

- Grand potential of an inhomogeneous system with a planar interface and no external potential

$$\Omega[\rho_k(z)] = F[\rho_k(z)] - \sum_{j=1}^{NS} \mu_{jc} \int \rho_j(z) \mathrm{d}z \tag{1}$$

- At thermodynamic equilibrium for given T, V, μ_{jc}

$$0 = \frac{\delta\Omega[\rho_k(z)]}{\delta\rho_i(z)} = \frac{\delta F[\rho_k(z)]}{\delta\rho_i(z)} - \mu_{ic}^{eq} \tag{2}$$

- The equilibrium density profiles are obtained by iterating the following equation

$$\rho_{is}(z) = \exp\left(\beta\mu_{ic}^{Eq} + D_{is}(z)\right) I_{1,is}(z) I_{2,is}(z) \tag{3}$$

Helmholtz Energy Functional

- Residual Helmholtz energy functional

$$F^{\mathrm{res}}[\rho_k(z)] = F^{\mathrm{hs}}[\rho_k(z)] + F^{\mathrm{hc}}[\rho_k(z)] + F^{\mathrm{disp}}[\rho_k(z)] + F^{\mathrm{asso}}[\rho_k(z)] \tag{4}$$

- Hard sphere contribution: modified fundamental measure theory[2][3]
- Chain formation: modified iSAFT (Jain, Dominik and Chapman[4])
- Dispersive contribution: weighted density approach (Sauer)

$$\beta F^{\mathrm{disp}}[\rho_k(z)] = \int \sum_{j=1}^{NS} \rho_j(z) \bar{a}_j^{\mathrm{disp,GC\text{-}PC\text{-}SAFT}}(\bar{\rho}_k(z)) \mathrm{d}z \tag{5}$$

$$\bar{\rho}_i(\mathbf{r}) = \frac{3}{4\pi\psi_i^3} \int \rho_i(\mathbf{r'}) \Theta(\psi_i - |\mathbf{r'} - \mathbf{r}|)(d)\mathbf{r'} \tag{6}$$

  - The value of ψ_i was adjusted for a DFT consistent with PC-SAFT REF and is used unchanged here
- Associative contribution: iSAFT (Bymaster and Chapman[5])

$$\beta F^{\mathrm{Asso}}[\rho_k(z)] = \int \sum_{j=1}^{NS} \rho_j(z) \sum_{A \in \Gamma^{(j)}} \left[\ln\chi_A^j(z) - \frac{\chi_A^j(z)}{2} + \frac{1}{2} \right] \mathrm{d}z \tag{7}$$

  - Equation for χ_A^i was modified to be consistent with bulk equation of state

$$\chi_A^i(z) = \frac{1}{1 + \frac{1}{2}\sum_{j=1}^{NS} \kappa_{ij}\sigma_{ij}^2 \int_{z-\sigma_{ij}}^{z+\sigma_{ij}} \rho_j(z') \sum_{B \in \gamma^{(j)}} \chi_B^j(z') \{[\exp(\beta\epsilon_{Ai,Bj}) - 1] y^{ij}(z, z')\} \mathrm{d}z'} \tag{8}$$

Numerical method

The resulting system of equations, eq. 3, is solved in parallel using an inexact Newton method from PETSc[6].

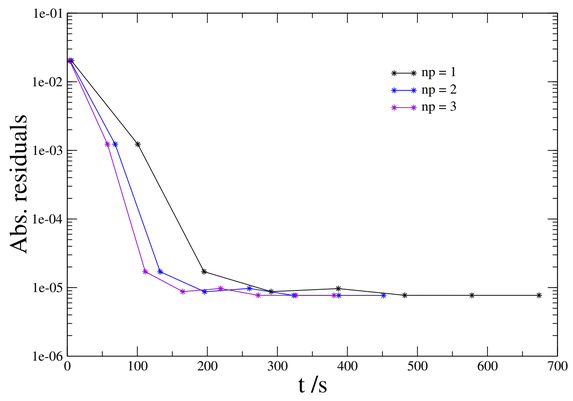

Figure : Absolute residuals over time for the surface tension calculation of dodecane at T = 450 K using different numbers of processors.

Results

- Surface Tensions of non-associating components

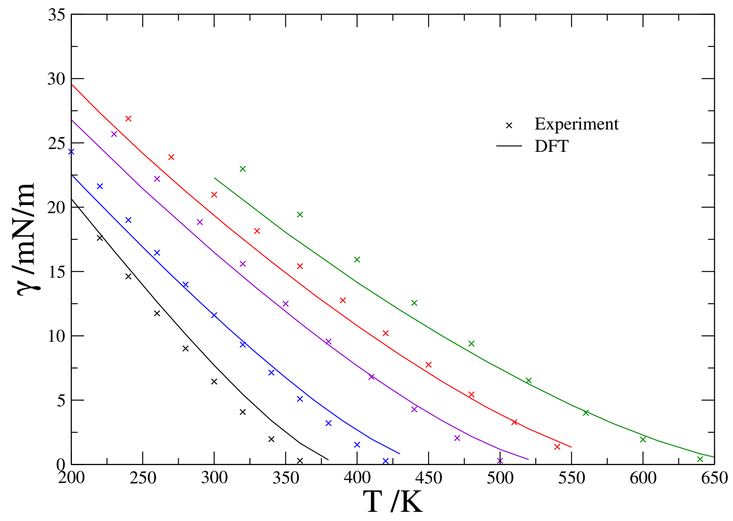

Figure : Comparison of DFT to experimental data of 1-propene[7], butane[7], hexane[7], octane[7] and dodecane[7] (from left to right).

- Surface Tensions of associating components

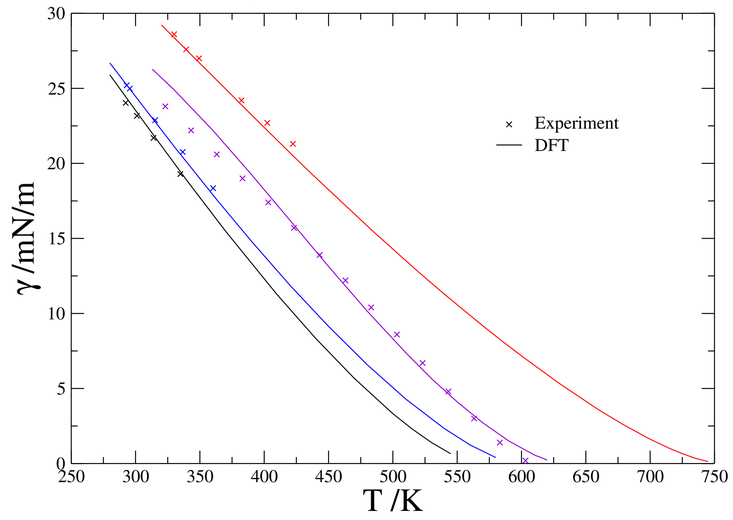

Figure : Comparison of DFT to experimental data of butylamine[8], pentylamine[8], 1-hexanol[9] and tetradecanoic acid[10] (from left to right).

- Density Profiles at Vapor-Liquid Interface

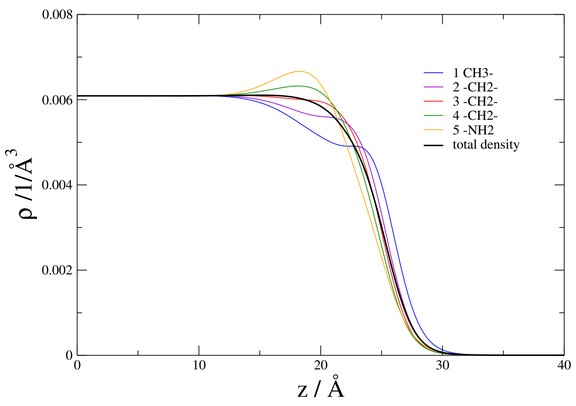

Figure : Density Profiles of the single segments of butylamine at T = 300K.

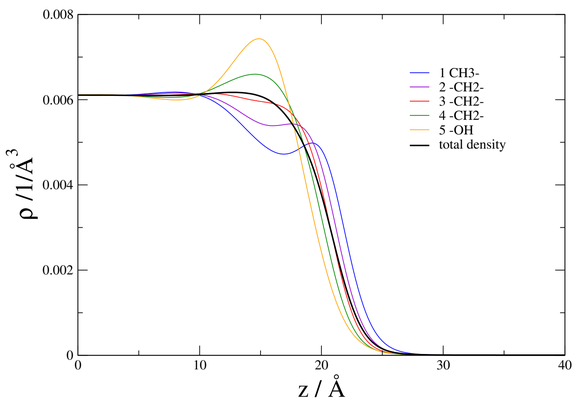

Figure : Density Profiles of the single segments of 1-butanol at T = 360K.

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