

Appendix for Thermodynamic Modeling of the Equilibrium Partitioning of Hydrocarbons in Nanoporous Kerogen Particles

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Appendix A: Free energy functionals

The ideal gas and chain formation contributions are the same as in interfacial Statistical Associating Fluid Theory (iSAFT), with the equations already presented in our previous work.¹ For the hard sphere contribution, we apply the White-Bear version of fundamental measure theory² to be consistent in the bulk with the hard sphere part in the PC-SAFT EoS. The temperature dependent hard sphere diameter of component i is,

$$d_i = \sigma_i \left[1 - 0.12 \exp \left(-3 \frac{\varepsilon_i}{k_b T} \right) \right] \quad (1)$$

The major challenge lies in approximating the long range attraction between molecules at the interface. In a non-local density functional theory (NLDFT), Weighted Density Approximation (WDA) is a method that approximates the free energy density at each location by the same macroscopic thermodynamic relation at a smoothed density. This smoothed

density can be evaluated in various ways in different recipes depending on the fluid intermolecular potentials and the purpose of modeling.³ The method by Sauer and Gross⁴ and similarly by Yu⁵ has been proved to be practically valuable for real fluid modeling, both at the vapor-liquid interface and fluid-solid interface. Considering the computational efficiency and practical interest of interfacial properties (i.e. interfacial tension and adsorption isotherms), we apply this approach to have the inhomogeneous fluid free energy reduce to PC-SAFT EoS in this study.

$$\Delta A^{\text{disp}}[\rho_s(\mathbf{r}); \rho(\mathbf{r})] = k_b T \int \bar{\rho}(\mathbf{r}_1) a^{\text{disp}}(\bar{\rho}(\mathbf{r}_1)) d\mathbf{r}_1 \quad (2)$$

where $\bar{\rho}(\mathbf{r}_1)$ is the total weighted density of both fluid and solid ($N + 1$ components) at position \mathbf{r}_1 ,

$$\bar{\rho}(\mathbf{r}_1) = \sum_{i=1}^{N+1} \bar{\rho}_i(\mathbf{r}_1) \quad (3)$$

$$\bar{\rho}(\mathbf{r}_1) = \sum_{i=1}^N \left[\frac{3}{4\pi(\varphi d_i)^3} \int \rho_i(\mathbf{r}_2) \Theta(\varphi d_i - |\mathbf{r}_1 - \mathbf{r}_2|) d\mathbf{r}_2 \right] + \frac{3}{4\pi(\varphi d_s)^3} \int \rho_s(\mathbf{r}_2) \Theta(\varphi d_s - |\mathbf{r}_1 - \mathbf{r}_2|) d\mathbf{r}_2 \quad (4)$$

Θ is the Heaviside function, d_i and d_s are the temperature dependent diameters of the i^{th} solvent and kerogen, and φ is an adjustable parameter that sets the volume range over which density is averaged. In this work, $\varphi = 1.21$ from our previous work^{6,7} was used.

$a^{\text{disp}}(\bar{\rho}(\mathbf{r}_1))$ is the bulk dispersion free energy per molecule evaluated at weighted density $\bar{\rho}(\mathbf{r}_1)$,

$$a^{\text{disp}}(\bar{\rho}(\mathbf{r}_1)) = -2\pi\bar{\rho}(\mathbf{r}_1) I_1(\bar{\eta}(\mathbf{r}_1), \bar{m}(\mathbf{r}_1)) \overline{m^2 \varepsilon \sigma^3}(\mathbf{r}_1) - \pi\bar{\rho}(\mathbf{r}_1) \bar{m}(\mathbf{r}_1) C_1 I_2(\bar{\eta}(\mathbf{r}_1), \bar{m}(\mathbf{r}_1)) \overline{m^2 \varepsilon^2 \sigma^3}(\mathbf{r}_1) \quad (5)$$

where van der Waals one-fluid mixing rule is used as shown below.

$$\overline{m^2 \varepsilon^\alpha \sigma^3}(\mathbf{r}_1) = \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \left(\frac{\bar{\rho}_i(\mathbf{r}_1)}{\bar{\rho}(\mathbf{r}_1)} \right) \left(\frac{\bar{\rho}_j(\mathbf{r}_1)}{\bar{\rho}(\mathbf{r}_1)} \right) m_i m_j \left(\frac{\varepsilon_{ij}}{k_b T} \right)^\alpha \sigma_{ij}^3; \quad \alpha = 1 \text{ or } 2 \quad (6)$$

The integrals over bulk correlation functions I_1 and I_2 and compressibility term are given by the following equations.

$$\bar{\eta} = \frac{\pi}{6} \sum_{i=1}^{N+1} \bar{\rho}_i(\mathbf{r}_1) m_i d_i^3 \quad (7)$$

$$C_1 = \left[1 + \frac{8\bar{\eta} - 2\bar{\eta}^2}{(1 - \bar{\eta})^4} \right]^{-1} \quad (8)$$

$$I_1 = \sum_{i=0}^6 a_i \bar{\eta}^i \quad (9)$$

$$I_2 = \sum_{i=0}^6 b_i \bar{\eta}^i \quad (10)$$

where values of a_i and b_i are the universal constants in PC-SAFT EoS.

Appendix B: Solve for the equilibrium fluid density distribution

Once the equilibrium bulk composition in kerogen/solvent phase and solvent phase are decided, a step function is used as the initial guess of the fluid density profile,

$$\rho_i^0(z) = \begin{cases} \rho_i^{\text{kerogen,b}} & -\frac{H_s}{2} \leq z < 0 \\ \rho_i^{\text{bulk}} & 0 \leq z \leq \frac{H_{\text{pore}}}{2} \end{cases} \quad \text{for } i = 1, 2, \dots, N \quad (11)$$

Considering the symmetry of the kerogen-pore composite, a reflective boundary condition is applied at both $z = -H_s/2$ and $z = -H_{\text{pore}}/2$. The calculation domain is discretized into $dz = 0.01\sigma_{ref}$, with σ_{ref} being one of the segment diameters of the mixture. Numerical integration in z direction is done by Simpson's rule. The calculation starts from eq 11 and Picard iteration is applied to eq 14 in the article until the sum of the absolute difference in all density points between the last two solutions is smaller than the tolerance of 3.0E-5.

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