

# Classical Density Functional Theory for Thermopack - Radial distribution function at contact from fundamental measure theory.

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# 1 Introduction

From statistical mechanics the compressibility in a hard sphere system is known from the virial theorem,

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3} \rho \sigma^3 g^c(\sigma), \quad (1)$$

where  $g^c(\sigma)$  is the radial distribution function (RDF) at contact. For additive mixtures, the virial theorem extends to a double sum over the contributions from all pairs,  $ij$ ,

$$\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3} \rho \sum_i \sum_j x_i x_j \sigma_{ij}^3 g^c(\sigma_{ij}), \quad (2)$$

where  $x_i$  is the mole fraction of component  $i$  [2, Eq. 5.14]. The excess pressure is then related to the RDF at contact through the algebraic relation,

$$\beta P_{\text{ex}} = \frac{2\pi}{3} \sum_i \sum_j \rho_i \rho_j \sigma_{ij}^3 g^c(\sigma_{ij}). \quad (3)$$

In a classical density functional theory (DFT) formulation, the Helmholtz free energy density can be calculated from fundamental measure theory (FMT). In FMT, the Helmholtz energy is a function of weighted densities,  $\mathbf{n}$ , ie.

$$\Phi = \Phi(\mathbf{n}). \quad (4)$$

The weighted densities are given as convolution integrals,

$$n_\alpha = \int d\mathbf{r}' \rho(\mathbf{r}') w_\alpha(\mathbf{r} - \mathbf{r}') = \rho(\mathbf{r}) \otimes w_\alpha(\mathbf{r}), \quad (5)$$

where  $w_\alpha$  is the a weight function.

The excess pressure is given from,

$$\beta P_{\text{ex}} = -\Phi + \sum_i \rho_i \frac{\partial \Phi}{\partial \rho_i}. \quad (6)$$

Here,

$$\frac{\partial \Phi}{\partial \rho_i} = \sum_\alpha \frac{\partial \Phi}{\partial n_\alpha} \frac{\partial n_\alpha}{\partial \rho_i}. \quad (7)$$

For mixtures, the RDF at contact are related to the Helmholtz energy [2, Eq. 5.29], [1] through the differentials,

$$g^c(\sigma_{ij}) = \frac{1}{2\pi(2 - \delta_{ij}) \rho_i \rho_j \sigma_{ij}^2} \frac{\partial \Phi}{\partial \sigma_{ij}} \quad (8)$$

The equation require the differential

$$\frac{\partial \Phi}{\partial \sigma_{ij}} = \sum_{\alpha} \frac{\partial \Phi}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial \sigma_{ij}}. \quad (9)$$

The differential  $\frac{\partial n_{\alpha}}{\partial \sigma_{ij}}$  requires integrals of the weight function differentials with respect to  $\sigma_{ij}$  and it is therefore not possible to derive a analytical relation for the RDF at contact. New weighted functions, similar to the weight functions used for the calculation of entropy are required to model the  $g^c(\sigma_{ij})$ .

The component densities,  $\rho_i$ , in Eq. 8 is in the FMT context can be either  $n_{0,i}$  or simply the local density,  $\rho_i(\mathbf{r})$ . This must be investigated.

## 2 The PCP-SAFT hard-chain functional

The hard-chain functional used in PCP-SAFT [3] is,

$$\begin{aligned} \beta F^{\text{hc}}[\rho_k] = & \sum_i (m_i - 1) \int \rho_i(\mathbf{r}) (\ln \rho_i(\mathbf{r}) - 1) d\mathbf{r} \\ & - \sum_i (m_i - 1) \int \rho_i(\mathbf{r}) \left( \ln \left[ y_{ii}^{\text{dd}} \left( \bar{\rho}_k^{\text{hc}}(\mathbf{r}) \right) \lambda_i(\mathbf{r}) \right] - 1 \right) d\mathbf{r}, \end{aligned} \quad (10)$$

where  $\lambda_i$  is a weighted density based on a normalized weight function and  $\bar{\rho}_k^{\text{hc}}$  are a dirac weighted density, both of width  $2d_i$ ,

$$\bar{\rho}_k^{\text{hc}}(\mathbf{r}) = \frac{3}{4\pi d_i^3} \int \rho_i(\mathbf{r}_2) \Theta(d_i - |\mathbf{r}_2 - \mathbf{r}_1|) d\mathbf{r}_2 \quad (11)$$

$$\lambda_i(\mathbf{r}) = \frac{1}{4\pi d_i^2} \int \rho_i(\mathbf{r}_2) \delta(d_i - |\mathbf{r}_2 - \mathbf{r}_1|) d\mathbf{r}_2 \quad (12)$$

Show entropy profile using the above functional.....

### 3 The association hard chain term used for PCP-SAFT

The associative attraction functional require a description of the  $ij$  RDF at contact. To describe RDF at contact for heterogeneous systems, Sauer and Gross used the term proposed by Yu and Wu [4]:

$$g_{ij}^c(\{n_\alpha(\mathbf{r})\}) = \frac{1}{1-n_3} + \frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}} \frac{\xi n_2}{2(1-n_3)^2} + \left( \frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}} \right)^2 \frac{\xi^2 n_2^2}{18(1-n_3)^3}, \quad (13)$$

where  $\xi = 1 - \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2 / n_2^2$ .

### 4 Test

Use equation Eq. 8 to test:

- Is  $g_{ij} = g_{ji}$ ?
- Resulting  $g_{ij}$  compared to the model version of both PCP-SAFT [3] and Yu and Wu [4].
- Effect on entropy

## References

- [1] Esam Hamad. Consistency test for mixture pair correlation function integrals. *J. Chem. Phys.*, 101(11):10195–10196, December 1994. ISSN 0021-9606, 1089-7690. doi:10.1063/1.468011.
- [2] Ángel Mulero, W. Beiglböck, J. Ehlers, K. Hepp, H. Weidenmüller, R. Beig, W. Domcke, B.-G. Englert, U. Frisch, P. Hänggi, G. Hasinger, W. Hillebrandt, R. L. Jaffe, W. Janke, H. v. Löhneysen, M. Mangano, J.-M. Raimond, D. Sornette, S. Theisen, W. Weise, and J. Zittartz, editors. *Theory and Simulation of Hard-Sphere Fluids and Related Systems*, volume 753 of *Lecture Notes in Physics*. Springer Berlin Heidelberg, Berlin, Heidelberg, 2008. ISBN 978-3-540-78766-2 978-3-540-78767-9. doi:10.1007/978-3-540-78767-9.
- [3] Elmar Sauer and Joachim Gross. Classical Density Functional Theory for Liquid–Fluid Interfaces and Confined Systems: A Functional for the Perturbed-Chain Polar Statistical Associating Fluid Theory Equation of State. *Ind. Eng. Chem. Res.*, 56(14):4119–4135, April 2017. ISSN 0888-5885, 1520-5045. doi:10/f95br5.
- [4] Yang-Xin Yu and Jianzhong Wu. A fundamental-measure theory for inhomogeneous associating fluids. *J. Chem. Phys.*, 116(16):7094–7103, April 2002. ISSN 0021-9606, 1089-7690. doi:10/cxh7vb.