SUPPLEMENTARY INFORMATION: An accurate density functional theory for the vapor-liquid interface of chain molecules based on the statistical associating fluid theory for potentials of variable range for Mie chainlike fluids

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(Dated: 3 May 2019)

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I. HOMOGENEOUS FLUID OF MIE CHAIN MOLECULES (SAFT-VR MIE)

Before presenting the Helmholtz free energy functional to deal with inhomogeneous fluids, we briefly summary the main equations and approximations developed by Lafitte *et al.*[1] to obtain the SAFT-VR Mie formalism. Here we follow the traditional SAFT formalism for the EOS of chain molecules formed from Mie segments. As in all SAFT approaches, a fluid of N chains of m_s Mie segments is formed from a total of $N_s = m_s N$ segments. In addition to that, the number density of chain molecules $\rho = N/V$ and of segments $\rho_s = N_s/V$ are related simply through the well-known relationship $\rho_s = m_s \rho$. It is convenient to use the dimensionless Helmholtz free energy of the fluid $a = A/(N k_B T)$, where k_B is the Boltzmann constant and T the temperature of the system. The dimensionless Helmholtz free energy a of the homogeneous fluid is written as a perturbation expansion which takes into account the various types of interactions, ideal, monomer segment, and chain:

$$a = a^{IDEAL} + a^{MONO} + a^{CHAIN} \tag{1}$$

A. Ideal contribution

The ideal-gas term is given in the standard form as[2]

$$a^{IDEAL}(\rho) = \ln(\rho \Lambda^3) - 1 \tag{2}$$

where Λ is a thermal de Broglie wavelength which contains the translational and rotational contributions to the partition function of the ideal chain; the kinetic contributions do not have to be specified explicitly as they do not contribute to the fluid-phase equilibria and interfacial properties.

B. Monomer contribution for Mie fluids

The term a^{MONO} combines the repulsive and dispersive contributions to the free energy of the reference monomeric spherical segments making up the chain molecules:

$$a^{MONO} = m_s a^M \tag{3}$$

where $a^M = A^M/(N_s k_B T)$ is the corresponding residual Helmholtz free energy per monomer. According to the perturbation series expansion in the inverse of the temperature $\beta = 1/(k_B T)$ up to third series developed by Lafitte et al.[1] (based on a high-temperature Barker and Henderson (BH)[3,4] perturbation expansion about a hard-sphere reference system), the free energy of the monomers can be written as,

$$a^M = a^{HS} + \beta a_1 + \beta^2 a_2 + \beta^3 a_3 \tag{4}$$

where a^{HS} is the reference hard-sphere free energy calculated by integrating the well-known Carnahan and Starling[5] EOS,

$$a^{HS} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{5}$$

Here $\eta = \rho_s \pi d^3/6$ is the packing fraction of the reference hard-sphere system. Here, d is the hard-sphere diameter of Barker and Henderson given by Eq. (7) in the work of Lafitte et al.[1]

The first-order perturbation term a_1 is calculated from the expression of the mean-attractive energy in the BH approach for a Mie potential obtained by Lafitte et al.,[1]

$$a_1 = \mathcal{C}\left[x_0^{\lambda_a}\left\{ a_1^S(\eta;\lambda_a) + B(\eta;\lambda_a)\right\} - x_0^{\lambda_r}\left\{ a_1^S(\eta;\lambda_r) + B(\eta;\lambda_r)\right\}\right] \tag{6}$$

Here, $x_0 = \sigma/d$ is the reduced diameter σ with respect to the diameter d. The first-order perturbation term depends basically on two main functions: a_1^S, that depends on η and λ_a, and B, that depends on η and λ_r.

The first function, a_1^S, is the first-order term of the Helmholtz free energy of a system of hard-core Sutherland particles of diameter d characterized by the range parameter λ. This expression was evaluated within the SAFT-VR by making use of the mean-value theorem by Gil-Villegas et al.,[6]

$$a_1^S = 2\pi\rho_s\epsilon d^3 \int_1^\infty \left(-\frac{1}{x^\lambda}\right) g_d^{HS}(xd)x^2 dx = 12\epsilon\eta \int_1^\infty \left(-\frac{1}{x^\lambda}\right) g_d^{HS}(xd)x^2 dx$$
$$= -12\epsilon\eta\left(\frac{1}{\lambda-3}\right) g_d^{HS}(\xi) = -12\epsilon\eta\left(\frac{1}{\lambda-3}\right) g_d^{HS}(d;\eta_{eff}) \tag{7}$$

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In the previous equation, the radial distribution function of the hard-sphere reference $g_d(xd)$ is calculated numerically by making use of an integral-equation theory. Once this is done, the integral in Eq. (7) is evaluated as a function of the exponent λ and packing fraction η. By using the mean-value theorem, it is possible to determine analytically the integral and, as in the original SAFT-VR formalism[6], to evaluate a_1^S as a function of the contact radial distribution function $g_d^{HS}(d)$ evaluated at an effective density η_{eff},

$$g_d^{HS}(d; \eta_{eff}) = \frac{1 - \eta_{eff}(\eta; \lambda)/2}{\left[1 - \eta_{eff}(\eta; \lambda)\right]^3} \tag{8}$$

Note that the above expression is consistent with the Carnahan and Starling[5] EOS. The analytic expression for a_1^S given by Eq. (7) is only possible if the dependence of the effective packing fraction η_{eff} on λ and η is known. We use here the new parametrization proposed by Lafitte et $al.$[1], that accounts for a broader range of exponents than the original parametrization of Gil-Villegas et $al.$[6], i.e., $5 \leq \lambda \leq 100$,

$$\eta_{eff} = c_1(\lambda)\eta + c_2(\lambda)\eta^2 + c_1(\lambda)\eta^3 + c_4(\lambda)\eta^4 \tag{9}$$

with

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} 0.81096 & 1.7888 & -37.578 & 92.284 \\ 1.0205 & -19.341 & 151.26 & -463.50 \\ -1.9057 & 22.845 & -228.14 & 973.92 \\ 1.0885 & -6.1962 & 106.98 & -677.64 \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 1/\lambda \\ 1/\lambda^2 \\ 1/\lambda^3 \end{pmatrix} \tag{10}$$

See the work of Lafitte et $al.$[1] to check the ability of the analytic Eq. (7) describing the dependence of a_1^S with ρ_s of the BH perturbation term of the Sutherland fluid with varying attractive exponent λ.

The first-order perturbation term a_1 also depends on the function $B(\eta; \lambda)$,[1]

$$B(\eta; \lambda) = 12\eta\epsilon \left[\frac{1 - \eta/2}{(1 - \eta)^3} I_\lambda(\lambda) - \frac{9\eta(1 + \eta)}{2(1 - \eta)^3} J_\lambda(\lambda) \right] \tag{11}$$

with $I_\lambda(\lambda)$ defined as,

$$I_\lambda(\lambda) = -\frac{(x_0)^{3-\lambda} - 1}{\lambda - 3} \tag{12}$$

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and $J_\lambda(\lambda)$ as,

$$J_\lambda(\lambda) = -\frac{(x_0)^{4-\lambda}(\lambda - 3) - (x_0)^{3-\lambda}(\lambda - 4) - 1}{(\lambda - 3)(\lambda - 4)} \tag{13}$$

As it will become clear in the next Section, it is useful to partition the mean-attractive energy or first-order perturbation to the free energy $a_1 = a_1^{SR} + a_1^{LR}$ into short-range, a_1^{SR}, and long-range, a_1^{LR} parts. The short-range contribution is written as

$$a_1^{SR} = a_1 - a_1^{VDW} \tag{14}$$

where a_1^{VDW} is the long-range contribution represented by the van der Waals attractive term (at the mean-field level of approximation) given by

$$a_1^{VDW} = 2\pi\beta\,\alpha\rho_s \tag{15}$$

α is a single dimensionless van der Waals-like attractive constant given in terms of the Mie intermolecular potential as

$$\alpha = \frac{1}{\epsilon\sigma^3}\int_\sigma^\infty \phi(r)r^2dr = \mathcal{C}\left(\frac{1}{\lambda_a - 3} - \frac{1}{\lambda_r - 3}\right) \tag{16}$$

The second-order term a_2 (fluctuation contribution) is much more difficult to obtain as it requires a knowledge of two-, three-, and four-body correlation functions of the reference system. Lafitte et al.[1] used the idea of Zhang[7] who proposed an improved macroscopic compressibility approximation (MCA) assuming that the number of molecules in neighboring coordination shells are correlated. Following this approach, a_2 may be written as an algebraic expression using the same procedure used for a_1,

$$a_2 = -\pi\rho_s\chi\int_\sigma^\infty g_d^{HS}(r)[\phi(r)]^2r^2dr = \frac{1}{2}K^{HS}(1 + \chi)\epsilon\mathcal{C}^2\left[x_0^{2\lambda_a}\left\{a_1^S(\eta; 2\lambda_a) + B(\eta; 2\lambda_a)\right\}\right.$$
$$\left. - 2x_0^{\lambda_a + \lambda_r}\left\{a_1^S(\eta; \lambda_a + \lambda_r) + B(\eta; \lambda_a + \lambda_r)\right\} - x_0^{2\lambda_r}\left\{a_1^S(\eta; 2\lambda_r) + B(\eta; 2\lambda_r)\right\}\right] \tag{17}$$

Here K^{HS} is the isothermal compressibility of the hard-sphere reference fluid, which is obtained form the density derivative of the Carnahan and Starling[5] expression for the compressibility factor,

$$K^{HS} = \frac{(1-\eta)^4}{1 + \eta + 4\eta^2 - 4\eta^3 + \eta^4} \tag{18}$$

The correction pre-factor χ used by Lafitte et al.[1] is a more-generic factor than that used originally by Zhang[7],

$$\chi = f_1(\alpha)\eta x_0^3 + f_2(\alpha)(\eta x_0^3)^5 + f_3(\alpha)(\eta x_0^3)^8 \tag{19}$$

The functions f_i $(i = 1, 2, 3)$ depend on both the attractive and repulsive exponents of the Mie potential through the single dimensionless van der Waals-like attractive constant α defined previously in Eq. (16). The specific functional dependence of f_i on α is given by,

$$f_i(\alpha) = \left(\sum_{n=0}^{3} \phi_{i,n}\alpha^n\right) \Big/ \left(1 + \sum_{n=4}^{6} \phi_{i,n}\alpha^{n-3}\right) \quad i = 1, \ldots 6 \tag{20}$$

Coefficients $\phi_{i,n}$ are given in Table II of the work of Lafitte et al.[1].

Finally, the third-order term a_3 proposed by Lafitte et al.[1] is expressed as an empirical expression similar to the correction pre-factor defined in Eq. (19),

$$a_3 = -\epsilon^3 f_4(\alpha)\eta x_0^3 \exp\left(f_5(\alpha)\eta x_0^3 + f_6(\alpha)\eta x_0^6\right) \tag{21}$$

Note that the expression has a functional form that is independent of temperature. Functions f_i $(i = 4, 5, 6)$ are functions of α as defined previously in Eq. (20).

C. Chain contribution

The term a^{CHAIN} takes into account the contribution to the free energy due to the formation of a chain molecule of m_s Mie monomers tangentially bonded at $r = \sigma$. It can be expressed in the standard Wertheim TPT1[8] form as,

$$a^{CHAIN} = -(m_s - 1)\ln g^{Mie}(\sigma) \tag{22}$$

where the radial distribution function of the Mie reference fluid at contact is given by,[1]

$$g^{Mie}(\sigma) = g_d^{HS}(\sigma)\exp\left[(\beta\epsilon)\frac{g_1(\sigma)}{g_d^{HS}(\sigma)} + (\beta\epsilon)^2\frac{g_2(\sigma)}{g_d^{HS}(\sigma)}\right] \tag{23}$$

The zeroth-order term $g_d^{HS}(\sigma)$ is given here by the semi-empirical representation proposed by Boublík[9], valid for $1 < x_0 < \sqrt{2}$,

$$g_d^{HS}(\sigma) = g_d^{HS}(x_0 d) = \exp\left[(k_0 + k_1 x_0 + k_2 x_0^2 + k_3 x_0^3)\right] \tag{24}$$

where the density-dependent coefficients k_i are given by,[9]

$$k_0 = -\ln(1 - \eta) + \frac{42\eta - 39\eta^2 + 9\eta^3 - 2\eta^4}{6(1 - \eta)^3} \tag{25}$$

$$k_1 = \frac{\eta^4 + 6\eta^2 - 12\eta}{2(1 - \eta)^3}, \tag{26}$$

$$k_2 = \frac{-3\eta^2}{8(1 - \eta)^2}, \tag{27}$$

and

$$k_3 = \frac{-\eta^4 + 3\eta^2 + 3\eta}{6(1 - \eta)^3} \tag{28}$$

The first- and second-order terms, $g_1(\sigma)$ and $g_2(\sigma)$, respectively, are given by,

$$g_1(\sigma) \approx g_1(d) = \frac{1}{2\pi\epsilon d^3}\left[3\frac{\partial a_1}{\partial \rho_s} - \mathcal{C}\lambda_a x_0^{\lambda_a}\frac{a_1^S(\eta; \lambda_a + B(\eta; \lambda_a)}{\rho_s} + \mathcal{C}\lambda_r x_0^{\lambda_r}\frac{a_1^S(\eta; \lambda_r + B(\eta; \lambda_a)}{\rho_s}\right] \tag{29}$$

and

$$g_2(\sigma) \approx g_2(d) = (1 + \gamma_c)\, g_2^{MCA}(d) \tag{30}$$

Lafitte *et al.*[1] propose a simple empirical correlation given by the previous equation, in which γ_c is a correction factor that is a function of both density and temperature,

$$\gamma_c = \phi_{7,0}\left[-\tanh\left\{\phi_{7,1}(\phi_{7,2} - \alpha)\right\} + 1\right]\eta x_0^3 \theta \times \exp\left[\phi_{7,3}\,\eta x_0^3 + \phi_{7,4}\,\eta^2 x_0^6\right] \tag{31}$$

where $\theta = \exp(\beta\epsilon) - 1$, and coefficients $\phi_{7,1}$, $\phi_{7,2}$, $\phi_{7,3}$, and $\phi_{7,4}$ are given in Table II of the work of Lafitte *et al.*[1]. $g_2^{MCA}(\sigma)$ may be expressed as,

$$g_2^{MCA}(\sigma) = \frac{1}{2\pi\epsilon^2 d^3}\left[3\frac{\partial}{\partial\rho_s}\left(\frac{a_2}{1+\chi}\right) - \epsilon K^{HS}\mathcal{C}^2\lambda_r x_0^{2\lambda_r}\frac{a_1^S(\eta;2\lambda_r)+B(\eta;2\lambda_r)}{\rho_s}\right.$$
$$+ \epsilon K^{HS}\mathcal{C}^2(\lambda_r+\lambda_a)x_0^{\lambda_r+\lambda_a}\frac{a_1^S(\eta;\lambda_r+\lambda_a)+B(\eta;\lambda_r+\lambda_a)}{\rho_s}$$
$$\left.- \epsilon K^{HS}\mathcal{C}^2\lambda_a x_0^{2\lambda_a}\frac{a_1^S(\eta;2\lambda_a)+B(\eta;2\lambda_a)}{\rho_s}\right] \tag{32}$$

II. INHOMOGENEOUS FLUID OF ASSOCIATING CHAIN MOLECULES (SAFT-VR MIE DFT)

The new Helmholtz free energy functional presented in this work, given by Eq. (5) in the paper, is expressed in terms of an ideal, $A^{IDEAL}[\rho(\mathbf{r})]$, a reference, $A^{REF}_{Mie,MF}[\rho(\mathbf{r})]$, and an attractive contribution, $A^{ATT}_{Mie,MF}[\rho(\mathbf{r})]$,

$$A^{SAFT-VR}_{Mie,MF}[\rho(\mathbf{r})] = A^{IDEAL}[\rho(\mathbf{r})] + A^{REF}_{Mie,MF}[\rho(\mathbf{r})] + A^{ATT}_{Mie,MF}[\rho(\mathbf{r})]. \tag{33}$$

where $A^{REF}_{Mie,MF}[\rho(\mathbf{r})]$ is the reference term that incorporates the repulsive hard-sphere, the perturbative terms due to the attractive interactions, and the chain term,

$$A^{REF}_{Mie,MF}[\rho(\mathbf{r})] = A^{HS}[\rho(\mathbf{r})] + A_1^{SR}[\rho(\mathbf{r})] + A_2[\rho(\mathbf{r})] + A_3[\rho(\mathbf{r})] + A^{CHAIN}[\rho(\mathbf{r})] \tag{34}$$

Here we explain in detail the particular functional forms of the ideal and all the reference contributions. The reduced ideal Helmholtz free energy of an inhomogeneous system of nonspherical particles can be written as[2,10],

$$A^{IDEAL} = k_B T \int d\mathbf{r}\, f^{IDEAL}(\rho(\mathbf{r})) = k_B T \int d\mathbf{r}\, \rho(\mathbf{r})\, a^{IDEAL}(\rho(\mathbf{r})) \tag{35}$$

The hard-sphere interaction is short ranged and is usually treated locally in a perturbative DFT treatment of the vapor-liquid interface[10-14]; such functionals based on the local density approximation (LDA) of the reference term provide a good description of the vapor-liquid interface, although the approach fails for fluids close to their triple points or for confined systems where a weighted-density approximation (WDA) has to be used. In our SAFT-VR Mie DFT the hard-sphere LDA free energy functional is given by

$$A^{\mathrm{HS}}[\rho(\mathbf{r})] = k_B T \int d\mathbf{r}\, f^{\mathrm{HS}}(\rho(\mathbf{r})) = k_B T \int d\mathbf{r}\, \rho(\mathbf{r})\, m\, a^{\mathrm{HS}}(\rho(\mathbf{r})), \tag{36}$$

where the expression for $a^{\mathrm{HS}}(\rho(\mathbf{r}))$ is written as a function of the packing fraction profile $\eta(\mathbf{r}) = (\pi d^3/6)\rho_s(\mathbf{r})$ in the Carnahan and Starling form (see Eq. (5)).

The first-order contribution to the free energy of Mie spheres due to the short-range part of the correlations in the attractive term, as well as the second- and third-order contributions are contained in $A_1^{SR}[\rho(\mathbf{r})]$, $A_2[\rho(\mathbf{r})]$, and $A_3[\rho(\mathbf{r})]$, respectively. The three contributions are defined in terms of the bulk terms a_1^{SR}, a_2, and a_3 given by Eqs. (14), (17), and (21), respectively. As all these contributions present a short-range interaction it can be treated locally as[12]

$$A_1^{SR}[\rho(\mathbf{r})] = k_B T \int d\mathbf{r}\, f_1^{SR}(\rho(\mathbf{r})) = k_B T \int d\mathbf{r}\, \rho(\mathbf{r})\, m\, a_1^{SR}(\rho(\mathbf{r})), \tag{37}$$

$$A_2[\rho(\mathbf{r})] = k_B T \int d\mathbf{r}\, f_2(\rho(\mathbf{r})) = k_B T \int d\mathbf{r}\, \rho(\mathbf{r})\, m\, a_2(\rho(\mathbf{r})), \tag{38}$$

and

$$A_3[\rho(\mathbf{r})] = k_B T \int d\mathbf{r}\, f_3(\rho(\mathbf{r})) = k_B T \int d\mathbf{r}\, \rho(\mathbf{r})\, m\, a_3(\rho(\mathbf{r})), \tag{39}$$

The chain contribution to the SAFT free energy, given by Eq. (22) can be written in terms of the contact value of the pair radial distribution function of the reference monomer system, which is clearly a 'short-range' contribution and can also be approximated by a local functional[12]. The contribution to the reference free energy functional for the formation of a chain of m Mie segments is written at the LDA level as

$$A^{CHAIN}[\rho(\mathbf{r})] = k_B T \int d\mathbf{r}\, f^{CHAIN}(\rho(\mathbf{r})) = k_B T \int d\mathbf{r}\, \rho(\mathbf{r})\, a^{CHAIN}(\rho(\mathbf{r})), \tag{40}$$

where $a^{CHAIN}(\rho(\mathbf{r}))$ is the function of density given by Eq. (22). This LDA treatment, that has been introduced and used by Gloor et al.[12], it provides a very good description of the vapor-liquid surface tension of moderately long chainlike molecules. In essence this approximation amounts to determining the average density profile for the segments making up the chain without specifying which chain the segments belong to. This is an alternative way of describing the density profiles of molecules in comparison with WDA treatments,

such as those developed by Kierlik and Rosinberg[15,16] and the iSAFT formalism of Tripathi and Chapman[17,18], in which the position of each segment of the chain is treated explicitly.

As was mentioned in the paper, the equilibrium interfacial profile is the one that minimizes the grand potential. In the case of the SAFT-VR Mie MF DFT that has just been described, the corresponding Euler-Lagrange equation is obtained as

$$
\begin{aligned}
\left. \frac{\delta\Omega[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \right|_{\text{eq}} &= \frac{\delta A[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} - \mu \\
&= \frac{\delta A^{IDEAL}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} + \frac{\delta A^{REF}_{Mie,MF}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} + \frac{\delta A^{ATT}_{Mie,MF}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} - \mu = 0
\end{aligned}
\tag{41}
$$

The variation of the ideal and reference contributions with respect to $\rho(\mathbf{r})$ correspond to the local chemical potentials $\mu^{IDEAL}(\rho(\mathbf{r})) = \frac{\delta A^{IDEAL}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}$ and $\mu^{REF}_{Mie,MF}(\rho(\mathbf{r})) = \frac{\delta A^{REF}_{Mie,MF}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}$ (which can be obtained from the corresponding expressions for the homogeneous system, through $\mu = k_B T\{a + \rho\partial a/\partial\rho\}$), while the variation of the attractive term requires a knowledge of the density derivative of the correlation function. The equilibrium profile can thus be determined by solving the equation

$$
\mu = \mu^{IDEAL}(\rho(\mathbf{r})) + \mu^{REF}_{Mie,MF}(\rho(\mathbf{r})) + \int \mathrm{d}\mathbf{r}' \, m^2 \, \rho(\mathbf{r}') \, \phi(|\mathbf{r} - \mathbf{r}'|),
\tag{42}
$$

which ensures that the chemical potential at each point in the profile is equal to the bulk chemical potential μ[11].

In order to achieve an accurate solution the region over which the density profile deviates from the vapor and liquid bulk densities (interfacial thickness) must be narrower than the interval over which Eq. (4) of the paper or Eq. (42) is solved. Widths ranging from $|z_{\max} - z_{\min}| \sim 2\sigma$ for states at a temperature $T \sim T_c/2$ (where T_c is the critical temperature) to $|z_{\max} - z_{\min}| \sim 15\sigma$ at $0.98\,T_c$. The integration in the z direction is performed numerically by selecting the range from $z_{\min}$ to $z_{\max}$ over which to integrate, and the interval is discretised into a large number of points z_i (typically 200 grid points *per* σ). A numerical integration of Eq. (41) is then performed by starting from a trial density profile ρ_{old} with limiting densities $\rho(z_{\max})$ and $\rho(z_{\min})$ which correspond to the vapor and liquid equilibrium bulk densities (the initial profile could be represented by a step profile), and solving the Euler-Lagrange equation numerically at each point z_i. This results in a new density profile ρ_{new} and the

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process is repeated until the density at each point z_i changes by no more than a specified tolerance.

REFERENCES

[1] T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. S. Adjiman, E. A. Müller and G. Jackson, *J. Chem. Phys.*, 2013, **139**, 154504.

[2] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids, 3rd Edition*, Academic Press, London, 2006.

[3] J. A. Barker and D. J. Henderson, *J. Chem. Phys.*, 1967, **47**, 2856.

[4] J. A. Barker and D. J. Henderson, *J. Chem. Phys.*, 1967, **47**, 4714.

[5] N. F. Carnahan and K. E. Starling, *J. Chem. Phys.*, 1969, **51**, 635–636.

[6] A. Gil-Villegas, A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson and A. N. Burgess, *J. Chem. Phys.*, 1997, **106**, 4168–4186.

[7] B.-J. Zhang, *Fluid Phase Equilibria*, 1999, **154**, 1–10.

[8] M. S. Wertheim, *J. Chem. Phys.*, 1987, **87**, 7323–7331.

[9] T. Boublík, *Molecular Physics*, 1986, **59(4)**, 775–793.

[10] R. Evans, *Density Functionals in the Theory of Nonuniform Fluids. In Fundamentals of Inhomogeneous Fluids*, Dekker, New York, 1992.

[11] J. Winkelmann, *Mol. Phys.*, 2001, **13**, 4739–4768.

[12] G. J. Gloor, G. Jackson, F. J. Blas, E. Martín Del Río and E. D. Miguel, *J. Chem. Phys.*, 2004, **121**, 12740–12759.

[13] F. J. Blas, E. Martín Del Río, E. de Miguel and G. Jackson, *Mol. Phys.*, 2001, **99**, 1851–1865.

[14] G. J. Gloor, F. J. Blas, E. M. D. Río, E. D. Miguel and G. Jackson, *Fluid Phase Equil.*, 2002, **194-197**, 521–530.

[15] E. Kierlik and M. L. Rosinberg, *J. Chem. Phys.*, 1992, **97(12)**, 9222–9239.

[16] E. Kierlik and M. L. Rosinberg, *J. Chem. Phys.*, 1993, **99(5)**, 3950–3965.

[17] S. Tripathi and W. G. Chapman, *J. Chem. Phys.*, 2005, **122**, 094506/1–11.

[18] S. Tripathi, A. Dominik and W. G. Chapman, *Ind. Eng. Chem. Res.*, 2006, **45**, 6785–6792.