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1 **A molecular Density Functional Theory for associating fluids in 3D geometries**2 Antoine Barthes,¹ Thomas Bernet,² David Grégoire,^{1,3} and Christelle Miqueu¹3 ¹*Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, LFCR, Anglet,*
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10 (Dated: 11 December 2023)

11 A new free-energy functional is proposed for inhomogeneous associating fluids. The gen-
12 eral formulation of Wertheim's thermodynamic perturbation theory is considered as the
13 starting point of the derivation. We apply the hypotheses of the statistical associating fluid
14 theory in the classical density functional theory (DFT) framework to obtain a tractable
15 expression of the free-energy functional for inhomogeneous associating fluids. Specific
16 weighted functions are introduced in our framework to describe association interactions
17 for a fluid under confinement. These weighted functions have a mathematical structure
18 similar to the weighted densities of the fundamental-measure theory (*i.e.*, they can be ex-
19 pressed as convolution products), such that they can be efficiently evaluated with Fourier
20 transforms in a 3D space. The resulting free-energy functional can be employed to deter-
21 mine the microscopic structure of inhomogeneous associating fluids of arbitrary 3D geom-
22 etry. The new model is first compared with Monte Carlo simulations and previous versions
23 of DFT for a planar hard wall system in order to check its consistency in a 1D case. As
24 an example of application in a 3D configuration, we investigate then the extreme confine-
25 ment of an associating hard-sphere fluid inside an anisotropic open cavity with a shape that
26 mimics a simplified model of zeolite. Both the density distribution and the corresponding
27 molecular bonding profile are given, revealing complementary information to understand
28 the structure of the associating fluid inside the cavity network. The impact of the degree of
29 association on the preferential positions of the molecules inside the cavity is investigated
30 as well as the competition between association and steric effect on adsorption.

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31 *List of acronyms*

32

TPT	thermodynamic perturbation theory
SAFT	statistical associating fluid theory
EoS	equation of state
PDF	pair distribution function
ref.	reference
HS / hs	hard sphere
RDF	radial distribution function
DFT	density functional theory
FMT	fundamental-measure theory
iSAFT	interfacial statistical associating fluid theory
aFMT	fundamental-measure theory for association
aWDA	weighted density approximation for association
33	
assoc.	association
dist.	distance
ang.	angular
ext.	external
eq.	equilibrium
id.	ideal
ex.	exces
WBII	White Bear version mark II of FMT
RHNC	reference hypernetted-chain approach
CG	coarse grained
FFT	fast Fourier transform
LTA	Linde Type A

34 **I. INTRODUCTION**

35 Within the domain of thermodynamics, associating fluids constitute a unique class of sub-
 36 stances known for their distinctive ability to form oriented interactions, *e.g.*, hydrogen bonds and
 37 strong polar interactions. When associating fluids are confined in porous media, a complex in-
 38 terplay ensues. The characterization of the fluid-solid interfaces and effects of confinement is

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39 not only of interest for fundamental research, but is also of great importance in a variety of ap-
40 plied fields, including nanotechnology, heterogeneous catalysis, gas storage and separation, and
41 environmental science¹⁻³.

42 In the 80's, Wertheim developed in its famous thermodynamic perturbation theory (TPT) a
43 rigorous framework that models highly directional attractive intermolecular interactions capable
44 of describing the thermodynamic properties of inhomogeneous associating fluids⁴⁻⁷. Within this
45 pioneering approach, these attractive forces are mediated by acentrically located sites within each
46 molecule, with the bonding constraints that two molecules can only form a single association with
47 each other due to steric effects. A detailed discussion about Wertheim's framework can be found
48 in the pedagogical review of Zmpitas *et al.*⁸. A few years later, Jackson *et al.*⁹ restated Wertheim's
49 TPT at first order, namely TPT1, in a framework for homogeneous fluids, such that the association
50 contribution to the free energy could be introduced in the so-called SAFT equation-of-state (EoS)
51 by Chapman *et al.*¹⁰⁻¹². Multiple bonding sites are considered in a tractable way in the SAFT
52 approach, by assuming the independence of the association interactions, such that the contribu-
53 tions to the free energy can be approximated as a sum over the different sites. Thus, estimating
54 the association contribution to the Helmholtz free energy requires only to solve the so-called non-
55 bonded fraction relation⁹. This latter is a key achievement of Wertheim's TPT and is formulated as
56 a self-consistent equation involving a pair-correlation integral, that can be interpreted as the bond-
57 ing probability, and requires the pair distribution function (PDF) of the reference inter-molecular
58 potential $g^{ref.}(\mathbf{r}_1, \mathbf{r}_2)$. The PDF quantifies the extent by which the probability of finding a set of
59 two molecules in the configuration $(\mathbf{r}_1, \mathbf{r}_2)$, *i.e.* the two-body density denoted as $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, de-
60 viates from the uncorrelated one-body densities $\rho(\mathbf{r}_1)$ and $\rho(\mathbf{r}_2)$, through the normalized relation
61 $[g(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) / [\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)]]$. In the TPT framework, the elaboration of non-ideal
62 contributions from the PDF allows us to obtain tractable formulations both without explicit con-
63 sideration of the partition function and also only expressed in terms of one-body density. Thus
64 defined, the difficulty has been shifted in determining the PDF and one can use the individual
65 properties of the target fluid to treat the pair correlation on a case-by-case basis. In the original
66 work⁹, as well as in our current work, a hard sphere (HS) fluid is considered as the reference
67 non-associated fluid of the perturbation approach⁴⁻⁷. In the case of a uniform fluid, the correla-
68 tion between two HS molecules only depends on the radial distance, designated as $g^{hs}(r_{12})$, and is
69 referred as the radial distribution function (RDF). An accurate description of the thermodynamic
70 properties of a homogeneous HS fluid¹³ along with the exact contact-value theorem¹⁴ give access

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71 to the particular value of the HS pair correlation at the contact distance $r_{12} = \sigma$, denoted here as
 72 $g_{\sigma}^{\text{hs}}(\eta_{\sigma})$, which only depends of the selected thermodynamic conditions, set by the packing factor
 73 η_{σ} . Because of the short-range intermolecular association, Jackson *et al.*⁹ could approximate the
 74 RDF with the contact-value approach, and the resulting pair-correlation integral could be com-
 75 pacted by introducing the bonding volume (*i.e.*, the volume available to two sites for bonding).
 76 Thus defined, any configurations of association under the bonding constraints fixed in the TPT
 77 development can be considered with the SAFT formalism, but an analytical solution of the non-
 78 bonded fraction relation is only available for particular association schemes *e.g.*, schemes 1A, 2B,
 79 and 4C defined later. Subsequent studies on parameterization have enabled SAFT (the original
 80 formulation^{11,12}, as well as alternative parameterizations¹⁵⁻²¹) to be applied to the thermodynamic
 81 description of many real associative fluids (water, alcohols, acids, *etc.*) under bulk conditions²²⁻²⁶.

82 In the more general case of inhomogeneous fluids, classical density functional theory²⁷ (DFT)
 83 has emerged as a powerful theoretical framework that provides the equilibrium density distribu-
 84 tions of a fluid submitted to an external potential (such as the one induced by solid surfaces). In the
 85 DFT framework, the Helmholtz free energy, intrinsic to molecular interactions within the fluid, is
 86 a functional of the density distribution that can be approximated with a perturbative approach from
 87 a reference fluid, which is most often the HS fluid. A succession of theoretical achievements has
 88 resulted in an accurate thermodynamic description of inhomogeneous HS fluids; the most accurate
 89 being certainly the fundamental-measure theory²⁸⁻³¹ (FMT). Chapman³² were the first to derive
 90 Wertheim's TPT into a tractable inhomogeneous form of the association free energy functional,
 91 the bulk limit of which was used in the development of SAFT briefly recalled above. However,
 92 this formulation is not directly applicable, as it requires both an inhomogeneous formulation of
 93 the PDF and a method for solving the integral equations arising from the inhomogeneity. In this
 94 respect, different paths have been followed in the literature, mainly using the bulk counterpart,
 95 not only as a guideline for constructing the inhomogeneous functional, but also as a homogeneous
 96 limit, such that the bulk parameterization can be employed in the inhomogeneous case. Segura *et al.*³³
 97 proposed two methods to approximate the association contribution to the free-energy func-
 98 tional: a first one starting from the inhomogeneous form of Wertheim's theory, and a second one,
 99 starting from the bulk form (SAFT EoS) and extending it to an inhomogeneous scenario.

100 In the first method, Segura *et al.*³⁴ managed to derive Chapman's inhomogeneous expression
 101 into a formulation that can be applicable to adsorption on a planar solid surface by making two as-
 102 sumptions. The first one deals with the PDF and corresponds to the approximation that Jackson *et*

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103 *al.*⁹ employed in SAFT for homogeneous fluids. The second one relates to the treatment of the in-
 104 homogeneous functions (*e.g.* local density) involved in the bonding probability in the non-bonded
 105 fraction, whose final expression is given in the form of a 1D formulation. This is the starting point
 106 of the interfacial statistical associating fluid theory (iSAFT) developed by Chapman and coworkers
 107 ^{35–37}. Bymaster *et al.*³⁷ improved the inhomogeneous treatment of the PDF but did not propose
 108 any alternative resolution than Segura's approximation to solve the non-bonded fraction (as pre-
 109 sented so far in the literature). In the second method, Segura *et al.*³³ used the bulk EoS as a starting
 110 point of the derivation, and replaced the bulk density by the weighted density introduced by Tara-
 111 zona³⁸. This method has also been adopted by Yu and Wu³⁹ who used Rosenfeld's FMT weighted
 112 densities (referred to as aFMT), and Camacho Vergara *et al.*⁴⁰ who used specific weighted density
 113 approximations (WDA) (referred to as aWDA). In contrast to iSAFT^{35,36}, the aFMT and aWDA
 114 formulations extend the bulk properties to an inhomogeneous framework at an earlier step of the
 115 derivation, thus making more difficult to adjudicate the treatment of the inhomogeneity.

116 A detailed inventory of these most common SAFT-based DFT versions for associating fluids
 117 can be found in the recent article of Camacho Vergara *et al.*⁴⁰ where they compared the iSAFT
 118 version of Bymaster *et al.*³⁷, aFMT, and aWDA approaches with molecular simulations for fluids
 119 in the neighborhood of a hard wall, for several thermodynamic conditions and several associa-
 120 tion schemes. Their study revealed that iSAFT shows slightly better agreement than aWDA with
 121 simulations for confined fluids when the association interactions are predominant. The aim of the
 122 present work is to propose a simpler and more general approach than the derivation of Chapman
 123 and coworkers^{37,41} employed in iSAFT by: i) starting from the inhomogeneous framework of
 124 Wertheim^{4–7} (as done in iSAFT); ii) following the recent formulations of Lurie-Cregg *et al.*⁴² to
 125 improve the description of the inhomogeneous PDF for EoS-based DFT approaches; iii) applying
 126 the necessary approximations to find the homogeneous limit corresponding to the RDF used in
 127 SAFT⁹. The advantage of this new formulation is that it introduces weighted functions, specific to
 128 the range of association, that can be efficiently evaluated with Fourier transforms in a 3D space.

129 In Section II, the new approach for inhomogeneous associating fluids is presented. In particu-
 130 lar, the intermolecular potential considered in our work is described in Section II A, the classical
 131 DFT framework is introduced in Section II B, and the new free-energy functional is detailed in
 132 Section II C. Results are shown in Section III for an associating fluid at contact with a hard planar
 133 wall (Section III A) and in an anisotropic 3D cavity (Section III B). In Section IV, we provide
 134 conclusions and closing remarks.

135 **II. THEORY**136 **A. Potential for inter-molecular repulsion and association interactions**

137 We consider a single-component system of associating monomers. The total pairwise potential
138 can be split into two contributions⁹

$$139 \quad \phi^{\text{hs}}(\mathbf{r}_{12}) + \sum_{a,b} \phi_{ab}^{\text{assoc.}}(\mathbf{r}_{1a2b}) \quad (1)$$

140 where ϕ^{hs} is the HS potential, with \mathbf{r}_{12} being the vector connecting the centers of the two particles
141 1 and 2. Denoting σ the diameter of the particles,

$$142 \quad \phi^{\text{hs}}(\mathbf{r}_{12}) = \begin{cases} \infty & \text{if } r_{12} < \sigma \\ 0 & \text{if } r_{12} \geq \sigma \end{cases} \quad (2)$$

143 where $r_{12} = |\mathbf{r}_{12}|$ is the center-center distance between two molecules. The second term of Eq. (1)
144 is a sum over all association pair site potentials $\phi_{ab}^{\text{assoc.}}$ with \mathbf{r}_{1a2b} being the vector connecting the
145 position of site a from molecule 1 to the position of site b from molecule 2 (as shown in FIG. 1).
146 Two standard formulations of $\phi_{ab}^{\text{assoc.}}$ exist. Association is simulated in the first simulation by
147 means of a square-well potential centered on a site position and having a given cutoff r_c . Let us
148 note d the distance between on site position and the center of the molecule (FIG. 1(a)). Considering
149 this distance formalism,

$$150 \quad \phi_{\text{dist.},ab}^{\text{assoc.}}(\mathbf{r}_{1a2b}) = \begin{cases} -\epsilon_{ab} & \text{if } r_{ab} \leq r_c \\ 0 & \text{if } r_{ab} > r_c \end{cases} \quad (3)$$

151 where $r_{ab} = |\mathbf{r}_{1a2b}|$ is the distance between association sites and ϵ_{ab} is the association degree
152 of interaction. A square-well potential which is centered on molecule positions is considered
153 as a second formulation of association (FIG. 1(b)), for a given cutoff $r_{12,c}$, and the following
154 angular parameters (θ_1, θ_2) are introduced to define the site orientations. Let θ_1 (respectively θ_2)
155 be the angle between \mathbf{r}_{12} and the vector from the center of molecule 1 (respectively 2) to site a
156 (respectively b),

$$157 \quad \phi_{\text{ang.},ab}^{\text{assoc.}}(\mathbf{r}_{1a2b}) = \begin{cases} -\epsilon_{ab} & \text{if } r_{12} \leq r_{12,c} \text{ and } \theta_1 \leq \theta_{1,c} \text{ and } \theta_2 \leq \theta_{2,c} \\ 0 & \text{if } r_{12} > r_{12,c} \text{ or } \theta_1 > \theta_{1,c} \text{ or } \theta_2 > \theta_{2,c} \end{cases} \quad (4)$$

158 where $\theta_{1,c}, \theta_{2,c}$ are angular cutoffs. In order to compare our new DFT approach with existing

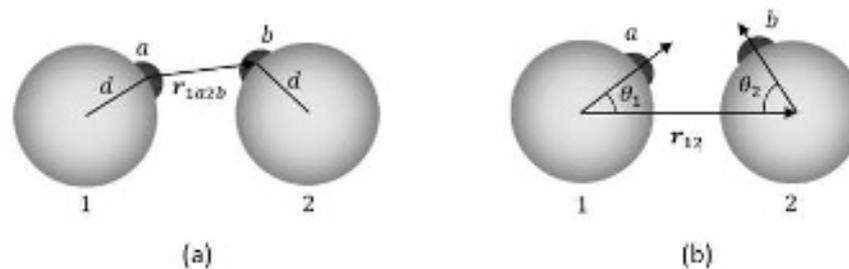


FIG. 1. Bonding description using distance parameters (a) and angular parameters (b).

159

160 Monte Carlo simulations^{33,34,43}, as well as previous DFT models^{37,39,40}, the angular formulation is
 161 employed in our current work, with $r_{12,c} = 1.05\sigma$ and $\theta_{1,c} = \theta_{2,c} = \theta_c = 27^\circ$ for each site. Studies
 162 mentioned above considered three different schemes of association illustrated in FIG. 2 : scheme
 163 1A for which there is one site A of each particle that can be bonded with another site ; in scheme
 164 2B, two sites A and B are placed on the particle and we assume that only site A can be bonded with
 165 site B, *i.e.*, $\epsilon_{AA} = \epsilon_{BB} = 0$; scheme 4C consists of four associating sites A, B, C, and D where only
 166 AC, AD, BC, and BD are allowed to be bonded, *i.e.*, $\epsilon_{AA} = \epsilon_{AB} = \epsilon_{BB} = \epsilon_{CC} = \epsilon_{CD} = \epsilon_{DD} = 0$.
 167 The scheme 4C is typically used to model hydrogen bonding in the water molecule.

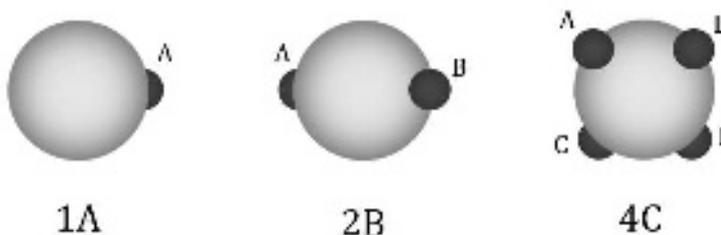


FIG. 2. Different schemes of association.

168

169

170 B. DFT treatment for spherical associating monomer

171 Let us consider an ensemble of molecules in a volume V at a given temperature T and bulk
 172 chemical potential μ which is the grand canonical ensemble suitable for adsorption studies. Putting
 173 this system under an external field $V^{\text{ext}}(\mathbf{r})$, the grand potential $\Omega[\rho]$ can be defined as a functional
 174 of the density profile $\rho(\mathbf{r})$ with the classical DFT framework²⁷:

175

$$\Omega[\rho] = \mathcal{F}[\rho] + \int \rho(\mathbf{r}) (V^{\text{ext}}(\mathbf{r}) - \mu) d\mathbf{r} \quad (5)$$

176 where $\mathcal{F}[\rho]$ is the Helmholtz free-energy functional that does not depend explicitly on the external
177 and bulk chemical potentials. The minimum of the grand potential is obtained for a unique density
178 profile $\rho_{\text{eq.}}(\mathbf{r})$, such that

$$179 \quad \left. \frac{\delta \Omega[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho(\mathbf{r})=\rho_{\text{eq.}}(\mathbf{r})} = 0 \quad (6)$$

180 and corresponds to the equilibrium state, for which the functional reduces to the grand-canonical
181 potential $\Omega[\rho_{\text{eq.}}] = \Omega$. The free-energy functional $\mathcal{F}[\rho]$, intrinsic to a given pair potential model,
182 can be split into an ideal part and an excess part, as $\mathcal{F} = \mathcal{F}^{\text{id.}} + \mathcal{F}^{\text{ex.}}$. The ideal part, correspond-
183 ing to the kinetic energy, is known exactly from statistical thermodynamics³⁸. The excess part,
184 corresponding here to the interactions between associative HS, can be obtained from a thermody-
185 namic expansion⁴⁻⁷, $\mathcal{F}^{\text{ex.}} = \mathcal{F}^{\text{hs}} + \mathcal{F}^{\text{assoc.}}$, where the HS free-energy functional \mathcal{F}^{hs} is defined
186 as a reference, and the association free-energy functional $\mathcal{F}^{\text{assoc.}}$ as a perturbation. Once an ex-
187 pression of $\mathcal{F}^{\text{ex.}}$ is considered, one can minimize the grand potential to obtain the self-consistent
188 density profile :

$$189 \quad \rho(\mathbf{r}) = \rho \exp \left(\beta \mu^{\text{ex.}} - \frac{\delta \beta \mathcal{F}^{\text{ex.}}[\rho]}{\delta \rho(\mathbf{r})} - \beta V^{\text{ext.}}(\mathbf{r}) \right) \quad (7)$$

190 where the density ρ is the bulk limit of the one-body density $\rho(\mathbf{r})$ and $\mu^{\text{ex.}}$ the excess part
191 of the bulk chemical potential. The functional derivative $\frac{\delta \mathcal{F}^{\text{ex.}}[\rho]}{\delta \rho(\mathbf{r})}$ estimates the response of
192 the intrinsic Helmholtz free energy functional with respect to the density changes, *i.e.*, corre-
193 sponds to the excess chemical potential for an inhomogeneous phase that can be decomposed
194 as $\mu^{\text{ex.}}(\mathbf{r}) = \mu^{\text{hs}}(\mathbf{r}) + \mu^{\text{assoc.}}(\mathbf{r})$. This estimation is also known as the singlet-direct correlation
195 function $c^{(1)}(\mathbf{r}) = -\mu^{\text{ex.}}(\mathbf{r})$. The bulk counterpart $\mu^{\text{ex.}}$ can be directly obtained by taking the
196 homogeneous limit and thus the microscopic structure of a fluid submitted to an external potential
197 can be completely determined only with an expression of $\mu^{\text{ex.}}(\mathbf{r})$.

198 Among the possible HS treatments, we consider here the HS free-energy functional of the FMT
199 approach²⁸, with the White Bear version mark II (WBII)³⁰ (that corresponds to the Carnahan-
200 Starling¹³ EoS as a bulk limit), such that

$$201 \quad \beta \mathcal{F}^{\text{hs}}[\rho] = \int \Phi^{\text{hs}}(n_{\alpha}(\mathbf{r})) \, d\mathbf{r} \quad (8)$$

202 where $\beta = 1/(k_{\text{B}}T)$ (k_{B} is the Boltzmann constant), and Φ^{hs} is the HS free-energy density, which
203 is postulated to be a function of the weighted densities $n_{\alpha}(\mathbf{r})$ (where α denotes the nature of the
204 weighting^{30,44}). The generic form of a weighted density is a convolution product

$$205 \quad n_{\alpha}(\mathbf{r}_1) = \int \rho(\mathbf{r}_2) p_{\alpha}^{\text{hs}}(\mathbf{r}_{12}) \, d\mathbf{r}_2 \quad (9)$$

206 where p_{α}^{hs} , that depends on the distance between the two positions \mathbf{r}_1 and \mathbf{r}_2 , corresponds to
207 the scalar- and vector-weight functions that describe the geometrical effects coming from the HS
208 potential model^{30,44}. Calculation of the inhomogeneous HS excess chemical potential functional
209 can also be evaluated as a sum of convolution products, such that

$$210 \quad \beta\mu^{\text{hs}}(\mathbf{r}_1) = \frac{\delta\beta\mathcal{F}^{\text{hs}}[\rho]}{\delta\rho(\mathbf{r}_1)} = \sum_{\alpha} \int \frac{\partial\Phi^{\text{hs}}}{\partial n_{\alpha}} \Big|_{(\mathbf{r}_2)} p_{\alpha}^{\text{hs}}(\mathbf{r}_{12}) d\mathbf{r}_2 \quad (10)$$

211 C. Association contribution to the free-energy functional

212 1. Wertheim's free-energy and chemical potential functionals

213 The TPT1 Wertheim's association free energy⁴⁻⁷ for a pure fluid of associating HS is given by

$$214 \quad \beta\mathcal{F}^{\text{assoc.}}[\rho] = \int \rho(\mathbf{r}_1) \sum_a \left[\ln X_a(\mathbf{r}_1) - \frac{X_a(\mathbf{r}_1)}{2} + \frac{1}{2} \right] d\mathbf{r}_1 \quad (11)$$

215 as derived by Chapman³² and Segura *et al.*⁴⁵. $X_a(\mathbf{r}_1)$ is the fraction of a non-bonded site a of a
216 molecule at position \mathbf{r}_1 ,

$$217 \quad X_a(\mathbf{r}_1) = \frac{1}{1 + \int \rho(\mathbf{r}_2) g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2) \sum_b X_b(\mathbf{r}_2) \bar{F}_{ab}(r_{12}) d\mathbf{r}_2} \quad (12)$$

218 where $g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2)$ is the HS PDF at positions \mathbf{r}_1 and \mathbf{r}_2 , and $\bar{F}_{ab}(r_{12})$ is an average of the Mayer
219 function $f_{ab}(\mathbf{r}_{1a2b}) = \left[\exp(-\beta\phi_{ab}(\mathbf{r}_{1a2b})) - 1 \right]$ over the orientations Ω_1 and Ω_2 of molecules 1
220 and 2, respectively, such that

$$221 \quad \bar{F}_{ab}(r_{12}) = \left\langle f_{ab}(\mathbf{r}_{1a2b}) \right\rangle_{\Omega_1, \Omega_2} \quad (13)$$

222 Because of the unweighted average over all orientations, the Mayer function only depends on r_{12} ,
223 and the considered one-body density $\rho(\mathbf{r}_1)$ and fraction $X_a(\mathbf{r}_1)$ do not depend on the orienta-
224 tions Ω_1 and Ω_2 . The function $\bar{F}_{ab}(r_{12})$ can be expressed with the distance association potential
225 model⁴⁶,

$$226 \quad \bar{F}_{\text{dist.},ab}(r_{12}) = F_{ab} \frac{(r_c + 2d - r_{12})^2 (2r_c - 2d + r_{12})}{24 d^2 r_{12}} \times \left(\Theta(2d + r_c - r_{12}) - \Theta(\sigma - r_{12}) \right) \quad (14a)$$

227 or with the angular potential model⁹,

$$228 \quad \bar{F}_{\text{ang.},ab}(r_{12}) = F_{ab} \frac{(1 - \cos\theta_c)^2}{4} \left(\Theta(r_{12,c} - r_{12}) - \Theta(\sigma - r_{12}) \right) \quad (14b)$$

229 where $F_{ab} = \exp(\beta \epsilon_{ab}) - 1$ represents the association strength, and the Heaviside step function Θ
 230 (such that $\Theta(x) = 1$ if $x > 0$, and $\Theta(x) = 0$ if $x < 0$) is used to take into account the association
 231 boundaries.

232
 233 Solving Eq. (7) requires a formulation of the chemical potential functional for the association
 234 contribution, $\mu^{\text{assoc.}}(\mathbf{r}_1) = \frac{\delta \mathcal{F}^{\text{assoc.}}}{\delta \rho(\mathbf{r}_1)}$. However, the derivative $\frac{\delta X_a(\mathbf{r}_1)}{\delta \rho(\mathbf{r}_1)}$ should not be expressed
 235 explicitly to avoid a self-consistent equation problem. This issue has been solved by Michelsen and
 236 Hendriks⁴⁷ for a homogeneous system, and by Chapman and coworkers^{36,37} for an inhomogeneous
 237 system, such that

$$238 \quad \beta \mu^{\text{assoc.}}(\mathbf{r}_1) = \sum_a \ln X_a(\mathbf{r}_1) - \frac{1}{2} \iint \rho(\mathbf{r}_2) \rho(\mathbf{r}_3) \sum_{a,b} X_a(\mathbf{r}_2) \quad (15)$$

$$\times X_b(\mathbf{r}_3) \frac{\delta g^{\text{hs}}(\mathbf{r}_2, \mathbf{r}_3)}{\delta \rho(\mathbf{r}_1)} \bar{F}_{ab}(\mathbf{r}_{23}) d\mathbf{r}_2 d\mathbf{r}_3$$

239 2. Approximations on the pair distribution function (PDF)

240 Exact expressions of the inhomogeneous PDF are unknown but they can be estimated by ap-
 241 proximation methods. In a bulk phase, the PDF only depends on the radial distance r_{12} and cor-
 242 responds to the RDF. Jackson *et al.*⁹ observed that for short distances beyond the contact value σ
 243 between two molecules 1 and 2, the RDF of a homogeneous HS fluid decreases as $1/r_{12}^2$, so that it
 244 can be approximated as

$$245 \quad g^{\text{hs}}(r_{12}; \eta_\sigma) \approx \frac{\sigma^2}{r_{12}^2} g_\sigma^{\text{hs}}(\eta_\sigma) \quad (16)$$

246 where $g_\sigma^{\text{hs}}(\eta_\sigma)$ is the contact value of the HS RDF, and $\eta_\sigma = \frac{\pi}{6} \rho \sigma^3$ is the bulk packing fraction.
 247 Dufal *et al.*^{20,21} showed that this approximation fits well the HS RDF obtained with the reference
 248 hypernetted-chain (RHNC) integral equation theory⁴⁸, under the range of bonding. The func-
 249 tion $g_\sigma^{\text{hs}}(\eta_\sigma)$ can be obtained by using the exact contact-value theorem for the Carnahan–Starling
 250 EoS¹³, such that

$$251 \quad g_\sigma^{\text{hs}}(\eta_\sigma) = \frac{1 - \eta_\sigma/2}{(1 - \eta_\sigma)^3} \quad (17)$$

252 for a homogeneous HS fluid.

253
 254 The treatment of the PDF for an inhomogeneous HS fluid is more complex than for its homo-
 255 geneous equivalent because $g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2)$ depends both on the positions \mathbf{r}_1 and \mathbf{r}_2 (and not only on

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256 the distance r_{12}), and on the density profile (and not only on a constant density). There is not
 257 currently a suitable PDF of an inhomogeneous HS fluid to be used in the association free-energy
 258 functional we develop here. Indeed, $\mathcal{F}^{\text{assoc.}}[\rho]$ has first to exactly correspond to the SAFT free en-
 259 ergy $F^{\text{assoc.}}$ in the homogeneous limit, which requires that the PDF corresponds to the SAFT RDF
 260 (Eq. (16)) in the bulk limit. It excludes approaches based on external potential as for instance the
 261 Percus' method^{49,50} which is unsuitable for SAFT-based free-energy functionals. Another strategy
 262 consists in extending the RDF to the inhomogeneous case. The simplest analytical approximation
 263 consists in replacing the PDF of the inhomogeneous system by the RDF of the homogeneous fluid
 264 at a specific density. Segura *et al.*⁴⁵ have already used this approximation, choosing the bulk
 265 density under the same thermodynamic conditions as the reference density, thus recovering the
 266 SAFT formulation of the non-bonded fraction in the bulk limit. However, this approximation is a
 267 rough estimate of the PDF since local densities near an interface may differ from the bulk value by
 268 several orders of magnitude. In addition, the free-energy functional should not depend explicitly
 269 on the bulk density to satisfy the Gibbs adsorption theorem³¹. Lurie-Gregg *et al.*⁴² discussed the
 270 advantages and shortcomings of several analytical approximations for inhomogeneous PDF that
 271 transform RDF into an inhomogeneous framework using position-dependent reference densities.
 272 They introduced the so-called contact value approach to compute the PDF of an inhomogeneous
 273 HS fluid that is suitable for DFTs based on TPT and that only requires a low computational cost.
 274 We are inspired by their approach but apply the necessary approximations to find the homoge-
 275 neous limit corresponding to the RDF used in the SAFT association term (Eq. (16)). We therefore
 276 use the mean-function approximation⁴² so that

$$277 \quad g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{g^{\text{hs}}(r_{12}; \eta_{\sigma}(\mathbf{r}_1)) + g^{\text{hs}}(r_{12}; \eta_{\sigma}(\mathbf{r}_2))}{2} \quad (18)$$

278 in which the position-dependant RDF $g(r_{12}; \eta_{\sigma}(\mathbf{r}_1))$ and $g(r_{12}; \eta_{\sigma}(\mathbf{r}_2))$ are approximated as in
 279 (Eq. (16)). Hence,

$$280 \quad g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{\sigma^2}{2r_{12}^2} \left(g_{\sigma}^{\text{hs}}(\mathbf{r}_1) + g_{\sigma}^{\text{hs}}(\mathbf{r}_2) \right) \quad (19)$$

281 where we only consider the inhomogeneous HS PDF at the contact distance^{51,52},

$$282 \quad g_{\sigma}^{\text{hs}}(\mathbf{r}_1) = \frac{1 - \eta_{\sigma}(\mathbf{r}_1)/2}{(1 - \eta_{\sigma}(\mathbf{r}_1))^3} \quad (20)$$

283 by analogy with Eq. (17), and where the bulk packing fraction η_{σ} is replaced by the weighted
 284 density

$$\eta_{\sigma}(\mathbf{r}_1) = \int \rho(\mathbf{r}_2) \frac{\Theta(R\psi - r_{12})}{\psi^3} d\mathbf{r}_2 \quad (21)$$

where $R = \sigma/2$ is the radius of the molecule, ψ is a parameter defining the size of the weighting and the denominator factor ψ^3 is here to ensure that the homogeneous limit of the functional corresponds to the bulk packing fraction. One could optimize the parameter ψ as it has already been done in some DFT work⁵³, but by simplicity we only consider here the traditional coarse-grained approach for which $\psi = 2$, and we define the coarse-grained weight $p^{\text{cg}}(r_{12}) = \frac{\Theta(\sigma - r_{12})}{8}$ to compact the notation in the remaining derivation.

3. Expression of the chemical potential functional with weighted functions

With the separation of the variables \mathbf{r}_1 and \mathbf{r}_2 in the approximated PDF (Eq. (19)), the pair correlation integrals in the non-bonded fraction (Eq. (12)) and the chemical potential functional (Eq. (15)) can be decomposed as a sum of one-center convolution products. The non-bonded fraction can then be expressed as

$$X_a(\mathbf{r}_1) = \frac{1}{1 + \sum_b \frac{1}{2} \left(g_{\sigma}^{\text{hs}}(\mathbf{r}_1) \chi_{ba}(\mathbf{r}_1) + G_{ba}^{\text{assoc.}}(\mathbf{r}_1) \right)} \quad (22)$$

where we introduce the weighted functions

$$\chi_{ba}(\mathbf{r}_1) = \int \rho(\mathbf{r}_2) X_b(\mathbf{r}_2) p_{ab}^{\text{assoc.}}(\mathbf{r}_{12}) d\mathbf{r}_2 \quad (23)$$

and

$$G_{ba}^{\text{assoc.}}(\mathbf{r}_1) = \int \rho(\mathbf{r}_2) X_b(\mathbf{r}_2) g_{\sigma}^{\text{hs}}(\mathbf{r}_2) p_{ab}^{\text{assoc.}}(\mathbf{r}_{12}) d\mathbf{r}_2 \quad (24)$$

which depend on the association weight, defined as follows

$$p_{ab}^{\text{assoc.}}(\mathbf{r}_{12}) = \frac{\sigma^2}{|\mathbf{r}_{12}|^2} \bar{F}_{ab}(|\mathbf{r}_{12}|) \quad (25)$$

regardless the choice made to describe association bonding (angular or distance potential formulation). The chemical potential functional can be expressed as

$$\beta\mu^{\text{assoc.}}(\mathbf{r}_1) = \sum_a \ln X_a(\mathbf{r}_1) - \frac{1}{2} \sum_{a,b} \iint \rho(\mathbf{r}_2) X_a(\mathbf{r}_2) \rho(\mathbf{r}_3) X_b(\mathbf{r}_3) \times \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \Big|_{(\mathbf{r}_2)} p^{\text{cg}}(\mathbf{r}_{12}) p_{ab}^{\text{assoc.}}(\mathbf{r}_{23}) d\mathbf{r}_2 d\mathbf{r}_3 \quad (26)$$

308 The last term in the right-hand side in Eq. (26) is simplified by introducing χ_{ba} , and by defining
309 the weighted function

$$310 \quad \bar{G}_{ab}^{\text{assoc.}}(\mathbf{r}_1) = \int \rho(\mathbf{r}_2) X_a(\mathbf{r}_2) \left. \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \right|_{(\mathbf{r}_2)} \chi_{ba}(\mathbf{r}_2) p^{\text{cg}}(r_{12}) d\mathbf{r}_2 \quad (27)$$

311 such that the chemical potential can be written as

$$312 \quad \beta\mu^{\text{assoc.}}(\mathbf{r}_1) = \sum_a \ln X_a(\mathbf{r}_1) - \frac{1}{2} \sum_{a,b} \bar{G}_{ab}^{\text{assoc.}}(\mathbf{r}_1) \quad (28)$$

313 4. Calculation of weighted functions

314 Two types of weighted functions have been introduced in the new expression of the association
315 functional proposed in our current work. Both have the same mathematical structure, similar to
316 the weighted densities for HS (Eq. (9)), that can be interpreted as the convolution product of a
317 local function f and a given weight.

318
319 The first type of weighted function depends on the association weight $p_{ab}^{\text{assoc.}}$, for which we
320 define the generic expression

$$321 \quad n^{\text{assoc.}}(\mathbf{r}_1) = \int f(\mathbf{r}_2) p_{ab}^{\text{assoc.}}(\mathbf{r}_{12}) d\mathbf{r}_2 \quad (29)$$

322 by analogy with Eqs. (23–24). One can explicit $p_{ab}^{\text{assoc.}}$ by replacing $\bar{F}_{ab}(r_{12})$ in Eq. (25) with the
323 expressions given in Eqs. (14a–14b), such that, for the distance formulation

$$324 \quad p_{\text{dist.},ab}^{\text{assoc.}}(\mathbf{r}) = \frac{\sigma^2}{r^2} F_{ab} \frac{(r_c + 2d - r)^2 (2r_c - 2d + r)}{24 d^2 r} \quad (30a)$$

$$\times \left(\Theta(2d + r_c - r) - \Theta(\sigma - r) \right)$$

325 and for the angular formulation

$$326 \quad p_{\text{ang.},ab}^{\text{assoc.}}(\mathbf{r}) = \frac{\sigma^2}{r^2} F_{ab} \frac{(1 - \cos \theta_c)^2}{4} \quad (30b)$$

$$\times \left(\Theta(r_{12,c} - r) - \Theta(\sigma - r) \right)$$

327 where $r = |\mathbf{r}|$. The weighted function can be solved by using fast Fourier transforms (FFT) in a
328 tridimensional space⁵⁴, as

$$329 \quad n^{\text{assoc.}}(\mathbf{r}_1) = \text{FFT}^{-1} [\text{FFT}[f] \times \hat{p}_{ab}^{\text{assoc.}}(\mathbf{k})] \quad (31)$$

330 Although the main interest of Fourier transforms to solve convolution products in DFT approach
 331 comes from the use of the FFT algorithm⁵⁵, there are others favourable features. In the Fourier
 332 space, the weight $\hat{p}_{ab}^{\text{assoc.}}(\mathbf{k})$ can be computed independently of the density profile and thus has to
 333 be evaluated only once for the iterative method used to solve Eq. (7), for a given size of the system.
 334 Also, a Fourier transform implies by definition a periodicity of the weighted functions that is an
 335 asset if one desires to introduce periodic boundary conditions (the simplified model of zeolite that
 336 we present in Section III B showcases this feature).

337 The analytical expressions of the Fourier transform of the association weight $\hat{p}_{ab}^{\text{assoc.}}(\mathbf{k})$ for the
 338 distance and angular formulations are

$$339 \quad \hat{p}_{\text{dist.},ab}^{\text{assoc.}}(\mathbf{k}) = \frac{4\pi\sigma^2}{k} F_{ab} \int_{\sigma}^{2d+r_c} \frac{\sin(kr)}{r} \times \frac{(r_c + 2d - r)^2 (2r_c - 2d + r)}{24 d^2 r} dr \quad (32a)$$

340 and

$$341 \quad \hat{p}_{\text{ang.},ab}^{\text{assoc.}}(\mathbf{k}) = \frac{4\pi\sigma^2}{k} F_{ab} \frac{(1 - \cos \theta_c)^2}{4} \int_{\sigma}^{r_{12,c}} \frac{\sin(kr)}{r} dr \quad (32b)$$

342 respectively, for $\mathbf{k} \neq \mathbf{0}$, such that the integrals are computed numerically. As already noticed, the
 343 weight in the Fourier space $\hat{p}_{ab}^{\text{assoc.}}(\mathbf{k})$ is independent of the molecular distribution, thus the DFT
 344 treatment of the two potential models (distance and angular) is identical (*i.e.*, the same density
 345 profile is obtained for both formulations) as long as the weight $\hat{p}_{ab}^{\text{assoc.}}(\mathbf{k})$ gives the same value
 346 for each potential formulation. An analogous result in the homogeneous framework of SAFT is
 347 explained by Jackson *et al.*⁹ with the definition of the bonding volume (the exact relation between
 348 the association weight in the homogeneous limit and the bonding volume is given in Appendix A).

349
 350 The second type of weighted function depends on the coarse-grained weight p^{cg} , used in
 351 Eqs. (21) and (27), for which we define the generic weighted function

$$352 \quad n^{\text{cg}}(\mathbf{r}_1) = \int f(\mathbf{r}_2) p^{\text{cg}}(\mathbf{r}) d\mathbf{r}_2 \quad (33)$$

353 that can be solved as

$$354 \quad n^{\text{cg}}(\mathbf{r}_1) = \text{FFT}^{-1} [\text{FFT}[f] \times \hat{p}^{\text{cg}}(\mathbf{k})] \quad (34)$$

355 where the Fourier transform of the coarse-grained weight is given analytically, as

$$356 \quad \hat{p}^{\text{cg}}(\mathbf{k}) = \frac{\pi\sigma^3}{2} \left(\frac{\sin(k\sigma)}{(k\sigma)^3} - \frac{\cos(k\sigma)}{(k\sigma)^2} \right) \quad (35)$$

357 for $\mathbf{k} \neq \mathbf{0}$.

358 III. RESULTS

359 A. Associating fluid against a planar hard wall

360 To check the consistency of the association free-energy functional we consider a fluid of asso-
361 ciating HS of radius $R = \sigma/2$ near a planar hard wall. The wall is perpendicular to the z -axis, and
362 placed at $z = 0$, such that the wall potential is given by

$$363 \quad V^{\text{ext.}}(z) = \begin{cases} \infty & \text{if } z \leq R^+ \\ 0 & \text{if } z > R^+ \end{cases} \quad (36)$$

364 The system has a 1D geometry, and all quantities vary along the axis z .

365
366 First, analytical verification can be done to check the thermodynamic coherence in the expres-
367 sion of a given functional. Sum rules³¹ are exact relationships between microscopic properties
368 that can be derived from a DFT model and from the macroscopic thermodynamic quantities that
369 can be obtained from an EoS. Satisfying them in the elaboration of an EoS-based DFT model
370 (SAFT-based in this case) corroborates that the EoS limit is well respected. The wall theorem is
371 an application of the contact-value theorem for this system and states that the density at the contact
372 with the wall is related to the pressure of the bulk phase (far from the wall) by³¹ $\rho(R^+) = \beta P$.
373 The pressure of an associating HS fluid can be expressed as $P = P^{\text{id.}} + P^{\text{hs}} + P^{\text{assoc.}}$, where the
374 three terms in the right-hand side represent respectively the ideal, the HS and the association
375 contribution to the bulk pressure. Lutsko⁵⁶ gave an analytical demonstration of the wall theorem
376 for a van der Waals fluid. We have followed this approach for an associating HS fluid, and we
377 have verified that the wall theorem is respected by the new functional (the detailed proof can be
378 found in Appendix B).

379
380 In addition, numerical comparisons are done with molecular simulations at equivalent potential.
381 An inventory of existing Monte Carlo simulations^{33,34,41,43} for the associating HS fluid system
382 can be found in the work of Camacho Vergara *et al.*⁴⁰. The schemes of association presented
383 in Section II A are considered with the angular cutoff $\theta_c = 27^\circ$, and the distance cutoff $r_{12,c} =$
384 1.05σ . Molecular simulations provide density profiles $\rho(z)$ for a wide range of thermodynamic
385 conditions, as well as the non-bonded fraction of monomers $X_0(z)$. To implement the hard wall
386 system we consider a slit pore large enough so that the bulk fluid can be recovered far from the

387 wall, such that we restrict our attention to the vicinity of the wall, where the variations in density
 388 are observed. Weighted functions and inhomogeneous excess chemical potentials of both HS and
 389 association contributions are evaluated by using FFT with a mesh width of $\sigma/125$. The density
 390 profile at equilibrium is obtained by solving the self-consistent equation (Eq. (7)) with the Picard
 391 iterative method³¹. For a pure fluid in presence of a non-associative external potential, assumptions
 392 made on the schemes imply that the non-bonded fractions of a site a (*i.e.* $X_a(z)$) are all identical
 393 for any site a , such that the non-bonded fraction of monomers $X_0(z)$ can be related to $X_a(z)$ by the
 394 approximation³⁹

$$395 \quad X_0(z) = (X_a(z))^M \quad (37)$$

396 with M being the number of sites for the molecule considered. The fraction $X_a(z)$ is expressed in
 397 Eq. (22) as a self-consistent equation. It is solved together with the density distribution, following
 398 the iteration steps of the Picard method such that the resulting non-bonded fraction profile is ob-
 399 tained for the equilibrium state. In addition to molecular simulation data, we compare the density
 400 profiles obtained in our current work to the density profiles predicted by aFMT³⁹, iSAFT³⁷ and
 401 aWDA⁴⁰. In works presenting the aFMT as well as the aWDA, the non-bonded fraction is calcu-
 402 lated using another method which is discussed in Appendix C 2. Thus, the non-bonded fraction
 403 profiles obtained with our functional are only compared to Monte Carlo simulations.

404

405 1. Density profiles

406 A selection of density profiles is shown in FIG. 3(a,b) for scheme 1A, in FIG. 3(c,d) for scheme
 407 2B, and in FIG. 3(e,f) for scheme 4C. The overall shape of a density profile depends on the selected
 408 thermodynamic conditions, set by the reduced bulk density $\rho^* = \rho\sigma^3$, and the reduced association
 409 energy $\varepsilon^* = \varepsilon/(k_B T)$. An increase of the density at contact with the wall is obtained when the HS
 410 contribution is predominant in the free-energy functional, as can be seen in FIG. 3(a,c,e). How-
 411 ever, a decrease in density in the vicinity of the wall is observed when the association contribution
 412 is predominant, as shown in FIG. 3(b,d,f). Indeed, increasing the association degree of interaction
 413 competes with the repulsion effect of the hard wall, which causes a depletion of the density near
 414 the wall. When considering more sites per particle (*e.g.*, scheme 2B rather than scheme 1A) a
 415 larger amount of associating clusters within the fluid is formed, which amplifies the depletion near
 416 the wall. More details about the behaviour of an associating fluid against a planar hard wall and

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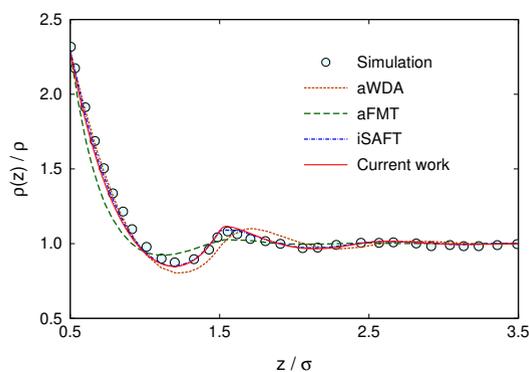
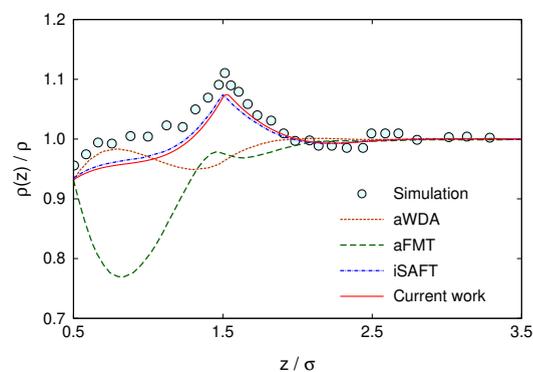
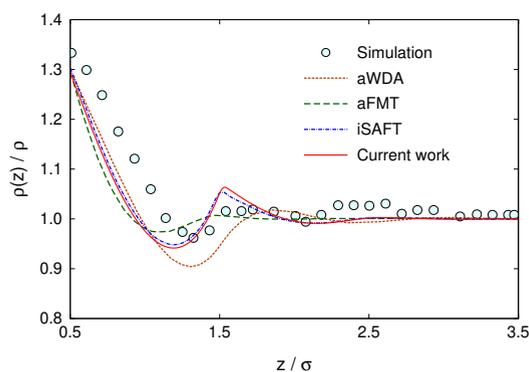
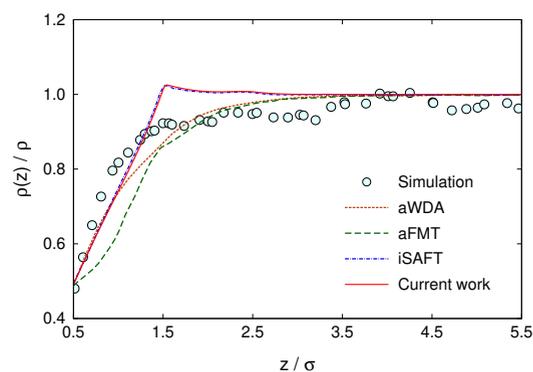
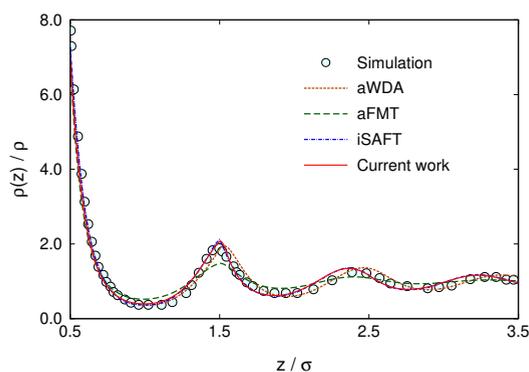
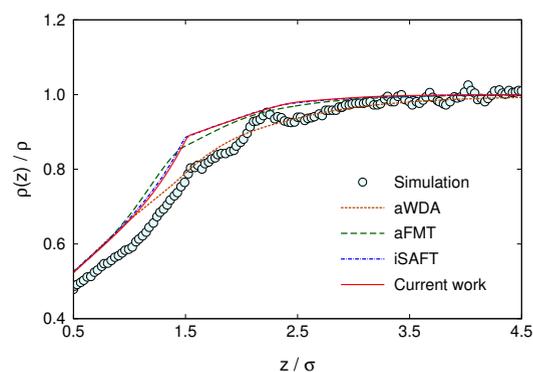
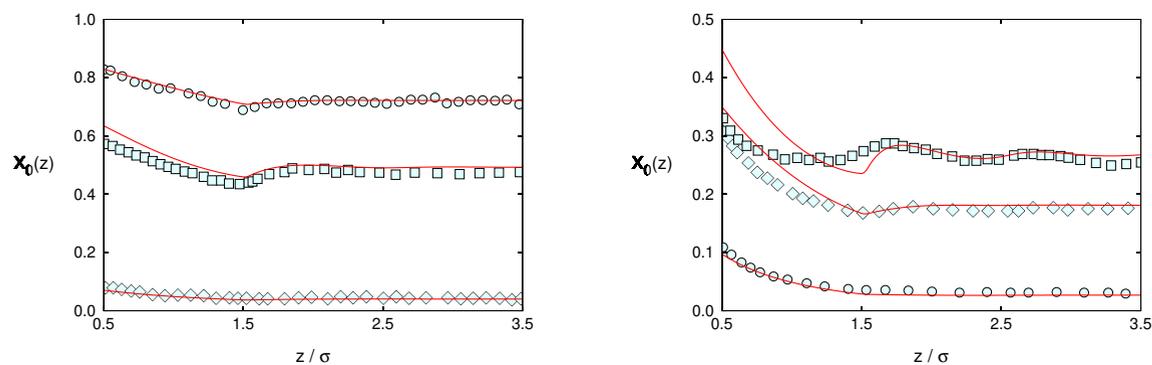
(a) Scheme 1A; $\rho^* = 0.4868$ and $\epsilon^* = 11$ (b) Scheme 1A; $\rho^* = 0.1999$ and $\epsilon^* = 14$ (c) Scheme 2B; $\rho^* = 0.3449$ and $\epsilon^* = 8$ (d) Scheme 2B; $\rho^* = 0.2084$ and $\epsilon^* = 11$ (e) Scheme 4C; $\rho^* = 0.9036$ and $\epsilon^* = 5$ (f) Scheme 4C; $\rho^* = 0.2112$ and $\epsilon^* = 7$

FIG. 3. Density profiles of an associating HS fluid in contact with a planar hard wall placed at $z = 0$. The results for systems described by Scheme 1A are shown in (a,b), by Scheme 2B in (c,d), and by Scheme 4C in (e,f). The profiles $\rho(z)/\rho$ are represented as a function of z/σ , where σ is the diameter of the fluid molecules. The circles represent the simulation data^{33,34,41,43}. The dotted orange line represents the aWDA calculation⁴⁰, the dashed green line represents aFMT calculation³⁹, the dotted-dashed blue line represents iSAFT calculation³⁷ and the continuous red line represents our current work.

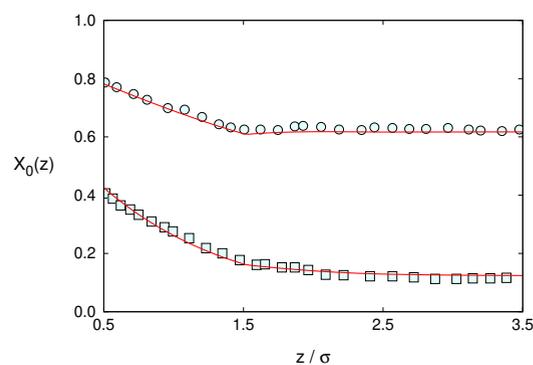
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417 the impact of the scheme can be found in the review of Camacho Vergara *et al.*⁴⁰. The results
 418 obtained with the free-energy functional proposed in our current work are in very good agree-
 419 ment with Monte Carlo simulations in all cases. As for the new functional, the density profiles
 420 are correctly captured by iSAFT, or are slightly overestimated while smoother profiles are given
 421 by both aFMT and aWDA (the peaks in density are underestimated by aFMT, while they are bet-
 422 ter reproduced by aWDA). Similar results can be observed in FIG. 3 for the new functional and
 423 iSAFT. It is not so surprising as both approaches follow a comparable guideline in the derivation
 424 : i) they use Wertheim's theory⁴⁻⁷ for inhomogeneous associating fluids as a starting point (see
 425 Eqs. (11) and (12)), ii) then, an analytical expression is introduced in the PDF by extending the
 426 bulk RDF to an inhomogeneous scenario, iii) in a final step, a method is proposed for both of them
 427 to treat the inhomogeneous functions involved in the bonding probability (*i.e.* the integral over
 428 the range of association in the unbonded equation Eq. (12)). The treatment of the PDF in iSAFT
 429 and the current work differs, on the one hand, in the combination of the position-dependent RDF
 430 (Eq. (18)) and, on the other hand, in the evaluation of the contact value of the HS RDF (Eq. (20)).
 431 We could easily check the influence of the choice of combination of RDF by implementing in the
 432 current functional the geometric mean function⁴⁰ used in iSAFT. We could observe that it does
 433 not significantly change the results for the considered thermodynamic conditions (see Appendix
 434 C). As for the method of solving the integral equations (Eqs. (12) and (15)), our formalism adds
 435 no additional approximation by considering Fourier transforms to perform the calculations, as ex-
 436 plained in section II C 4, whereas iSAFT with Segura's approximation (*cf.* Eq. (4-28) in Segura's
 437 thesis⁴⁵) results in a 1D formulation applicable to planar geometry. As presented in appendix C 1,
 438 we managed to reformulate the original derivation of Segura⁴⁵ in a more general 3D formalism
 439 to make comparable the effects of both methods related to the inhomogeneous treatment of as-
 440 sociation. By assuming that the cutoff $r_{12,c}$ tends to the lowest limit in the range of association
 441 (*i.e.* the contact value σ), we show that solely surfacic effects are treated in an inhomogeneous
 442 manner to estimate the bonding probability in iSAFT framework. In comparison, volume effect
 443 of association is taken into account in our framework by weighting the inhomogeneous functions
 444 over the exact range of association. Segura's approximation is reliable for the cutoff used in our
 445 current work, 1.05σ , which explains the close results compared to the new association function.



(a) Scheme 1A; from top to bottom: $\rho^* = 0.1984$ and $\epsilon^* = 7$; $\rho^* = 0.4868$ and $\epsilon^* = 7$; $\rho^* = 0.1999$ and $\epsilon^* = 14$ (b) Scheme 2B; from top to bottom: $\rho^* = 0.7177$ and $\epsilon^* = 6$; $\rho^* = 0.3449$ and $\epsilon^* = 8$; $\rho^* = 0.2084$ and $\epsilon^* = 11$



(c) Scheme 4C; from top to bottom: $\rho^* = 0.1994$ and $\epsilon^* = 5$; and $\rho^* = 0.2112$ and $\epsilon^* = 7$

FIG. 4. Fraction of monomers of an associating HS fluid in contact with a planar hard wall placed at $z = 0$. The results for systems described by Scheme 1A are shown in (a), by Scheme 2B in (b), and by Scheme 4C in (c). The circles, squares, and diamonds represent the simulation data^{33,34,41,43}. The continuous red line represents the results obtained in the current work.

446 2. Non-bonded fraction profiles

447 The non-bonded fractions of monomers related to the system considered in the current sec-
 448 tion are shown in FIG. 4(a) for scheme 1A, in FIG. 4(b) for scheme 2B, and in FIG. 4(c) for
 449 scheme 4C. A set of thermodynamic conditions is considered for each scheme, with an increase
 450 of the association degree of interaction (from top to bottom), which tends to have a fully bonded
 451 monomer (corresponding to X_0 tending to 0). According to Monte Carlo simulation data^{33,34,41,43},
 452 the non-bonded fraction of monomers decreases from the wall at $z = R^+$ until $z \approx 1.5\sigma$, and

453 remains almost constant for higher distances, for the three association schemes considered. This
 454 structure close to the wall can be easily understood as the monomers have a reduced opportunity
 455 to establish association bonds (because the wall is considered as non associative), in comparison
 456 with the monomers located far from the wall that are surrounded by other associative monomers.
 457 The results obtained with the new free-energy functional fit well the Monte Carlo simulations.
 458 Weighting the inhomogeneous functions on the exact bonding volume captures the change in the
 459 slope around 1.5σ . The fraction of monomers seems overestimated for the scheme 2B for the set
 460 $\rho^* = 0.7177$ and $\epsilon^* = 6$ (as can be seen in FIG.4(b)). However, the simulations⁴⁵ in that case can
 461 be questionable as it is the only case where no change in the slope can be seen around 1.5σ , and
 462 because the fraction near the wall is similar to the fraction for the set $\rho^* = 0.3449$ and $\epsilon^* = 8$,
 463 corresponding to a lower packing fraction.

464 B. Associating fluid confined inside an anisotropic open cavity

465 We investigate a pure HS fluid with four associating sites (modeled by Scheme 4C), confined
 466 in a network of interconnected spherical cavities, as illustrated in FIG. 5, that mimics the shape of
 467 a Linde Type A (LTA) zeolitic nanoporous adsorbent. The open cavity was created as proposed
 468 by Bernet *et al.*⁵⁷ by considering a spherical cavity of radius $R_{\text{sph}} \approx 1.7\sigma$, truncated by a cube of
 469 edge length $a = 3.2\sigma$ placed at the center of the sphere, thus creating six spherical apertures of
 470 diameter $D_{\text{ap}} = 1.1\sigma$ along each Cartesian axis. Molecules are able to go from a cavity to another
 471 by assuming periodic boundary conditions (which is taken into account by the Fourier transforms
 472 considered for calculations). A discrete Cartesian 3D grid is created with 128 points along each
 473 axis and a mesh width of $\sigma/40$, and the origin is placed at the center of the cubic box. The WBII
 474 version of FMT³⁰ is used for the HS contribution, as presented in Section II B. A tensorial term⁴⁴
 475 is added to avoid numerical divergences due to the extreme confinement of the molecules inside
 476 the cavity⁵⁷ (the tensorial contributions were not considered for the systems described in Section
 477 III A, as they can be found to be negligible, and to ensure that DFT approaches were defined
 478 at equivalent HS description). The association contribution is the one depicted in the previous
 479 Sections. The weighted functions and the chemical potential functionals of both the HS and the
 480 association contributions are evaluated with FFT. The Picard method is used to solve Eq. (7) to
 481 find the density distribution at equilibrium. For an easier interpretation, we define the bonded-
 482 fraction of monomers, $X_{0,\text{bond}}(\mathbf{r}) = 1 - X_0(\mathbf{r})$, where the non-bonded fraction of monomers $X_0(\mathbf{r})$
 483

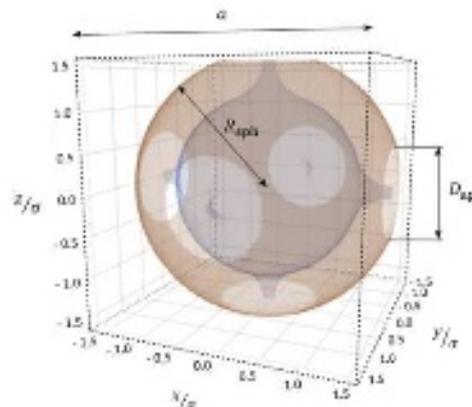


FIG. 5. Left: network of interconnected nanometer-sized hard cavities in a 3D cartesian space. Right: cubic computational box of edge length a containing one cavity of the network, represented as a contour plot. A spherical cavity of radius $R_{\text{sph}} > a/2$ is placed at the center of the box, creating apertures of diameter D_{ap} on the six faces of the cube. The surface of the open spherical cavity is represented in brown with a low opacity, revealing the volume accessible to the mass center of the fluid molecules, in blue.

484 is evaluated such as for the hard wall system.

485 The density distributions of the associating HS inside the cavity are shown in FIG. 6 (a,b,c) for
 486 a given bulk packing fraction of $\eta = 0.3$ and different degrees of association $\epsilon^* = 3, 5, 7$. A low
 487 value of association strength ($\epsilon^* = 3$) leads to important variations of the molecular density inside
 488 the cavity (FIG. 6(a)). In that case, the preferential positions of the fluid molecules are mainly
 489 determined by the predominance of the HS contribution. The main density peaks are situated at
 490 preferential locations : in the center of the cavity, in the shell at the contact of the hard wall in eight
 491 symmetric positions distributed on the diagonals at equal distance of the channels, and inside each
 492 channel. The highest densities are respectively in the channels (eight times the bulk density), in
 493 the center (six times the bulk density), and at the eight locations at the contact of the hard cavity
 494 (five times the bulk density). The density is very close to zero between these preferential locations,
 495 except in the layer in contact with the hard cavity. The presence of association bonds leads to a
 496 smaller value of the density maxima, in comparison with the non-associating HS fluid confined in
 497 the same cavity at the same conditions⁵⁷. When increasing the degree of association to $\epsilon^* = 5$, the
 498 density maxima decreases in the center of the cavity, the difference in density between the eight
 499 preferential positions and the rest of the shell at the contact of the hard cavity becomes smaller
 500 (FIG. 6(b)), and the density in the channels becomes similar to the density in the center. For

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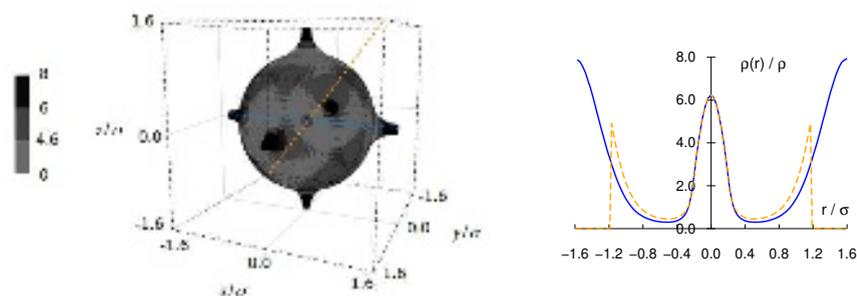
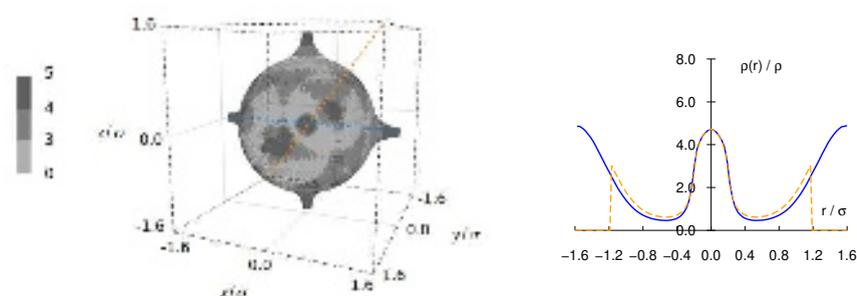
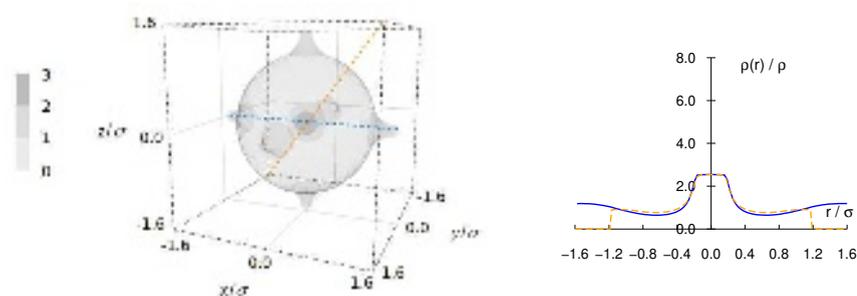
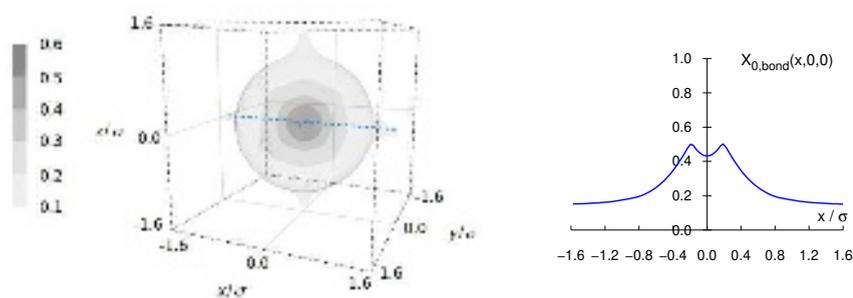
(a) Density distribution for $\eta = 0.3$ and $\epsilon^* = 3$ (b) Density distribution for $\eta = 0.3$ and $\epsilon^* = 5$ (c) Density distribution for $\eta = 0.3$ and $\epsilon^* = 7$

FIG. 6. Left: normalized molecular density $\rho(r)/\rho$ inside the computational box as a contour plot, the darker the higher the density. The contour values have been chosen to spotlight the preferential positions of the fluid molecules in the cavities. Right: as a quantitative supplementary information is given the density profile along the direction $(x, 0, 0)$ (represented with the dashed blue line in the contour plot) in continuous blue line, and the density profile along the diagonal of the box (represented with the dashed orange line in the contour plot) in dashed orange line.

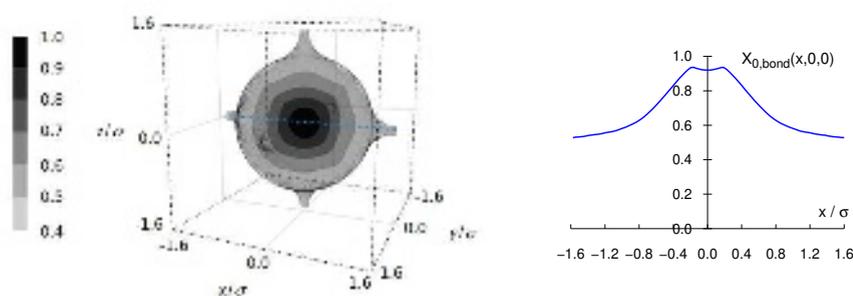
501 $\epsilon^* = 7$ (FIG. 6(c)), the eight preferential locations of the density peaks at the contact with the
502 cavity disappear, leaving only a slightly higher probability in finding molecules in the center and

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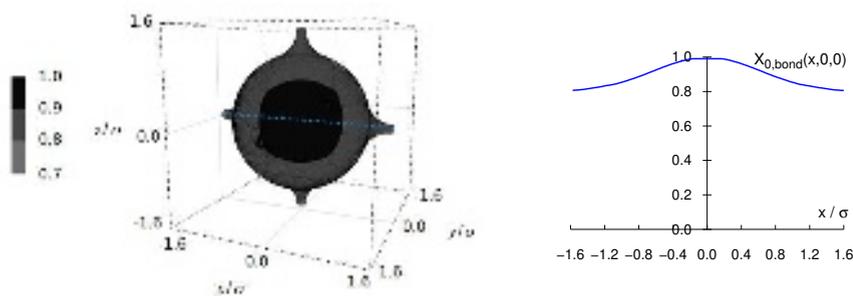
503 in the channels.



(a) Bonding fraction of monomers for $\eta = 0.3$ and $\epsilon^* = 3$



(b) Bonding fraction of monomers for $\eta = 0.3$ and $\epsilon^* = 5$



(c) Bonding fraction of monomers for $\eta = 0.3$ and $\epsilon^* = 7$

FIG. 7. Bonded-fraction of monomer corresponding to the density profiles shown in FIG. 6. Left: the fraction is presented as a contour plot where the higher bonded fraction corresponds to the darker and opaques regions. Right: bonded fraction profile along the direction $(x, 0, 0)$, represented with the blue dash line in the contour plot.

504 The bonded fraction of monomers corresponding to the same set of thermodynamic conditions
505 are shown in FIG. 7(a,b,c). For a small value of association strength ($\epsilon^* = 3$), the bonded fraction
506 of molecules is only 20% at the contact of the hard cavity and inside the channels, and it gradually

507 increases from this value to reach a maximum value of 50% in the center of the cavity where
 508 the molecules have the more neighbors to bond with (FIG. 7(a)). When increasing the degree of
 509 association to $\epsilon^* = 5$, the bonded fraction of monomers is then higher than 60% and reaches more
 510 than 90% in the center (FIG. 7(b)), which are the values typically found in dense bulk associating
 511 liquids²⁰. For $\epsilon^* = 7$, fully bonded monomers are found in the major part of the cavity (FIG. 7(c)).
 512 In that case, the association energy clearly competes with the steric effect.

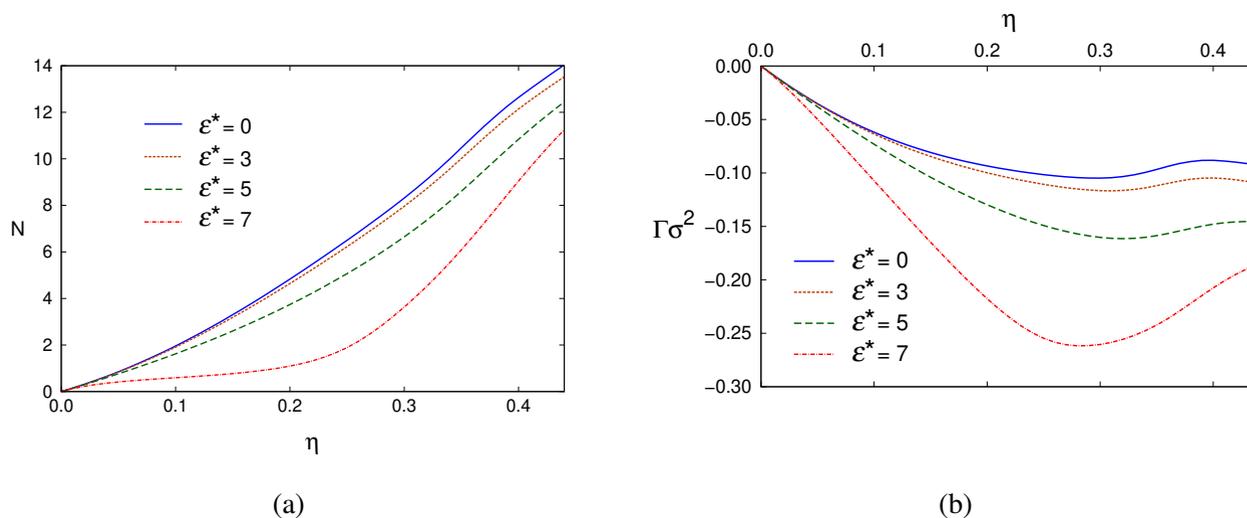


FIG. 8. (a) Average number N of associating HS inside the computational box and (b) excess adsorption Γ as a function of the packing fraction for $\epsilon^* = 0$ in blue (HS), $\epsilon^* = 3$ in a dash dark-orange line, $\epsilon^* = 5$ in a dash green line, $\epsilon^* = 7$ dotted red line.

513 The average number of molecules inside the cavity, N , and the corresponding excess adsorption,
 514 Γ , are shown in FIG. 8. The excess adsorption is defined as

$$515 \quad \Gamma = \frac{1}{A} \int (\rho(\mathbf{r}) - \rho) d\mathbf{r} = \frac{N - \rho V_{\text{open sphere}}}{A_{\text{open sphere}}} \quad (38)$$

516 where we made the choice to take into account the excluded volume in the range of integra-
 517 tion, such that the accessible volume inside the cavity corresponds to the volume of the open
 518 sphere $V_{\text{open sphere}}$. The surface area A , that corresponds here to the inner envelope of surface area
 519 $A_{\text{open sphere}}$ of this volume, is introduced in Eq. (38) to return an average excess number per unit
 520 of surface. The analytical expressions of $V_{\text{open sphere}}$ and $A_{\text{open sphere}}$ are given by Bernet *et al.*⁵⁷.
 521 The average number of molecules N is evaluated numerically by integrating the molecular density
 522 $\rho(\mathbf{r})$ over all the computational box. For a given bulk packing fraction, the increase in the degree
 523 of association leads to a decrease in the global number of molecules that can be accommodated

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524 inside the cavity, and thus a decrease in excess adsorption. Including association is more visible
525 on excess adsorption for medium densities than for high densities (as steric effects are dominant);
526 it can be interpreted as a competition between repulsive and attractive interactions.

527 **IV. CONCLUSIONS**

528 A new density free-energy functional theory is proposed in this work for associating fluids.
529 Wertheim's thermodynamics perturbation theory (TPT) is considered as the starting point of the
530 derivation with the constraint to recover the statistical associating fluid theory (SAFT) in the bulk
531 limit. Our framework introduces weighted functions specific to association that have a mathemati-
532 cal structure similar to the weighted densities of the fundamental measure theory (FMT). As these
533 latter are convolution products, they can be easily evaluated numerically with Fourier transforms
534 in a 3D space, thus allowing to investigate complex 3D systems. A comparison is done with exist-
535 ing Monte Carlo simulations and previous density functional theory formulations for a planar hard
536 wall system (1D geometry) in order to check the consistency of the new association functional.
537 As an example of 3D application, we investigate the extreme confinement of an associating hard
538 sphere (HS) fluid confined in a network of 3D interconnected spherical cavities that mimics the
539 shape of a zeolitic nanoporous adsorbent made of spherical cavities connected via channels. The
540 impact of the degree of association on the preferential positions of the particles inside the cavity
541 is investigated as well as the competition between on the association and the steric effect on the
542 adsorption. For low values of association strength, the density distribution is mainly governed by
543 the HS contribution and corresponds to a highly structured fluid with preferential positions of the
544 molecules. While the association strength increases, the density gradients decrease and the cavity
545 is occupied by a cluster of nearly fully bonded monomers. This leads to a lower adsorption of the
546 associating fluid in comparison with the HS one. Although there is no available molecular simu-
547 lation for this system so we could compare with, the consistency of the results we found suggests
548 that our model is reliable to describe associating fluids confined in porous materials with complex
549 geometry. The method we proposed to treat the inhomogeneous functions involved in the associ-
550 ation contribution is general and can be extended to other non-associated fluid references such as
551 square-well or soft-core potentials (*e.g.*, Lennard-Jones and Mie potentials).

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556 simulation data that are used in this work for the comparison with our results.

557 DATA AVAILABILITY STATEMENT

558 Data underlying this article can be accessed on Zenodo at <https://doi.org/10.5281/zenodo.10276406>
559 and used under the Creative Commons Attribution license.

560 REFERENCES

- 561 ¹H. Li, K. Wang, Y. Sun, C. T. Lollar, J. Li, and H.-C. Zhou, “Recent advances in gas storage
562 and separation using metal–organic frameworks,” *Materials Today* **21**, 108–121 (2018).
- 563 ²Y. Ma, Z. Wang, X. Xu, and J. Wang, “Review on porous nanomaterials for adsorption and
564 photocatalytic conversion of CO_2 ,” *Chinese Journal of Catalysis* **38**, 1956–1969 (2017).
- 565 ³M. Ouda, F. Banat, S. W. Hasan, and G. N. Karanikolos, “Recent advances on nanotechnology-
566 driven strategies for remediation of microplastics and nanoplastics from aqueous environments,”
567 *Journal of Water Process Engineering* **52**, 103543 (2023).
- 568 ⁴M. S. Wertheim, “Fluids with highly directional attractive forces. I. Statistical thermodynamics.”
569 *J. Stat. Phys.* **35**, 19–34 (1984).
- 570 ⁵M. S. Wertheim, “Fluids with highly directional attractive forces. II. Thermodynamic perturba-
571 tion theory and integral equations,” *J. Stat. Phys.* **35**, 35–37 (1984).
- 572 ⁶M. S. Wertheim, “Fluids with highly directional attractive forces. III. Multiple attraction sites,”
573 *J. Stat. Phys.* **42**, 459–476 (1986).
- 574 ⁷M. S. Wertheim, “Fluids with highly directional attractive forces. IV. Equilibrium polymeriza-
575 tion,” *J. Stat. Phys.* **42**, 477–492 (1986).
- 576 ⁸W. Zmpitas and J. Gross, “Detailed pedagogical review and analysis of Wertheim’s thermody-
577 namic perturbation theory,” *Fluid Phase Equilib.* **428**, 121 (2016).
- 578 ⁹G. Jackson, W. G. Chapman, and K. E. Gubbins, “Phase equilibria of associating fluids spherical
579 molecules with multiple bonding sites,” *Mol. Phys.* **65**, 1–31 (1988).
- 580 ¹⁰W. G. Chapman, G. Jackson, and K. E. Gubbins, “Phase equilibria of associating fluids chain
581 molecules with multiple bonding sites,” *Mol. Phys.* **65**, 1057 (1988).
- 582 ¹¹W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, “SAFT: equation-of-state solution
583 model for associating fluids,” *Fluid Phase Equilib.* **52** (1989).

This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0180795

- 584 ¹²W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, “New reference equation of state
585 for associating liquids,” *Ind. Eng. Chem. Res.* **29** (1990).
- 586 ¹³N. F. Carnahan and K. E. Starling, “Equation of state for nonattracting rigid spheres,” *J. Chem.*
587 *Phys.* **51**, 635–636 (1969).
- 588 ¹⁴J. B. Schulte, P. A. Kreitzberg, C. V. Haglund, and D. Roundy, “Using fundamental measure
589 theory to treat the correlation function of the inhomogeneous hard-sphere fluid,” *Phys. Rev. E*
590 **86** (2012), 10.1103/PhysRevE.86.061201.
- 591 ¹⁵A. Gil-Villegas, A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson, and A. N. Burgess, “Sta-
592 tistical associating fluid theory for chain molecules with attractive potentials of variable range,”
593 *J. Chem. Phys.* **106**, 4168–4186 (1997).
- 594 ¹⁶J. Gross and G. Sadowski, “Perturbed-Chain SAFT: an equation of state based on a perturbation
595 theory for chain molecules,” *Ind. Eng. Chem. Res.* **40**, 1244–1260 (2001).
- 596 ¹⁷J. Gross and J. Vrabec, “An equation-of-state contribution for polar components: dipolar
597 molecules,” *AIChE Journal* **52**, 1194–1204 (2006).
- 598 ¹⁸T. Lafitte, A. Apostolakou, C. Avendaño, A. Galindo, C. S. Adjiman, E. A. Müller, and G. Jack-
599 son, “Accurate statistical associating fluid theory for chain molecules formed from Mie seg-
600 ments,” *J. Chem. Phys.* **139**, 154504 (2013).
- 601 ¹⁹V. Papaioannou, T. Lafitte, C. Avendaño, C. S. Adjiman, G. Jackson, E. A. Müller, and
602 A. Galindo, “Group contribution methodology based on the statistical associating fluid theory
603 for heteronuclear molecules formed from Mie segments,” *J. Chem. Phys.* **140**, 54107 (2014).
- 604 ²⁰S. Dufal, T. Lafitte, A. J. Haslam, A. Galindo, G. N. I. Clark, C. Vega, and G. Jackson, “The
605 A in SAFT: developing the contribution of association to the Helmholtz free energy within a
606 Wertheim TPT1 treatment of generic Mie fluids,” *Mol. Phys.* **113**, 948–984 (2015).
- 607 ²¹S. Dufal, T. Lafitte, A. J. Haslam, A. Galindo, G. N. I. Clark, C. Vega, and G. Jackson, “Cor-
608 rrigendum: The A in SAFT: developing the contribution of association to the Helmholtz free
609 energy within a Wertheim TPT1 treatment of generic Mie fluids,” *Mol. Phys.* **116**, 283–285
610 (2018).
- 611 ²²H. S. Huang and M. Radosz, “Equation of state for small, large, polydisperse, and associating
612 molecules,” *Ind. Eng. Chem. Res.* **29**, 2284–2294 (1990).
- 613 ²³S. Dufal, V. Papaioannou, M. Sadeqzadeh, T. Pogiatis, A. Chremos, C. S. Adjiman, G. Jack-
614 son, and A. Galindo, “Prediction of thermodynamic properties and phase behavior of fluids and
615 mixtures with the SAFT- γ Mie group-contribution equation of state,” *J. Chem. Eng. Data* **59**,

This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0180795

616 3272–3288 (2014).

617 ²⁴S. Di Lecce, G. Lazarou, S. H. Khalit, C. S. Adjiman, G. Jackson, A. Galindo, and L. McQueen,
618 “Modelling and prediction of the thermophysical properties of aqueous mixtures of choline ger-
619 anate and geranic acid (CAGE) using SAFT- γ Mie,” *RSC Adv.* **9**, 38017–38031 (2019).

620 ²⁵A. J. Haslam, A. Gonzalez-Perez, S. Di Lecce, S. H. Khalit, F. A. Perdomo, S. Kournopoulos,
621 M. Kohns, T. Lindeboom, M. Wehbe, S. A. Febra, G. Jackson, C. S. Adjiman, and A. Galindo,
622 “Expanding the applications of the SAFT- γ Mie group-contribution equation of state: prediction
623 of thermodynamic properties and phase behaviour of mixtures,” *J. Chem. Eng. Data* **65**, 5862–
624 5890 (2020).

625 ²⁶S. A. Febra, T. Bernet, C. Mack, J. McGinty, I. I. Onyemelukwe, S. J. Urwin, J. Sefcik, J. H.
626 ter Horst, C. S. Adjiman, G. Jackson, and A. Galindo, “Extending the SAFT- γ Mie approach to
627 model benzoic acid, diphenylamine, and mefenamic acid: solubility prediction and experimental
628 measurement,” *Fluid Phase Equilib.* **540**, 113002 (2021).

629 ²⁷R. Evans, “The nature of the liquid-vapour interface and other topics in the statistical mechanics
630 of non-uniform, classical fluids,” *Adv. Phys.* **28**, 143 (1979).

631 ²⁸Y. Rosenfeld, “Free-energy model for the inhomogeneous hard-sphere fluid mixture and density-
632 functional theory of freezing,” *Phys. Rev. Lett.* **63**, 980 (1989).

633 ²⁹Y.-X. Yu and J. Wu, “Structures of hard-sphere fluids from a modified fundamental-measure
634 theory,” *J. Chem. Phys.* **117** (2002).

635 ³⁰H. Hansen-Goos and R. Roth, “Density functional theory for hard-sphere mixtures: the White
636 Bear version mark II,” *J. Phys.: Condens. Matter* **18**, 8413 (2006).

637 ³¹R. Roth, “Fundamental measure theory for hard-sphere mixtures: a review,” *J. Phys.: Condens.*
638 *Matter* **22**, 063102 (2010).

639 ³²W. G. Chapman, “Theory and Simulation of Associating Liquid Mixtures,” Ph.D. Dissertation,
640 Cornell University (1988).

641 ³³C. J. Segura, W. G. Chapman, and K. Shukla, “Associating fluids with four bonding sites against
642 a hard wall: density functional theory,” *Mol. Phys.* **90**, 759–771 (1997).

643 ³⁴C. J. Segura, E. V. Vakarín, W. G. Chapman, and M. F. Holovko, “A comparison of density
644 functional and integral equation theories vs Monte Carlo simulations for hard sphere associating
645 fluids near a hard wall,” *Mol. Phys.* **108**, 4837–4848 (1998).

646 ³⁵S. Tripathi and W. G. Chapman, “Microstructure of inhomogeneous polyatomic mixtures from
647 a density functional formalism for atomic mixtures,” *J. Chem. Phys.* **122**, 094506 (2005).

This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0180795

- 648 ³⁶S. Jain, A. Dominik, and W. G. Chapman, “Modified interfacial statistical associating fluid
649 theory: a perturbation density functional theory for inhomogeneous complex fluids,” *J. Chem.*
650 *Phys.* **127**, 244904 (2007).
- 651 ³⁷A. Bymaster and W. G. Chapman, “An iSAFT density functional theory for associating poly-
652 atomic molecules,” *J. Phys. Chem.* **114**, 12298–12307 (2010).
- 653 ³⁸R. Evans, “Fundamentals of inhomogeneous fluids,” Marcel-Dekker, New York (1992).
- 654 ³⁹Y.-X. Yu and J. Wu, “A fundamental-measure theory for inhomogeneous associating fluids,” *J.*
655 *Chem. Phys.* **116**, 7094 (2002).
- 656 ⁴⁰E. L. Camacho Vergara, G. M. Kontogeorgis, and X. Liang, “A new study of associating in-
657 homogeneous fluids with classical density functional theory,” *Mol. Phys.* **118**, 12298–12307
658 (2020).
- 659 ⁴¹C. J. Segura and W. G. Chapman, “Associating fluids with four bonding sites against solid sur-
660 faces: Monte Carlo simulations,” *Mol. Phys.* **86**, 415–442 (1995).
- 661 ⁴²P. Lurie-Gregg, J. B. Schulte, and D. Roundy, “Approach to approximating the pair distribution
662 function of inhomogeneous hard-sphere fluids,” *Physical Review E* **90**, 042130 (2014).
- 663 ⁴³A. Patrykiewicz, S. Sokolowski, and D. Henderson, “The structure of associating fluids restricted
664 by permeable walls: a density functional approach,” *Mol. Phys.* **95**, 211–218 (1998).
- 665 ⁴⁴P. Tarazona, “Density functional for hard sphere crystals: A fundamental measure approach,”
666 *Phys. Rev. Lett.* **84**, 694–697 (2000).
- 667 ⁴⁵C. J. Segura, “Associating fluids near solid surfaces,” Ph.D. Dissertation, Rice University (1997).
- 668 ⁴⁶M. S. Wertheim, “Fluids of dimerizing hard spheres, and fluid mixtures of hard spheres and
669 dispheres,” *J. Chem. Phys.* **85**, 2929 (1986).
- 670 ⁴⁷M. L. Michelsen and E. M. Hendriks, “Physical properties from association models,” *Fluid Phase*
671 *Equilib.* **180**, 165–174 (2000).
- 672 ⁴⁸A. Malijevský and S. Labík, “The bridge function for hard spheres,” *Mol. Phys.* **60**, 663–669
673 (1987).
- 674 ⁴⁹J. K. Percus, “The Equilibrium Theory of Classical Fluids,” (by H. L. Frisch and J. L. Lebowitz,
675 editors, Benjamin, New York, 1964).
- 676 ⁵⁰J. K. Percus, “Approximation methods in classical statistical mechanics,” *Phys. Rev. Lett.* **8**, 462
677 (1962).
- 678 ⁵¹J. B. Schulte, P. A. Kreitzberg, C. V. Haglund, and D. Roundy, “Using fundamental measure
679 theory to treat the correlation function of the inhomogeneous hard-sphere fluid,” *Phys. Rev. E*

This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0180795

680 **86**, 061201 (2012).

681 ⁵²J. Gross, “A density functional theory for vapor-liquid interfaces using the PCP-SAFT equation
682 of state,” *J. Chem. Phys.* **131**, 204705 (2009).

683 ⁵³E. Sauer and J. Gross, “Classical density functional theory for liquid–fluid interfaces and con-
684 fined systems: A functional for the perturbed-chain polar statistical associating fluid theory
685 equation of state,” *Ind. Eng. Chem. Res.* **56**, 4119–4135 (2017).

686 ⁵⁴T. Bernet, M. M. Piñeiro, F. Plantier, and C. Miqueu, “A 3D non-local density functional theory
687 for any pore geometry,” *Mol. Phys.* **118**, e1767308 (2020).

688 ⁵⁵W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, “Numerical Recipes in
689 Fortran,” Cambridge University Press (1992).

690 ⁵⁶J. F. Lutsko, “Recent developments in classical density functional theory,” *Adv. Chem. Phys.*
691 **144**, 1 (2010).

692 ⁵⁷T. Bernet, E. A. Müller, and G. Jackson, “A tensorial fundamental measure density functional
693 theory for the description of adsorption in substrates of arbitrary three-dimensional geometry,”
694 *J. Chem. Phys.* **152**, 224701 (2020).

695 **Appendix A: Bulk limit**

696 The bulk limit of the generic association weighted function defined in Eq. (29) is

697
$$n^{\text{assoc.}} = f \int p_{ab}^{\text{assoc.}}(r) d\mathbf{r} = f \hat{p}_{ab}^{\text{assoc.}}(\mathbf{0}) \quad (\text{A1})$$

698 where we employ the Fourier transform of $p_{ab}^{\text{assoc.}}$ for $\mathbf{k} = \mathbf{0}$, corresponding to the integration⁹ of
699 the distance and angular association weights (Eqs. (30a–30b)), as

700
$$\begin{aligned} \hat{p}_{\text{dist.},ab}^{\text{assoc.}}(\mathbf{0}) &= \frac{4\pi\sigma^2}{72d^2} F_{ab} \left[\ln \left(\frac{r_c + 2d}{\sigma} \right) \right. \\ &\quad \times (6r_c^3 + 18r_c^2d - 24d^3) + (r_c + 2d - \sigma) \\ &\quad \left. \times (22d^2 - 5r_cd - 7d\sigma - 8r_c^2 + r_c\sigma + \sigma^2) \right] \end{aligned} \quad (\text{A2a})$$

701 and

702
$$\hat{p}_{\text{ang.},ab}^{\text{assoc.}}(\mathbf{0}) = 4\pi\sigma^2 F_{ab} \frac{(1 - \cos\theta_c)^2}{4} (r_{12,c} - \sigma) \quad (\text{A2b})$$

703 respectively. It is convenient to define the bonding volume⁹ K_{ab} between sites a and b , such
704 that $\hat{p}_{ab}^{\text{assoc.}}(\mathbf{0}) = 4\pi K_{ab} F_{ab}$ regardless the choice of potential. We finally obtain the usual SAFT
705 expression of the non-bonded fraction for a homogeneous fluid,

706
$$X_a = \frac{1}{1 + \rho \sum_b X_b \Delta_{ab}} \quad (\text{A3})$$

707 where $\Delta_{ab} = 4\pi g_{\sigma}^{\text{hs}} K_{ab} F_{ab}$. The bulk limit of Eq. (28) corresponds to the bulk chemical potential
708 given by Michelsen and Hendriks⁴⁷ (under the assumption made for the contact RDF), expressed
709 as

710
$$\beta\mu^{\text{assoc.}} = \sum_a \ln X_a - \frac{\rho\eta}{2} \frac{\partial \ln g_{\sigma}^{\text{hs}}}{\partial \eta} \sum_{a,b} X_a X_b \Delta_{ab} \quad (\text{A4})$$

711 and the pressure is given by

712
$$\beta P^{\text{assoc.}} = -\frac{\rho^2}{2} \left(1 + \eta \frac{\partial \ln g_{\sigma}^{\text{hs}}}{\partial \eta} \right) \sum_{a,b} X_a X_b \Delta_{ab} \quad (\text{A5})$$

713 **Appendix B: Proof of the wall theorem for associating hard spheres**714 The derivation of the wall theorem to check the consistency of our new functional is detailed in
715 this appendix. We consider a fluid of associative HSs of diameter $\sigma = 2R$ in the vicinity of a planar
716 hard wall located at $z = 0$, such that the external potential $V^{\text{ext.}}(z)$ vanishes for $z > R^+$ (Eq. (36)).

717 Due to the one-dimensional geometry, the inhomogeneous quantities vary only along the axis z *i.e.*
718 perpendicular to a surface of area A defined by the (infinite) planar wall. In this configuration, the
719 Euler–Lagrange equation is given by the minimization of the grand potential Ω , as

$$720 \quad \frac{\delta\Omega/A}{\delta\rho(z_1)} = \frac{\delta\mathcal{F}/A}{\delta\rho(z_1)} + V^{\text{ext.}}(z_1) - \mu = 0 \quad (\text{B1})$$

721 where μ is the bulk chemical potential and the derivative of the free-energy functional \mathcal{F} is

$$722 \quad \begin{aligned} \frac{\delta\mathcal{F}/A}{\delta\rho(z_1)} &= \frac{\delta\mathcal{F}^{\text{id.}}/A}{\delta\rho(z_1)} + \frac{\delta\mathcal{F}^{\text{hs}}/A}{\delta\rho(z_1)} + \frac{\delta\mathcal{F}^{\text{assoc.}}/A}{\delta\rho(z_1)} \\ &= \mu^{\text{id.}}(z_1) + \mu^{\text{hs}}(z_1) + \mu^{\text{assoc.}}(z_1) \end{aligned} \quad (\text{B2})$$

723 For $z > R^+$

$$724 \quad 0 = \ln\rho(z_1) + \mu^{\text{hs}}(z_1) + \mu^{\text{assoc.}}(z_1) - \mu \quad (\text{B3})$$

725 The derivation proposed by Lutsko⁵⁶ is adapted for the next steps. Both distance and angular
726 formulations of the potential are tested, by considering a generic distance/angular associative
727 cutoff, denoted as $r_c^{\text{assoc.}}$. Let us assume that there is a point z_B such that the density is homo-
728 geneous ($\rho(z) = \rho$) for $z > z_B$, and another point, z_b , sufficiently far in the bulk region, so that
729 $z_b > z_B + r_c^{\text{assoc.}}$, and $z_b > z_B + \sigma$. To bring up both the contact value of the density $\rho(R^+)$, as well
730 as the ideal bulk pressure, Eq. (B3) is differentiated with respect to z_1 , and multiplied by $\rho(z_1)$, as

$$731 \quad 0 = \frac{d\rho(z_1)}{dz_1} + \rho(z_1) \frac{d\mu^{\text{hs}}(z_1)}{dz_1} + \rho(z_1) \frac{d\mu^{\text{assoc.}}(z_1)}{dz_1} \quad (\text{B4})$$

732 and integrated from R^+ to z_b , as

$$733 \quad 0 = \rho(z_b) - \rho(R^+) + \int_{R^+}^{z_b} \rho(z_1) \frac{d\mu^{\text{hs}}(z_1)}{dz_1} dz_1 + \int_{R^+}^{z_b} \rho(z_1) \frac{d\mu^{\text{assoc.}}(z_1)}{dz_1} dz_1 \quad (\text{B5})$$

734 Under our assumptions, $\rho(z_b) = \rho$, such that

$$735 \quad \rho(R^+) = \rho + I_{\text{hs}} + I_{\text{assoc.}} \quad (\text{B6})$$

736 where I_{hs} and $I_{\text{assoc.}}$ are the HS and association integrals, respectively. The bulk density is related to
737 the ideal pressure by $\rho = \beta P^{\text{id.}}$, and $I_{\text{hs}} = \beta P^{\text{hs}}$ according to Lutsko's review⁵⁶. By using Eq. (28)
738 the association integral becomes

$$739 \quad \begin{aligned} I_{\text{assoc.}} &= \int_{R^+}^{z_b} \rho(z_1) \frac{d\mu^{\text{assoc.}}(z_1)}{dz_1} dz_1 \\ &= \sum_a \int_{R^+}^{z_b} \rho(z_1) \frac{d \ln X_a(z_1)}{dz_1} dz_1 - \frac{1}{2} \sum_{a,b} \int_{R^+}^{z_b} \rho(z_1) \frac{d\bar{G}_{ab}^{\text{assoc.}}(z_1)}{dz_1} dz_1 \\ &= \sum_a I_1 - \frac{1}{2} \sum_{a,b} I_2 \end{aligned} \quad (\text{B7})$$

740 Using Eq. (22), integral I_1 becomes

$$\begin{aligned}
 I_1 &= -\frac{1}{2} \sum_b \left[\int_{R^+}^{z_b} \rho(z_1) X_a(z_1) \frac{dG_{ba}^{\text{assoc.}}(z_1)}{dz_1} dz_1 + \int_{R^+}^{z_b} \rho(z_1) g_{\sigma}^{\text{hs}}(z_1) X_a(z_1) \frac{d\chi_{ba}(z_1)}{dz_1} dz_1 \right. \\
 &\quad \left. + \int_{R^+}^{z_b} \rho(z_1) \chi_{ba}(z_1) X_a(z_1) \frac{dg_{\sigma}^{\text{hs}}(z_1)}{dz_1} dz_1 \right] \\
 &= -\frac{1}{2} \sum_b [I_{11} + I_{12} + I_{13}]
 \end{aligned} \tag{B8}$$

742 Using Eq. (27), integral I_2 becomes

$$I_2 = \int_{R^+}^{z_b} \rho(z_1) \int_{-\infty}^{+\infty} \rho(z_2) X_a(z_2) \left. \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \right|_{(z_2)} \chi_b(z_2) \frac{dp^{\text{cg}}(z_{12})}{dz_1} dz_2 dz_1 \tag{B9}$$

744 such that Eq. (B7) can be expressed as

$$I_{\text{assoc.}} = -\frac{1}{2} \sum_{a,b} [I_{11} + I_{12} + I_{13} + I_2] \tag{B10}$$

746 The weight $p_{1D}^{\text{cg}}(z) = \iint p_{3D}^{\text{cg}}(x, y, z) dx dy$, which is the coarse-grained weight integrated over the
747 axes x and y (the indices 1D are omitted for in a sake of simplify) is used in Eq. (B9). In this
748 section, we also consider the integrated association weight $p_{ab,1D}^{\text{assoc.}}(z) = \iint p_{ab,3D}^{\text{assoc.}}(x, y, z) dx dy$.

749 Using Eqs. (23–24), we consider

$$\begin{aligned}
 \sum_{a,b} [I_{11} + I_{12}] &= \sum_{a,b} \left[\int_{R^+}^{z_b} \rho(z_1) X_a(z_1) \int_{-\infty}^{+\infty} \rho(z_2) X_b(z_2) g_{\sigma}^{\text{hs}}(z_2) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right. \\
 &\quad \left. + \int_{R^+}^{z_b} \rho(z_1) g_{\sigma}^{\text{hs}}(z_1) X_a(z_1) \int_{-\infty}^{+\infty} \rho(z_2) X_b(z_2) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right]
 \end{aligned} \tag{B11}$$

751 by analogy with Lutsko's treatment for the van der Waals fluid⁵⁶. Lower bounds of all the integrals
752 in Eq. (B11) can be replaced by $z = R^+$ because $\rho(z) = 0$ for $z < R^+$. The integrals having $+\infty$ as
753 the upper limit can be splitted by introducing the point z_b , so that

$$\begin{aligned}
 \sum_{a,b} [I_{11} + I_{12}] &= \sum_{a,b} \left[\int_{R^+}^{z_b} \rho(z_1) X_a(z_1) \int_{R^+}^{z_b} \rho(z_2) X_b(z_2) g_{\sigma}^{\text{hs}}(z_2) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right. \\
 &\quad + \int_{R^+}^{z_b} \rho(z_1) X_a(z_1) \int_{z_b}^{\infty} \rho(z_2) X_b(z_2) g_{\sigma}^{\text{hs}}(z_2) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \\
 &\quad + \int_{R^+}^{z_b} \rho(z_1) g_{\sigma}^{\text{hs}}(z_1) X_a(z_1) \int_{R^+}^{z_b} \rho(z_2) X_b(z_2) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \\
 &\quad \left. + \int_{R^+}^{z_b} \rho(z_1) g_{\sigma}^{\text{hs}}(z_1) X_a(z_1) \int_{z_b}^{\infty} \rho(z_2) X_b(z_2) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right]
 \end{aligned} \tag{B12}$$

755 that can be rearranged as

$$\begin{aligned} \sum_{a,b} [I_{11} + I_{12}] &= \sum_{a,b} \left[\int_{R^+}^{z_b} \int_{R^+}^{z_b} \rho(z_1) \rho(z_2) X_a(z_1) X_b(z_2) (g_\sigma^{\text{hs}}(z_1) + g_\sigma^{\text{hs}}(z_2)) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right] \\ &+ \sum_{a,b} \left[\int_{R^+}^{z_b} \rho(z_1) X_a(z_1) \int_{z_b}^{+\infty} \rho(z_2) X_b(z_2) g_\sigma^{\text{hs}}(z_2) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right] \\ &+ \sum_{a,b} \left[\int_{R^+}^{z_b} \rho(z_1) g_\sigma^{\text{hs}}(z_1) X_a(z_1) \int_{z_b}^{+\infty} \rho(z_2) X_b(z_2) \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right] \end{aligned} \quad (\text{B13})$$

756

757 The first sum on the right-hand side can be cancelled since it is odd by permutation of z_1 into z_2 .758 The last sum can also be rearranged since $\rho(z_2)$, $X_b(z_2)$ and $g_\sigma^{\text{hs}}(z_2)$ become constant and equal to759 their bulk value in the region $z_2 > z_b$, such that

$$\begin{aligned} \sum_{a,b} [I_{11} + I_{12}] &= \rho \sum_{a,b} X_b \left[g_\sigma^{\text{hs}} \int_{R^+}^{z_b} \rho(z_1) X_a(z_1) \int_{z_b}^{+\infty} \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right. \\ &+ \left. \int_{R^+}^{z_b} \rho(z_1) g_\sigma^{\text{hs}}(z_1) X_a(z_1) \int_{z_b}^{+\infty} \frac{dp_{ab}^{\text{assoc.}}(z_{12})}{dz_1} dz_2 dz_1 \right] \\ &= \rho \sum_{a,b} X_b \left[g_\sigma^{\text{hs}} \int_{R^+}^{z_b} \rho(z_1) X_a(z_1) p_{ab}^{\text{assoc.}}(z_1 - z_b) dz_1 \right. \\ &+ \left. \int_{R^+}^{z_b} \rho(z_1) g_\sigma^{\text{hs}}(z_1) X_a(z_1) p_{ab}^{\text{assoc.}}(z_1 - z_b) dz_1 \right] \end{aligned} \quad (\text{B14})$$

760

761 Making use of the associative cutoff

$$\begin{aligned} \sum_{a,b} [I_{11} + I_{12}] &= \rho \sum_{a,b} X_b \left[g_\sigma^{\text{hs}} \int_{z_b - r_c^{\text{assoc.}}}^{z_b} \rho(z_1) X_a(z_1) p_{ab}^{\text{assoc.}}(z_1 - z_b) dz_1 \right. \\ &+ \left. \int_{z_b - r_c^{\text{assoc.}}}^{z_b} \rho(z_1) g_\sigma^{\text{hs}}(z_1) X_a(z_1) p_{ab}^{\text{assoc.}}(z_1 - z_b) dz_1 \right] \end{aligned} \quad (\text{B15})$$

762

763 Under the considered assumptions, $\rho(z_1)$, $X_a(z_1)$ and $g_\sigma^{\text{hs}}(z_1)$ become constant and equal to their764 bulk value in the region $z_1 > z_b$, such that

$$\begin{aligned} \sum_{a,b} [I_{11} + I_{12}] &= 2\rho^2 g_\sigma^{\text{hs}} \sum_{a,b} X_a X_b \int_0^{r_c^{\text{assoc.}}} p_{ab}^{\text{assoc.}}(z_1) dz_1 \\ &= \rho^2 \sum_{a,b} X_a X_b \Delta_{ab} \end{aligned} \quad (\text{B16})$$

765

766 by using $4\pi K_{ab} F_{ab} = \int_{-r_c^{\text{assoc.}}}^{r_c^{\text{assoc.}}} p_{ab}^{\text{assoc.}}(z_1) dz_1$. The two remaining integrals in Eq. (B10) can be

767 simplified in a similar way, and give

$$\begin{aligned} \sum_{a,b} [I_{13} + I_2] &= \sum_{a,b} \left[\int_{0^+}^{z_b} \rho(z_1) \chi_{ba}(z_1) X_a(z_1) \frac{dg_\sigma^{\text{hs}}(z_1)}{dz_1} dz_1 \right. \\ &+ \left. \int_{R^+}^{z_b} \rho(z_1) \int_{-\infty}^{+\infty} \rho(z_2) X_a(z_2) \frac{\partial g_\sigma^{\text{hs}}}{\partial \eta} \Big|_{(z_2)} \chi_{ba}(z_2) \frac{dp^{\text{cg}}(z_{12})}{dz_1} dz_2 dz_1 \right] \end{aligned} \quad (\text{B17})$$

768

769 where we used

$$770 \quad \frac{dg_{\sigma}^{\text{hs}}(z_1)}{dz_1} = \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \bigg|_{(z_1)} \frac{\partial \eta}{\partial z_1} \\ = \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \bigg|_{(z_1)} \int_{-\infty}^{+\infty} \rho(z_2) \frac{dp^{\text{cg}}(z_{12})}{dz_1} dz_2 \quad (\text{B18})$$

771 With the same methodology used in Eqs. (B12–B13), we obtain

$$\begin{aligned} \sum_{a,b} [I_{13} + I_2] &= \sum_{a,b} \left[\int_{R^+}^{z_b} \int_{R^+}^{z_b} \rho(z_1) \rho(z_2) \left(X_a(z_1) \chi_{ba}(z_1) \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \bigg|_{(z_1)} + X_a(z_2) \chi_{ba}(z_2) \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \bigg|_{(z_2)} \right) dz_2 dz_1 \right] \\ &+ \sum_{a,b} \left[\int_{R^+}^{z_b} \rho(z_1) \chi_{ba}(z_1) X_a(z_1) \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \bigg|_{(z_1)} \int_{z_b}^{+\infty} \rho(z_2) \frac{dp^{\text{cg}}(z_{12})}{dz_1} dz_2 dz_1 \right. \\ &\left. + \int_{R^+}^{z_b} \rho(z_1) \int_{z_b}^{+\infty} \rho(z_2) X_a(z_2) \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \bigg|_{(z_2)} \chi_{ba}(z_2) \frac{dp^{\text{cg}}(z_{12})}{dz_1} dz_2 dz_1 \right] \end{aligned} \quad (\text{B19})$$

772
773 Performing a derivation similar to the one done in Eqs. (B14–B16) with the CG cutoff σ allows to
774 obtain

$$\begin{aligned} \sum_{a,b} [I_{13} + I_2] &= 2\rho^2 \frac{\partial g_{\sigma}^{\text{hs}}}{\partial \eta} \int_0^{\sigma} p^{\text{cg}}(z_1) dz_1 \sum_{a,b} X_a \chi_{ba} \\ &= \rho^2 \eta \frac{\partial \ln g_{\sigma}^{\text{hs}}}{\partial \eta} \sum_{a,b} X_a X_b \Delta_{ab} \end{aligned} \quad (\text{B20})$$

776 and Eq. (B10) becomes

$$\begin{aligned} I_{\text{assoc.}} &= -\frac{\rho^2}{2} \left(1 + \eta \frac{\partial \ln g_{\sigma}^{\text{hs}}}{\partial \eta} \right) \sum_{a,b} X_a X_b \Delta_{ab} \\ &= \beta P^{\text{assoc.}} \end{aligned} \quad (\text{B21})$$

778 such that Eq. (B6) reduces to $\rho(R^+) = \beta P$ and the wall theorem is verified.

779 Appendix C: Inhomogeneous treatment of the bonding fraction

780 The probability of finding an eligible bonding partner, for a site a on a given molecule at
781 position \mathbf{r}_1 , is expressed through a complex pair correlation integral in the non-bonded fraction
782 relation, that we recall here:

$$783 \quad X_a(\mathbf{r}_1) = \frac{1}{1 + \int \rho(\mathbf{r}_2) g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2) \sum_b X_b(\mathbf{r}_2) \bar{F}_{ab}(\mathbf{r}_{12}) d\mathbf{r}_2} \quad (\text{C1})$$

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784 In the original derivation proposed by Wertheim⁴⁻⁷, this bonding probability depends on both the
 785 position of the associating molecules and the orientation of their respective sites. An average over
 786 sites orientations is convenient so that the formalism is simplified to a position-dependant density
 787 functional theory. The range of association around a given molecule in a spherical envelope, repre-
 788 sented in FIG. 9, is defined by the orientation-averaged Mayer function $\bar{F}_{ab}(r_{12})$. For the angular
 789 potential formulation, this range corresponds to an interval from the contact value between two
 790 molecules (*i.e.*, the diameter σ) to the cutoff $r_{12,c}$, such that the bonding is restricted to a dimer
 791 formation⁹ (*i.e.*, $\sigma < r_{12,c} \leq \sigma/[2 \sin(\theta_c)]$). To estimate the bonding probability in an inhomogeneous
 792 fluid, one requires the values of the local functions (*e.g.*, local density) in the defined
 793 region. Segura *et al.*⁴¹ was the first to drive Wertheim's unbonded fraction relation to a tractable
 794 equation for inhomogeneous fluid. It was later enhanced by Chapman and coworkers³⁷ in iSAFT
 795 framework.

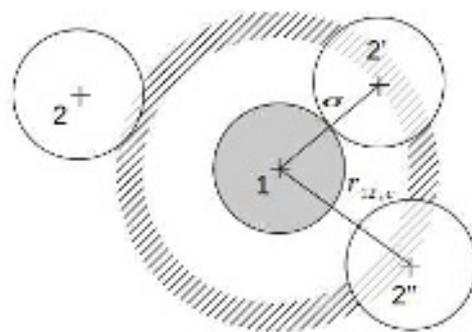


FIG. 9. Schematic representation of the range of association between two molecules placed at r_1 and r_2 , respectively. The lower limit of the range is represented with molecule $2'$, and the upper limit of the range is represented with molecule $2''$. A non-bonded case is represented with molecule 2 .

796 A reformulation of the original derivation⁴⁵, under the same assumptions, is given in Sec-
 797 tion C 1 of this appendix to make clear the improvements provided by our current work concern-
 798 ing the inhomogeneous treatment of association. In Section C 2, we discuss the method proposed
 799 by Yu and Wu³⁹ (and employed by Camacho Vergara *et al.*⁴⁰) to calculate the unbonded fraction
 800 profiles.

801 1. Surface and volume effect of association

802 We consider here the case of an associating fluid with four sites within the scheme 4C. The

803 expression of the non-bounded fraction obtained by Segura *et al.*^{41,45} is given as a 1D formulation
804 as

$$805 \quad X_a^{\text{Segura}}(z_1) = \frac{1}{1 + \frac{4\pi F_{aa} K_{aa} g^{\text{hs}}(\sigma; \rho_{\text{bulk}})}{\sigma} \int_{z_1 - \sigma}^{z_1 + \sigma} \rho(z_2) X_a(z_2) dz_2} \quad (\text{C2})$$

806 Two assumptions are made to obtain Eq. (C2) from Eq. (C1). The first assumption deals with
807 the pair correlation function (and corresponds to the approximation that Jackson *et al.*⁹ employed
808 in SAFT for homogeneous fluids), treated as $g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{\sigma^2}{r_{12}^2} g^{\text{hs}}(\sigma; \rho_{\text{bulk}})$, where ρ_{bulk} is the
809 bulk density for the considered chemical potential μ (introduced in Eq. (5)), and $g^{\text{hs}}(\sigma; \rho_{\text{bulk}})$ is
810 the contact-value of the pair distribution function of the homogeneous hard-sphere (HS) fluid for
811 ρ_{bulk} . By using these assumptions in Eq. (C1), this latter becomes

$$812 \quad X_a(\mathbf{r}_1) = \frac{1}{1 + 2 g^{\text{hs}}(\sigma; \rho_{\text{bulk}}) F_{aa} K_{aa} \int \rho(\mathbf{r}_2) X_a(\mathbf{r}_2) \frac{1}{r_{12}^2} \frac{\Theta(r_{12,c} - r_{12}) - \Theta(\sigma - r_{12})}{r_{12,c} - \sigma} d\mathbf{r}_2} \quad (\text{C3})$$

813 where we express the average Mayer function $\bar{F}_{aa}(r_{12})$ with the weights defined in Eq. (14b) (for
814 the angular formulation of the potential) and introduce the bonding volume K_{aa} , defined by Segura
815 *et al.*^{41,45} as $K_{aa} = \frac{(1 - \cos \theta_c)^2}{4} \sigma^2 (r_{12,c} - \sigma)$ (which in turn introduces the factor $(r_{12,c} - \sigma)$ in
816 the denominator).

817 The second approximation consists in simplifying the integral in Eq. (C3) by considering that
818 the bonding range is small. If $r_{12,c}$ tends to σ^+ , one can note that

$$819 \quad \lim_{r_{12,c} \rightarrow \sigma^+} \frac{\Theta(r_{12,c} - r_{12}) - \Theta(\sigma - r_{12})}{r_{12,c} - \sigma} = \delta(\sigma - r_{12}) \quad (\text{C4})$$

820 where $\delta(\sigma - r_{12})$ is a Dirac distribution. As a consequence, the term r_{12}^2 in Eq. (C3) can be
821 replaced by σ^2 , such that the non-bonded fraction can be expressed as

$$822 \quad X_a^{3\text{D,Segura}}(\mathbf{r}_1) = \frac{1}{1 + \frac{2 g^{\text{hs}}(\sigma; \rho_{\text{bulk}}) F_{aa} K_{aa}}{\sigma^2} \int \rho(\mathbf{r}_2) X_a(\mathbf{r}_2) \delta(\sigma - r_{12}) d\mathbf{r}_2} \quad (\text{C5})$$

823 This expression is equivalent to the 1D formulation (Eq. (C2)) in a more general 3D form, where
824 the local functions $\rho(\mathbf{r})$ and $X_a(\mathbf{r})$ are weighted (*i.e.*, averaged) on the surface of a sphere of radius
825 σ , that corresponds to the accessible surface area surrounding the molecule at position \mathbf{r}_1 . The
826 approximation used by Jackson *et al.*⁹ to estimate the pair correlation beyond the contact value
827 vanishes by using the Dirac distribution. Bymaster *et al.*³⁷ improved the initial formulation of
828 Segura, by replacing the homogeneous pair correlation function with an inhomogeneous scenario

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829 by using position-reference densities, but retained the second approximation (using of the Dirac
830 distribution defined in Eq. (C4)) within a 1D-equivalent formulation³⁷).

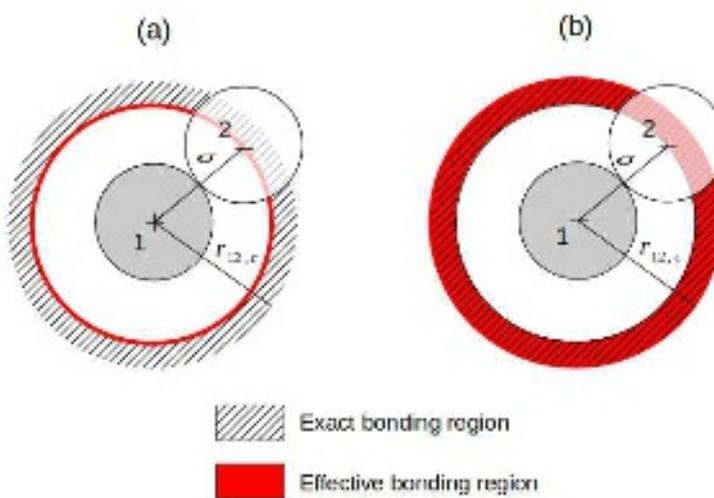


FIG. 10. Schematic representation of the exact and effective regions of association between molecules 1 and 2, measured in r_1 (the region of association occurs in the estimation of the unbonded fraction $X_a(r_1)$ for molecule 1). The exact bonding region, represented as a hatched zone, is delimited radially by the contact distance between molecule 1 and molecule 2, *i.e.*, the diameter σ , and by the cutoff $r_{12,c}$. Case (a) refers to the approximation employed by Segura^{41,45} and iSAFT³⁷ models, where the inhomogeneous functions are weighed on the accessible surface only, and where volume effects are neglected for association in an inhomogeneous manner. Case (b) refers to the new treatment proposed in our current work, where the inhomogeneous functions are weighed over the exact bonding volume of association.

831 With this second approximation, the treatment of inhomogeneous functions involved in the
832 bonding volume is restricted to surface effects (due to the Dirac distribution), as it is illustrated
833 in FIG. 10. The effects of the approximation are not negligible when the cutoff $r_{12,c}$ is no longer
834 similar to the contact value σ^+ . We compared the formulation proposed in the current work
835 (normalized by the bonding volume and denoted as $\bar{n}^{\text{assoc.}}(r_1)$ here), which depends on the cutoff
836 $r_{12,c}$,

$$\begin{aligned}
 \bar{n}^{\text{assoc.}}(r_1) &= \frac{\int f(r_2) \frac{1}{r_{12}^2} \left(\Theta(r_{12,c} - r_{12}) - \Theta(\sigma - r_{12}) \right) dr_2}{\int \frac{1}{r_{12}^2} \left(\Theta(r_{12,c} - r_{12}) - \Theta(\sigma - r_{12}) \right) dr_2} \\
 &= \frac{1}{4\pi} \int f(r_2) \frac{1}{r_{12}^2} \frac{\Theta(r_{12,c} - r_{12}) - \Theta(\sigma - r_{12})}{r_{12,c} - \sigma} dr_2
 \end{aligned}
 \tag{C6}$$

838 with the approximate function obtained by considering $r_{12,c} \rightarrow \sigma^+$ (also normalized by the bond-

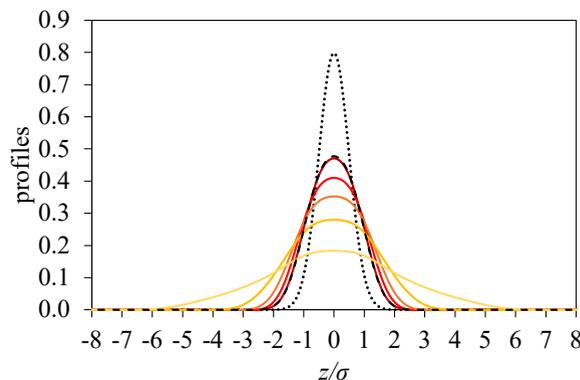


FIG. 11. Illustration of the cutoff influence in the association weight. A Gaussian profile $f(z)$ of reference is represented by a dotted curve. The corresponding weighted function $\bar{n}^{\text{Segura}}(z)$ defined from Segura's treatment⁴⁵ is represented by a dashed curve. The corresponding weighted function $\bar{n}^{\text{assoc.}}(z)$ introduced in our current work is represented by continuous curves for several cutoffs: 1.05σ (dark red), 1.46σ (red), 1.93σ (dark orange), 2.88σ (orange), and 5.74σ (yellow).

839 ing volume, and denoted as $\bar{n}^{\text{Segura}}(r_1)$ here), that is independent of the cutoff,

$$840 \quad \bar{n}^{\text{Segura}}(r_1) = \frac{\int f(r_2) \delta(\sigma - r_{12}) dr_2}{\int \delta(\sigma - r_{12}) dr_2} = \frac{1}{4\pi\sigma^2} \int f(r_2) \delta(\sigma - r_{12}) dr_2 \quad (\text{C7})$$

841 For a 1D Gaussian profile centered in zero,

$$842 \quad f(z) = \frac{1}{\sqrt{2\pi\Delta}} \exp\left(-\frac{z^2}{2\Delta^2}\right) \quad (\text{C8})$$

843
844 we show the results in fig. 11, for $\Delta = \sigma/2$. For the cutoff employed in our current work, 1.05σ ,
845 the difference between $\bar{n}^{\text{Segura}}(z)$ and $\bar{n}^{\text{assoc.}}(z)$ is negligible, explaining the close results between
846 the new association functional and iSAFT. The larger the cutoff is, the more spread out is the
847 function $\bar{n}^{\text{assoc.}}(z)$. In addition, we consider the following cutoff radius: 1.46σ , 1.93σ , 2.88σ , and
848 5.74σ , that correspond to the maximum possible cutoffs (to respect the dimerization condition)
849 for angles θ_c of 20° , 15° , 10° , and 5° , respectively.

850 2. Two methods for the calculation of the non-bonded fraction

851 Yu and Wu³⁹ developed a DFT model for associating fluids, denoted as aFMT here, by introduc-

852 ing the weighted densities of the fundamental-measure theory (FMT), $n_\alpha(\mathbf{r})$ in their framework
853 (where α denotes the nature of the weighting^{30,44}). The non-bonded fraction of an associating
854 fluid described by scheme 4C with the aFMT approach is expressed

$$855 \quad X_a^{\text{aFMT}}(\mathbf{r}) = \frac{1}{1 + 2n_0(\mathbf{r})\zeta(\mathbf{r})X_a(\mathbf{r})\Delta_{aa}(\mathbf{r})} \quad (\text{C9})$$

856 where $\zeta(\mathbf{r})$ is a function of scalar and vectorial FMT's weighted densities. The association
857 strength function $\Delta_{aa}(\mathbf{r})$ is given by

$$858 \quad \Delta_{aa}(\mathbf{r}) = 4\pi K_{aa} F_{aa} g(\sigma, n_\alpha) \quad (\text{C10})$$

859 where K_{aa} is the constant bonding volume, defined above, F_{aa} is the Mayer function, and $g(\sigma, n_\alpha)$
860 is the pair correlation between two HS molecules at contact, expressed as a function of the FMT's
861 weighted densities $n_\alpha(\mathbf{r})$. The inhomogeneous functions used to estimate the bonding fraction
862 of the monomer correspond to averages over the surface area and volume of the monomer itself
863 through the FMT's weighted densities. These contributions are then multiplied by the bonding
864 volume. Another formulation of the non-bonding fraction is proposed by Yu and Wu³⁹, consisting
865 in applying Segura's expression (*i.e.*, Eq. (C2)) to the density profile obtained with the aFMT
866 approach. The resulting non-bonded fraction is denoted as $X_a^{\text{aFMT-Segura}}(\mathbf{r})$.

867 We show in FIG.12 the 1D non-bonded fraction profiles, $X_0(z)$ (calculated with Eq. (37) from
868 the fractions $X_a(z)$), of an associating HS fluid against a planar hard wall for two sets of thermo-
869 dynamic conditions, characterized by $\rho^* = 0.1994$ and $\varepsilon^* = 5$, and by $\rho^* = 0.2112$ and $\varepsilon^* = 7$,
870 respectively. We compare the prediction obtained with the aFMT approach, the aFMT-Segura
871 approach, the new functional developed in the current work, and molecular simulations at equiv-
872 alent potential. A change of slope is observed in molecular simulations at $z \approx 1.5\sigma$, which is
873 correctly predicted by the new functional and by the aFMT-Segura approach. A change of slope
874 at $z \approx \sigma$ is however observed with the aFMT approach, which does not correspond to the trend
875 of the molecular simulations. These differences can be explained by the weighted functions used
876 in the approaches considered here: for a hard wall placed at $z = 0$ (*i.e.*, for an accessible region
877 of $z > \sigma/2$ for the center of fluid particles) and a weight characterized by a radius \mathcal{R} , a change
878 in slope can be observed at $z \approx \sigma/2 + \mathcal{R}$. In particular, the fraction $X_0^{\text{aFMT}}(z)$ (Eq. (C9)) depends
879 on weights of radius $\sigma/2$ only. By contrast, an effective weight using the contact distance σ is
880 introduced by the aFMT-Segura approximation (Eq. (C2)) to calculate $X_0^{\text{aFMT-Segura}}(z)$. The asso-
881 ciation contribution in the new free-energy functional depends on weights employing the contact

882 distance σ , and the bonding volume of association from σ to $r_{12,c} = 1.05\sigma$ (Eq. (22)), which
883 explains that the change in slope occurs at $z \approx 1.5\sigma$.

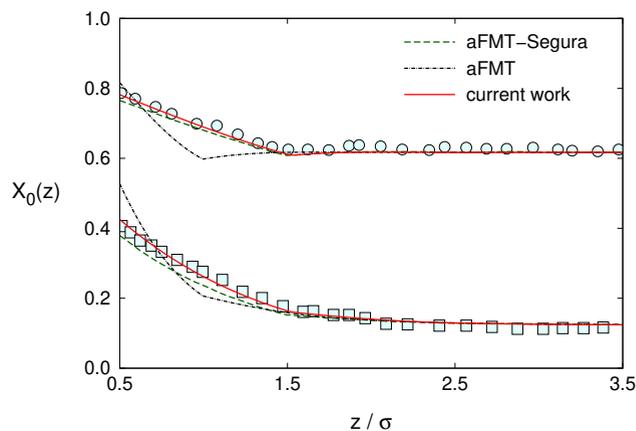


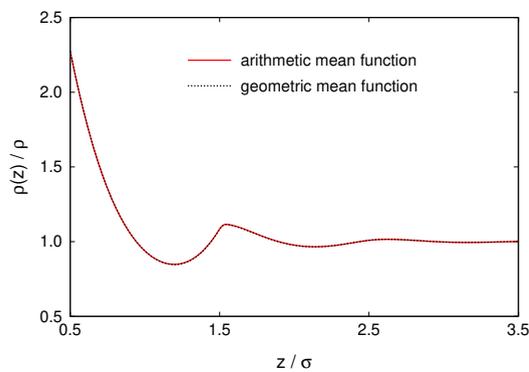
FIG. 12. Fraction of non-bonded monomers of an associated fluid with four associating sites (*i.e.*, scheme 4C) in contact with a planar hard wall placed at $z = 0$. From top to bottom: $\rho^* = 0.1994$ and $\epsilon^* = 5$; and $\rho^* = 0.2112$ and $\epsilon^* = 7$. The circles and squares represent the simulation data^{33,34,41,43}. The dashed green line represents the aFMT-Segura calculation (Eq. (C2)). The dotted-dashed black line represents aFMT result with the unbonded fraction expression obtained by Yu and Wu³⁹ (Eq. (C9)). The continuous red line represents the results obtained in the current work (Eq. (22)).

884 Appendix D: Two mean functions to approximate the pair distribution function (PDF)

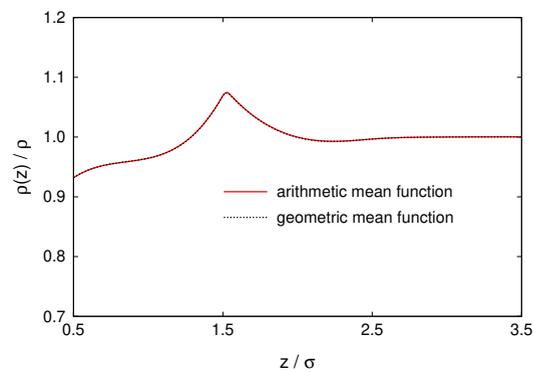
885 As discussed by Lurie-Gregg *et al.*⁴², a separation of the variables \mathbf{r}_1 and \mathbf{r}_2 in the PDF,
886 $g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2)$, is convenient so that the pair correlation integrals reduce to one-centers convolu-
887 tion products. To derive our association DFT model that we detailed in Section IIC, we em-
888 ployed the arithmetic mean function by analogy with the contact-value approach proposed by
889 Lurie-Gregg *et al.*⁴². However one could also use a geometric mean function, $g^{\text{hs}}(\mathbf{r}_1, \mathbf{r}_2) \approx$
890 $\left[g^{\text{hs}}(r_{12}; \eta_\sigma(\mathbf{r}_1)) g^{\text{hs}}(r_{12}; \eta_\sigma(\mathbf{r}_2)) \right]^{1/2}$, as it has been done in iSAFT calculation³⁷, by keeping
891 the remaining part of the derivation unchanged. We compare in FIG.13 both formulations applied
892 to the hard wall system that we presented in Section IIC for the same association scheme and
893 identical thermodynamic conditions, and we do not obtain significant changes in the results.

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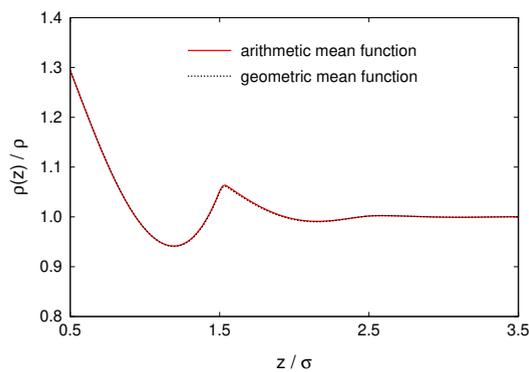
PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0180795



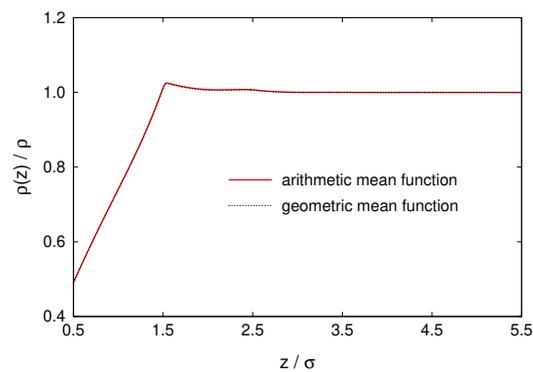
(a) Scheme 1A; $\rho^* = 0.4868$ and $\epsilon^* = 11$



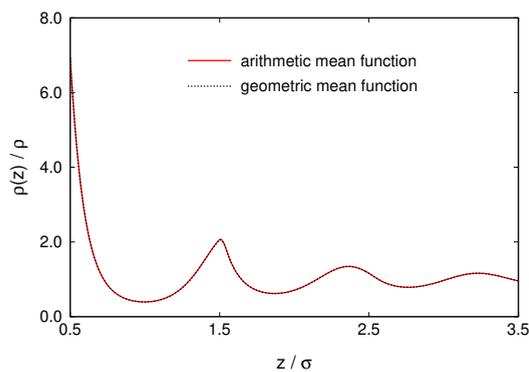
(b) Scheme 1A; $\rho^* = 0.1999$ and $\epsilon^* = 14$



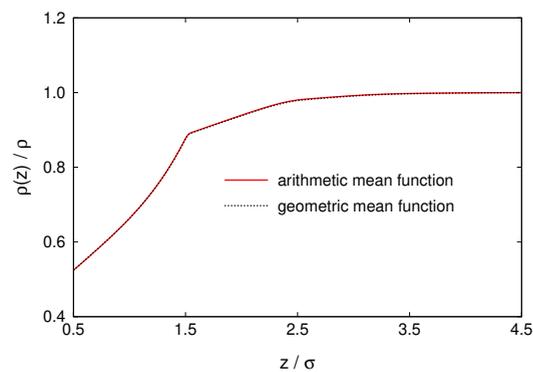
(c) Scheme 2B; $\rho^* = 0.3449$ and $\epsilon^* = 8$



(d) Scheme 2B; $\rho^* = 0.2084$ and $\epsilon^* = 11$



(e) Scheme 4C; $\rho^* = 0.9036$ and $\epsilon^* = 5$



(f) Scheme 4C; $\rho^* = 0.2112$ and $\epsilon^* = 7$

FIG. 13. Density profiles of an associating HS fluid in contact with a planar hard wall placed at $z = 0$, for the identical thermodynamic conditions presented in Section III A. The continuous red line represents our current work detailed in Section II C where an arithmetic mean function is employed to evaluate the PDF, the dash black line corresponds to the results where the arithmetic mean function has been changed with the geometric mean function that is employed in iSAFT calculation³⁷.