Properties of a soft-core model of methanol: An integral equation theory and computer simulation study

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Thermodynamic and structural properties of a coarse-grained model of methanol are examined by Monte Carlo simulations and reference interaction site model (RISM) integral equation theory. Methanol particles are described as dimers formed from an apolar Lennard-Jones sphere, mimicking the methyl group, and a sphere with a core-softened potential as the hydroxyl group. Different closure approximations of the RISM theory are compared and discussed. The liquid structure of methanol is investigated by calculating site-site radial distribution functions and static structure factors for a wide range of temperatures and densities. Results obtained show a good agreement between RISM and Monte Carlo simulations. The phase behavior of methanol is investigated by employing different thermodynamic routes for the calculation of the RISM free energy, drawing gas-liquid coexistence curves that match the simulation data. Preliminary indications for a putative second critical point between two different liquid phases of methanol are also discussed. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4899316>]

I. INTRODUCTION

Alcohols and their aqueous solutions are important in all aspects of modern life. They are used in food industry and preservation, transportation, medicine, and chemical industry as solvents and reactants. Methanol is the simplest example of alcohols and the smallest amphiphilic organic solute. The hydroxyl group is strongly polarized and can participate in hydrogen bonding with other methanol or water molecules. The methyl group has small polarizability and eschews polar environment. Due to its small size, both effects are noticeable in methanol. Thus, methanol is miscible with very polar solvents, such as water or acetic acid, and weakly polar solvents, such as benzene.

Properties of water have already been extensively studied with simulations. As computing power has increased exponentially, it is possible to employ atomistic models where each atom and lone electronic pair is dealt with explicitly (such as SPC or TIP5P). The methanol molecule contains twice as many atoms and demands roughly four times as much computing power, yet in principle the employment of atomistic models for methanol can be done in a similar manner. One of the earliest methanol models, the so-called optimized potential for liquid simulations (OPLS) model was proposed by Jorgensen,¹ followed by the work of van Leeuwen and Smiton on L1 model.² Also popular are H1 model of Haughey *et al.*^{3,4} and L2 model of Hasse *et al.*^{5,6} These models treat methanol on atomic level and use short-range Lennard-Jones interactions for repulsive and Coulomb law for long-range interactions, as atoms are ascribed positive or nega-

tive charges. The model we used (see details below) treats methanol molecules as rods of two fused pseudoatoms, interacting exclusively through short-range interactions.

Simulations can be expedited significantly when models with fewer particles are used. Recently, it has been shown that many structural, thermodynamic, and dynamic properties of water can be reproduced using soft-core spherically symmetrical potentials^{7–10} although certain tradeoffs are necessary due to the transferability issue.^{11,12} Angular dependence of hydrogen bonding is necessarily forgone and compensated for with two characteristic lengths that these models must have. Examples of such potentials are repulsive shoulder potentials,¹³ honeycomb potential,¹⁴ Lennard-Jones-Gaussian potentials,^{15,16} Jagla potential,^{17–20} and continuous shouldered well potential (CSW).²¹

Soft-core spherically symmetric potentials can be used as a starting point for the construction of coarse-grained methanol models. They represent the hydroxyl group and have an additional particle glued to them at a fixed distance, representing the methyl group. Stanley *et al.* used a two-particle model with Jagla and Lennard-Jones potential to simulate methanol in molecular dynamics.²² In their work, emphasis was placed on parameterizing the model in order to correctly predict excess volume and enthalpy of mixing.

In this context, integral equation theories of the liquid state²³ may play an important role in the study of structure and thermodynamics of simple and complex fluids, being generally able to provide a good description of the liquid structure and the fluid phase equilibria.²⁴ In this study, we adopt the Reference Interaction Site Model (RISM) theory of molecular fluids, developed by Chandler and Andersen²⁵ as a generalization of the Ornstein-Zernike theory of simple fluids.²³

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Originally, the theory was developed to deal only with molecular fluids consisting of hard spheres rigidly bonded together²⁶ or with simple Lennard-Jones dimers.²⁷ Later on, the theory has been extended to deal with more realistic representation of complex liquids, including associating fluids such as water^{28,29} and methanol,^{30–32} and their solvation properties.³³ More recently, RISM theory has been successfully implemented in the world of colloidal physics, investigating the phase behaviors and the self-assembly properties of a wide class of molecules, including tetrahedral colloidal particles,³⁴ Janus rods,³⁵ and colloidal dumbbells.^{36,37}

In this work, we apply and test the validity of RISM approach for a methanol model, consisting of two spherical particles, one mimicking the hydroxyl group and the other one the methyl group. The hydroxyl group is a CSW particle, interacting via the soft-core potential, while the methyl group is approximated by a Lennard-Jones particle. Data from Monte Carlo (MC) simulation are systematically compared with results from RISM theory, complemented by different closure approximations, namely, hypernetted chain (HNC),²³ soft-MSA (SMSA)²⁴ and Kovalenko-Hirata (KH).^{38,39} Also, we implement different thermodynamic routes to calculate the free energy of methanol and to draw the gas-liquid coexistence curve.

This paper consists of five sections. In Sec. II, the model is explained. We continue with the theoretical background of RISM theory and the details of Monte Carlo simulations in Sec. III. Results are gathered, compared, and discussed in Sec. IV, followed by Conclusions in Sec. V.

II. MODEL DETAILS

In our scheme, methanol is modeled as a rigid molecule consisting of two pseudo-atoms at a fixed distance $1.0a$ where a is the unit length. Hydroxyl groups are represented as spherical particles, interacting according to the CSW potential,²¹

$$U_{CSW}(r) = \frac{U_R}{1 + \exp(\Delta(r - R_R)/a)} - U_A \exp\left(-\frac{(r - R_A)^2}{2\delta_A^2}\right) + U_A \left(\frac{a}{r}\right)^{24}, \quad (1)$$

where U_A is the unit of energy. Model parameters have been kept unchanged since our last studies (see Refs. 9 and 10, and references therein): $U_R/U_A = 2$, $R_R/a = 1.6$, $R_A/a = 2$, $(\delta_A/a)^2 = 0.1$, $\Delta = 15$. Methyl groups are approximated as Lennard-Jones like particles, interacting pairwise as

$$U_{LJ}(r) = \frac{4}{3} \cdot 2^{\frac{2}{3}} \epsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r}\right)^{24} - \left(\frac{\sigma_{LJ}}{r}\right)^6 \right]. \quad (2)$$

Still following Refs. 9 and 10, Lennard-Jones parameters read as $\sigma_{LJ}/a = 1.0$ and $\epsilon_{LJ}/U_A = 0.1$. The interaction between hydroxyl and methyl groups is of Lennard-Jones type and follows classical Lorentz-Berthelot mixing rules $\sigma_{\text{mix}} = (\sigma_{LJ} + a)/2$ and $U_{\text{mix}} = \sqrt{\epsilon_{LJ} U_A}$ (see Fig. 1).

Finally, we define the reduced temperature, density, and pressure, respectively, as $T^* = k_B T/U_A$ (where k_B is the Boltz-

FIG. 1. Potentials used to represent interaction between two hydroxyl groups (solid line), hydroxyl and methyl groups (dot-dashed line) and two methyl groups (dotted line).

mann constant), $\rho^* = (N/V)a^3$ (where N is the number of the particles and V is the volume), and $P^* = Pa^3/U_A$.

III. THEORETICAL APPROACH AND SIMULATION STRATEGIES

A. Reference interaction site model

In the RISM theoretical framework, the pair structure of a fluid, composed of identical molecules, formed by n interaction sites, is characterized with a set of $n(n+1)/2$ site-site intermolecular pair correlation functions $h_{ij}(r) = g_{ij}(r) - 1$, where $g_{ij}(r)$ are the site-site radial distribution functions. $h_{ij}(r)$ are related to a set of intermolecular direct correlation functions $c_{ij}(r)$ by a Ornstein-Zernike-like matrix equation, which in k -space reads

$$\mathbf{H}(k) = \mathbf{W}(k)\mathbf{C}(k)\mathbf{W}(k) + \rho\mathbf{W}(k)\mathbf{C}(k)\mathbf{H}(k). \quad (3)$$

Since we investigate two-site models ($i, j = 1, 2$), Eq. (3) can be written in terms of 2×2 symmetric matrices as $\mathbf{H}(k) \equiv [h_{ij}(k)]$, $\mathbf{C}(k) \equiv [c_{ij}(k)]$, and $\mathbf{W}(k) \equiv [w_{ij}(k)]$. Elements $w_{ij}(k)$ are the Fourier transforms of the intramolecular correlation functions,

$$w_{ij}(k) = \frac{\sin[kL_{ij}]}{kL_{ij}}, \quad (4)$$

where bond length L_{ij} is $L_{ij} = a$ if $i \neq j$ and $L_{ij} = 0$ otherwise. In order to solve the RISM equation (Eq. (3)), we need an additional relation between the total and direct correlation functions, called the closure relation. In our case, the RISM equation has been solved with different approximation closures. First, we have tested the well-known hypernetted chain (HNC) closure, which can be written as

$$c_{ij}(r) = \exp[-\beta U_{ij}(r) + \gamma_{ij}(r)] - \gamma_{ij}(r) - 1. \quad (5)$$

Here, $\beta = 1/T^*$, and $U_{ij}(r)$ are the site-site interaction potentials and $\gamma_{ij}(r) = h_{ij}(r) - c_{ij}(r)$. The other classical approximation closure is the so-called mean spherical approximation (MSA), which is generally written (for a discontinuous potential) as

$$\begin{cases} g_{ij}(r) = 0 & \text{if } r \leq \sigma \\ c_{ij}(r) = -\beta U_{ij}(r) & \text{if } r > \sigma, \end{cases} \quad (6)$$

where σ is the hard-sphere diameter. However, this formula is not suitable for continuous potentials, therefore we adopted the soft-MSA (SMSA) closure where the intermolecular potential is split into a reference part and a perturbative contribution (for more details see Refs. 24 and 40 and references therein). Finally, we underscore that several other closures have been developed to address the shortcomings of HNC and MSA, especially the narrow region of convergence and the inherent thermodynamic inconsistency. One of these extensions is the Kovalenko-Hirata (KH) closure,^{38,39} which employs a combination of the MSA and of the HNC closure

$$c_{ij}(r) = \begin{cases} \text{HNC} & \text{if } g_{ij}(r) \leq 1 \\ \text{MSA} & \text{if } g_{ij}(r) > 1. \end{cases} \quad (7)$$

KH has been proposed to provide a more efficient convergence of the numerical algorithm, enabling a more detailed investigation of the fluid phase equilibria.

For the calculation of the free energy and pressure within the RISM/KH formalism, closed formulas (i.e., not requiring a thermodynamic integration) were derived by Kovalenko and Hirata,^{38,39} closely following the corresponding relations deduced for the HNC theory of simple fluids.^{41,42}

$$\begin{aligned} \frac{\beta A^{\text{ex}}}{N} = & -\frac{\rho^2}{2} \sum_{i,j} \int d\mathbf{r} \left[\frac{1}{2} h_{ij}^2(r) \Theta(-h_{ij}(r)) - c_{ij}(r) \right] \\ & + \frac{1}{2(2\pi)^3} \int d\mathbf{k} \{ \text{Tr} \rho \mathbf{W}(k) \mathbf{C}(k) \} \\ & + \ln \det[1 - \rho \mathbf{W}(k) \mathbf{C}(k)], \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{\beta P}{\rho} = & 1 + \frac{\rho}{2} \sum_{i,j} \int d\mathbf{r} \left[\frac{1}{2} h_{ij}^2(r) \Theta(-h_{ij}(r)) - c_{ij}(r) \right] \\ & + \frac{1}{2(2\pi)^3} \int d\mathbf{k} \{ \rho^{-1} \ln \det [\mathbf{I} - \rho \mathbf{W}(k) \mathbf{C}(k)] \\ & - \text{Tr} [\mathbf{W}(k) \mathbf{C}(k)] [\mathbf{I} - \rho \mathbf{W}(k) \mathbf{C}(k)]^{-1} \}, \end{aligned} \quad (9)$$

where Θ is the Heaviside step function. The chemical potential is then easily obtained from the standard thermodynamic relation

$$\beta \mu = \frac{\beta A}{N} + \frac{\beta P}{\rho}. \quad (10)$$

For the SMSA closure, no closed-form relation is available. Instead, we have calculated free energy and pressure with thermodynamic integration along constant-density paths according to²³

$$\frac{\beta A^{\text{ex}}(\beta)}{N} = \frac{\beta A^{\text{ex}}(\beta_0)}{N} + \int_{\beta_0}^{\beta} \frac{U(\beta')}{N} d\beta', \quad (11)$$

where the internal energy of the system is given by

$$\frac{U}{N} = 2\pi\rho \sum_{i,j=1}^2 \int_0^{\infty} U_{ij}(r) g_{ij}(r) r^2 dr. \quad (12)$$

In Eq. (11), $\beta A^{\text{ex}}(\beta_0)$ corresponds to a certain (known) value that the excess free energy attains at $\beta = \beta_0$. Once the free energy is known, the pressure can be deduced from the

derivation

$$\frac{\beta P}{\rho} = \rho \frac{\partial(\beta A/N)}{\partial \rho} \bigg|_T. \quad (13)$$

We have implemented the numerical solution by means of a standard iterative Picard algorithm, on a mesh of 8192 points with a spacing $\Delta r = 0.005\sigma$.

B. Monte Carlo simulations

Monte Carlo simulations were run in the canonical (NVT) ensemble with a fixed number of particles, volume and temperature. The bulk of simulations is comprised of 1000 methanol molecules. To check for possible finite-size effects, some initial simulations were also run with 500 molecules, and the results were found to be in agreement within the statistical uncertainty. Equilibration runs that started from random configurations lasted for 100 000 cycles and were followed by five runs of 1 000 000 cycles for gathering data. One cycle means an attempt to move each particle. The maximum displacement was adjusted for each simulation to get a 50% acceptance ratio in the Metropolis sampling.

Pressure was calculated via the virial route for rigid molecules as

$$\beta P = \rho - \frac{1}{3} \beta \sum_{i < j} \sum_{a < b} \frac{dU_{ab}}{dr} \frac{\mathbf{r}_{ab} \cdot \mathbf{r}_{ij}}{r_{ab}}, \quad (14)$$

where a and b denote the hydroxyl and methyl group in a molecule i , respectively. Vector $\mathbf{r}_{ab}$ is defined by the two groups in a molecule, while vector $\mathbf{r}_{ij}$ stretches between the center of masses of the molecules i and j . Note that we write one only summation sign for each double summation for greater clarity.

Virial pressure was compared with pressure from the test volume method. After each cycle, the system is temporarily blown-up and scaled-down for ΔV . Centers of masses of molecules are accordingly displaced. Energy of both new systems is averaged throughout the simulation and the average pressure is obtained as

$$\beta P = \rho + \frac{1}{2\Delta V} \log(\exp(\beta(U_{V+\Delta V} - U_{V-\Delta V}))). \quad (15)$$

At extremely low densities, the system can be approximated as an ideal gas and Helmholtz free energy is estimated as

$$\frac{\beta A}{N} \approx \frac{\beta A^{id}}{N} = \log(\Lambda^3 \rho) - 1. \quad (16)$$

Thermal de Broglie wavelength Λ has been absorbed into the potential definition and can be treated as unity for this purpose. At progressively higher densities, isothermal thermodynamic integration was employed

$$\frac{\beta A(\beta)}{N} = \frac{\beta A(\beta_0)}{N} + \int_{\rho_0}^{\rho} \frac{\beta p(\rho')}{\rho'^2} d\rho'. \quad (17)$$

Structure factor, being defined as autocorrelation function of density

$$S(\mathbf{k}) = \frac{1}{N} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle, \quad (18)$$

FIG. 2. Main figure: stable region of the HNC closure is separated from the unstable region by a border line in the $T^* - \rho^*$ plane. (Upper inset) Same for SMSA closure. (Lower inset) Same for KH closure.

is calculated for integer multiples of $k = \frac{2\pi}{L}$ for all combinations of particles a and b as

$$S_{ab}(\mathbf{k}) = \frac{N_a + N_b}{N_a N_b} \sum_a \sum_b \exp(-i\mathbf{k} \cdot (\mathbf{r}_a - \mathbf{r}_b)). \quad (19)$$

IV. RESULTS AND DISCUSSION

To test the RISM accuracy in predicting the fluid structure of methanol, we have first located, in the $T^* - \rho^*$ plane, the regions where the different closures properly work. The theories usually encounter ample difficulties to get the numerical convergence if the temperature is low or if the critical point is approached. In such conditions, the algorithm shows some instabilities that are reflected in the behavior of radial distribution functions and the static structure factors. The appearance of such instabilities usually predicts the fail-

ure of the numerical algorithm. We show in Fig. 2 the different operational ranges of HNC, SMSA, and KH. One can observe that the instability region of HNC is significant large than that of the other two closures. This precludes the possibility to perform HNC calculations on a large portion of the $T^* - \rho^*$ plane. Hence, in the spirit of sampling this space in more detail, we have adopted KH and SMSA closures to investigate the fluid structure and the phase behavior of methanol. Interestingly, the SMSA border line shows a minimum at $\rho^* = 0.15$: this feature could suggest the presence of two different instability regions, at low and high density, which will be further discussed afterwards.

The fluid structure of methanol is reported in Fig. 3. We show the radial distribution functions $g_{ij}(r)$ for two different thermodynamic states, with varying temperature and density. Results show an overall good agreement between theory and simulations in both cases. SMSA provides more accurate predictions at high temperature and intermediate density (panels (a) and (b)), while KH seems to work better at low temperature and high density (panels (c) and (d)). The behavior of the $g_{ij}(r)$ suggests a strong correlation between the hydroxyl groups at all temperatures and densities reported in the figure, with a double-peak behavior that changes upon lowering T^* and increasing ρ^* . Interestingly, such a feature could suggest a possible density anomaly in liquid methanol. Also, the double-peak behavior may be reminiscent of the presence of two possible orderings between methanol molecules, whose structuring is influenced essentially by the hydroxyl group. In fact, both the hydroxyl-methyl and methyl-methyl correlations show no structuring upon lowering T^* and increasing ρ^* , and no preferential orientation is observed.

To provide a description of phase equilibria and critical behavior of the CSW model for methanol, we report in Fig. 4

FIG. 3. Site-site radial distribution functions $g_{ij}(r)$ from MC (symbols) KH (full lines) and SMSA (dashed lines) at $T^* = 0.90 - \rho^* = 0.148$ (panels (a) and (b)) and $T^* = 0.60 - \rho^* = 0.200$ (panels (c) and (d)). Subscripts h and m refer to the hydroxyl group and the methyl group, respectively. For greater clarity, $g_{hh}(r)$ are plotted separately.

FIG. 4. Equations of state (a) and free energies (b) from MC (symbols), KH (full lines) and SMSA (dashed lines) for several isotherms. KH data are obtained by employing the closed formula (full lines), while SMSA results are calculated via thermodynamic integration (dashed lines).

equations of state (EOS) (panel (a)) and free energy (panel (b)) for four different isotherms. Theoretical predictions have been calculated by employing the closed formulas (8)–(9) for KH closure, as well as the thermodynamic integration according to Eqs. (11)–(13) for SMSA approximation. We set $\beta_0 = 0.5$, corresponding to $T^* = 2$. For the value of $\beta A^{ex}(\beta_0)$ we used the output of KH closed form, since it turned out to be very accurate at high temperatures. As shown in both panels of Fig. 4, KH predictions qualitatively reproduce simulation data for the pressure, providing also quantitative predictions of the free energy in a wide range of temperatures. The thermodynamic integration with the KH closure (not shown here) yields results fully comparable with the closed form, providing evidence of a good thermodynamic consistency. On the

FIG. 5. Gas-liquid coexistence points from the RISM theory, obtained by employing the closed formula and from MC simulations. Full lines are best fits calculated according to the scaling law for the density and the law of rectilinear diameter. The critical point estimated is indicated by the cross.

TABLE I. Critical parameters for MC, KH, and SMSA gas-liquid critical points.

	T_{crit}^*	ρ_{crit}^*	P_{crit}^*
MC	1.076	0.0753	0.0206
KH	1.028	0.0595	0.0211
SMSA	1.138	0.0667	0.0304

other hand, SMSA predictions appear less accurate than KH, underestimating free energy and pressure for a wide range of densities.

The monotonic increase of the free energy at $T^* = 1.30$ with density becomes increasingly flatter as the temperature is decreased, heralding a bend towards lower values at $T^* \leq 0.90$. The pressure exhibits a van der Waals loop at $T^* < 1.09$ that becomes progressively more pronounced upon lowering the temperature. This evidence provides a first indication for the critical temperature. The coexistence points are estimated by plotting the chemical potential, obtained from Eq. (10), as a function of the pressure: in sub-critical conditions, the chemical potentials of the gas and liquid phases cross at a specific pressure, whose value provides the two coexisting densities. In Monte Carlo simulation, coexistence points were calculated by Maxwell construction.

Results for the gas-liquid coexistence curve are reported in Fig. 5: theoretical predictions for critical values of temperature, density, and pressure agree very well with simulation data (see Table I). In particular, the gas-liquid critical point appears to be located at low values of reduced density, compared with standard isotropic liquids, allowing for the existence of a rather large liquid pocket.

It may be worth noting that, compared with previous RISM studies of different models of methanol,^{30,32}

FIG. 6. Typical snapshots from MC simulations at different conditions of temperatures and densities, namely, $T^* = 1.20 - \rho^* = 0.01$ (a), $T^* = 1.20 - \rho^* = 0.20$ (b), $T^* = 0.52 - \rho^* = 0.20$ (c), and $T^* = 0.52 - \rho^* = 0.28$ (d). Blue and red spheres indicate methyl and hydroxyl group, respectively.

FIG. 7. Equations of state from MC simulations (symbols), KH (full lines), and SMSA (dashed lines) at low temperatures. The second minimum of the pressure is visible in MC simulations around $\rho^* \simeq 0.27$.

theoretical predictions now agree much better with simulation data in describing both the structure and the thermodynamics of methanol.

Some snapshots of methanol molecules taken from MC simulations at high and low temperatures and densities are shown in the four panels of Fig. 6: the different values of T^* and ρ^* locate four thermodynamic state points in the $T^* - \rho^*$ plane close to liquid-gas and liquid-liquid critical points. In all panels, methanol molecules show a homogeneous arrangement in the simulation box: at low density (panel (a)) the attractive interactions are too weak to develop any kind of structuring. A high density, both at high (panel (b)) and low (panels (c) and (d)) temperatures, the packing effects dominate and the molecules arrange themselves in a closer configuration, regardless of the temperature. Interestingly, when the T^* is lowered to 0.54, the MC equation of state becomes flat around $\rho^* \simeq 0.27$ (see Fig. 7). This behavior hints at the appearance of a second minimum at $T^* = 0.52$. Unfortunately, as shown in Fig. 4, both KH and SMSA predictions lose accuracy upon lowering the temperature. As a consequence, the second minimum displayed by simulations is not reproduced by any of the closures. The appearance of such a minimum could suggest the presence of a second (liquid-liquid) critical point in methanol.⁴³ This hypothesis is corroborated by the trend of the site-site structure factors (defined by Eq. (18)), plotted in Fig. 8: by looking at the behavior of $S_{hh}(k)$ (the same holds for $S_{hm}(k)$ and $S_{mm}(k)$, not reported here) when $k \rightarrow 0$, it is possible to observe a progressive increase from $\rho^* = 0.20$ to $\rho^* = 0.25$. Conversely, for higher

FIG. 8. Hydroxyl-hydroxyl structure factors from MC simulations at fixed $T^* = 0.52$ and increasing densities.

densities, the $k \rightarrow 0$ limit of $S_{hh}(k)$ decreases as ρ^* increases. Since the increase of $S(k \rightarrow 0)$ usually signals an approach to a metastable region of the phase diagram, this behavior is compatible with the presence of a second critical point located around $T^* = 0.52$ and $\rho^* = 0.25$.

In Fig. 9, we report the three radial distribution functions at $T^* = 0.52$ and increasing densities from MC simulations: the first peak in the g_{hh} (panel (a)), centered around $r \simeq 1.05a$ becomes more and more defined upon increasing ρ^* . At the same time, the second peak of the g_{hh} , centered around $r \simeq 1.95a$, well defined at low densities, is lowered when ρ^* increases, until it is surpassed in height by the first peak at $\rho^* = 0.28$. This suggests that a different ordering is forming in the fluid structure. This hypothesis is also supported by the appearance of a small peak in the g_{hm} (panel (b)), centered around $r \simeq 2.30a$, visible at high densities but not at low densities. Finally, low structure is observed in methyl-methyl correlation (panel (c)).

All these findings are observed at temperatures where the RISM algorithm hardly gets the convergence and, hence, theoretical predictions are generally not suitable. Numerical troubles at low temperatures represent a typical weakness of the integral equation approach and they have been observed also in previous investigations of other models of methanol (see, e.g., Ref. 32). However, the numerical algorithm is still able to achieve the convergence if the density is high enough: in Fig. 10, we report SMSA predictions for $S_{hh}(k = 0)$, as a function of the density at different temperatures. Some oscillations appear and become more enhanced upon lowering of temperature. The reason why such oscillations develop

FIG. 9. Site-site radial distribution functions $g_{ij}(r)$ from MC simulations at $T^* = 0.52$ and increasing densities. The hydroxyl-hydroxyl correlation is reported in panel (a), the hydroxyl-methyl in panel (b), and the methyl-methyl in panel (c).

FIG. 10. $S_{hh}(k=0)$ from SMSA closure as a function of the density at different temperatures.

has not been completely clarified: they could be an artifact of the basic MSA scheme, which is generally inconsistent from the thermodynamic point of view, or they could signal the approach to the instability region of SMSA shown in Fig. 2. However, such oscillations are not observed inside the KH context. Anyway, a direct evidence of a liquid-liquid critical point in the theoretical framework is lacking: this is not completely surprising, since previous theoretical studies (see Refs. 44 and 45) have shown that simple fluid theory closures, such as HNC (and hence KH), hardly reproduce the liquid-liquid critical point and more refined closures are required. Specifically, such studies have shown that HMSA closure, which interpolates between SMSA and HNC (see Ref. 24 for more details) is able to provide the liquid-liquid critical point for atomic fluids with ramp and soft-core potentials. In those cases, the second critical point is found by imposing the thermodynamic consistency by the virial equation and the compressibility route.²³ However, such a consistency cannot be imposed inside the RISM formalism, because there is no virial equation available in the interaction site model (while such equation is available in the general context of molecular fluids), but for very specific cases like homonuclear hard dumbbells.^{46–48} On the other hand, the closed formula (9) is valid only in the KH closure and cannot be extended to the HMSA closure.

V. CONCLUSIONS

The behavior of CSW potential for methanol has been investigated by means of both MC simulations and RISM integral equation theory. A spherically symmetric coarse-grained model for methanol was used since its analogues have already been successfully adopted to investigate methanol non-idealities and water anomalies. The hydroxyl group is modeled with continuous shouldered well potential, while the methyl group is described by a Lennard-Jones-like potential. Different closures to the RISM equation (namely HNC, KH, and SMSA) have been compared and two thermodynamic routes have been employed to calculate the phase equilibria.

We have studied the fluid structure, analyzing the radial distribution functions $g(r)$ and the static structure factors $S(k)$, as well as the thermodynamics and the phase behavior of this model. Since HNC showed intrinsic weaknesses in obtaining

the numerical convergence, we have opted for the KH and SMSA as closure approximations, having found a satisfactory agreement with MC in predicting the behavior of $g(r)$.

As for the thermodynamics, remarkably both KH and SMSA predictions for free energy and pressure match very well the simulation data, with the KH being slightly more predictive than SMSA. MC results for gas-liquid coexistence curve and critical points are also well reproduced by both the closures. Interestingly, MC simulations also provide predictions for the presence of a liquid-liquid critical point, not observed experimentally so far. These indications are provided by the density-dependence of the pressure, that shows the presence of two minima, and the behavior of the site-site structure factors. Unfortunately, the RISM theory is not able to reproduce this kind of behavior in the context of both KH and SMSA closures; this may be due to the fact that, as demonstrated in earlier works,^{44,45} more refined, thermodynamically consistent closures, such as HMSA, are necessary to ascertain the presence of a liquid-liquid critical point in the framework of integral equation theories. However, HMSA closure is not straightforward to implement in the model at issue, since it requires imposing the thermodynamic consistency between virial equation and compressibility route, a task that, as previously explained, cannot be accomplished within the RISM approach.

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