Riccardo Fantoni and Giorgio Pastore

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Wertheim and Bjerrum-Tani-Henderson theories for associating fluids: A critical assessment

Riccardo Fantoni[1,a)] and Giorgio Pastore[2,b)]

[1]*Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Calle Larga S. Marta DD2137, I-30123 Venezia, Italy*
[2]*Dipartimento di Fisica dell' Università and IOM-CNR, Strada Costiera 11, 34151 Trieste, Italy*

Two theories for associating fluids recently used to study clustering in models for self-assembling patchy particles, Wertheim's and Bjerrum-Tani-Henderson theories, are carefully compared. We show that, for a fluid allowing only for dimerization, Wertheim theory is equivalent to the Bjerrum-Tani-Henderson theory neglecting intercluster correlations. Nonetheless, while the former theory is able to account for percolation and condensation, the latter is not. For the Bjerrum-Tani-Henderson theory we also rigorously prove the uniqueness of the solution for the cluster's concentrations and the reduction of the system of equations to a single one for a single unknown. We carry out Monte Carlo simulations of two simple models of dimerizing fluids and compare quantitatively the predictions of the two theories with the simulation data. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4892878]

I. INTRODUCTION

Recent advances in the experiments and modeling of patchy colloids,[1,2] i.e., colloidal particles whose interaction is dominated by the presence of selective, short range interaction sites on their surface, have renewed interest in theories able to describe liquid and vapour phases of associating fluids.

Fluid phase theories able to cope with the strong attractions of associating fluids have been developed starting from the seventies, when hydrogen bond in molecular liquids was a prototype problem. Two of the approximations developed a few decades ago, namely, the approach developed by Tani and Henderson,[3] extending Bjerrum's theory[4] for electrolytic solutions, and the more ambitious statistical mechanics approach by Wertheim[5] have been recently applied to the study of simple models of patchy colloids.[6–19] The novelty introduced by applications to self-assembling colloids is the huge variety of interactions which can be engineered and consequently the richness of the behaviors as far as the cluster population and its dependence on the thermodynamic state are concerned. Both approaches identify in the fluid and predict populations of suitably defined clusters.

In both theories, a cluster is defined on the basis of bonding in configuration space. For example, if we describe the fluid, as made by particles interacting with a certain pair-potential $\phi(12)$ between particles 1 and 2, we may consider two particles as bonded whenever their pair-potential is less than a given negative value $-\epsilon_{bond}$. Clusters made of one particle are called "monomers," the ones formed by two particles "dimers," the ones formed of three particles "trimers," … and the ones formed by a higher but small number of particles "oligomers." A cluster made of a number i of particles can also be denoted as an i-mer. If we measure the concentrations of the i-mers in an associating fluid we will find that these are functions of the thermodynamic state: The temperature T and the density ρ of the fluid. One can give various definitions of a cluster[20] either of a geometrical nature or of a topological one, depending on the spatial arrangement of the bonded particles. A more physical approach would require to introduce the concept of physical cluster[21,22] but virtually all the existing calculations have been based on clusters defined in configuration space.

In this work we will compare Wertheim's theory[5] and the one of Bjerrum-Tani-Henderson (BTH).[3,4] The former one starts from a thorough theoretical analysis, from which it is possible to derive a thermodynamic perturbation theory. Here, we will only discuss the first order term. At high temperature the associating fluid reduce to the "reference" fluid that can also be considered as the one obtained from the associating fluid sending to zero all attractions. The theory is only applicable when some "steric incompatibility" conditions are fulfilled by the associating fluid. The latter starts already by the description of the associating fluid as a mixture of n_c different species of oligomers where the numbers N_i of i-mers are allowed to vary subject to the constraint of a fixed total number of particles. One only assumes that the canonical partition function as a function of all the N_i, the volume and the temperature be factorisable into the product of n_c intra-cluster partition functions and an inter-cluster partition function. Moreover the clusters are assumed to interact weakly with each other.

We will show that for $n_c = 2$ Wertheim theory coincides with the Bjerrum-Tani-Henderson theory when the clusters are described as an ideal gas. Bjerrum-Tani-Henderson theory, on the other hand, allows to improve on this first level of approximation since one can always build better approximations to describe the inter-cluster partition function.

a)Electronic mail: rfantoni@ts.infn.it
b)Electronic mail: pastore@ts.infn.it

In this work we will only consider the Carnahan-Starling approximation,[23] i.e., we approximate intercluster correlations with effective spherically symmetric ones. On the other hand the simple and elegant theory of Wertheim is able, unlike the Bjerrum-Tani-Henderson theory, to describe fluids with percolating ($n_c \to \infty$) clusters. Due to this fact Wertheim's theory is able to describe in a consistent way the liquid phase while the Bjerrum-Tani-Henderson one is not. So, for n_c finite, Bjerrum-Tani-Henderson theory is expected to be more powerful and flexible than Wertheim theory since it allows to have more accurate results and it is not restricted to systems obeying the steric incompatibility conditions. Instead, Wertheim's theory is the method of choice whenever a consistent picture of the phase diagram is required.

We will then present a comparison and a critical assessment of the two theories by comparison with new Monte Carlo simulation results for two model fluids with $n_c = 2$: a binary mixture and a one-component system, both particularly suitable for comparing theories for association. In particular we will show an, apparently unavoidable, subtle short-come that may appear in the Bjerrum-Tani-Henderson when applied to multicomponent fluid mixtures: At high temperatures, when the fluid is dissociated, in the Bjerrum-Tani-Henderson theory one is left with a one-component mixture of monomers which may differ strongly from the original multicomponent mixture.

The paper is organized as follows: In Sec. II we introduce the thermodynamic quantities we will take in consideration in the following; in Sec. III we describe the two association theories discussing the problem of finite and infinite clusters (Sec. III B 1) and the problem of one attractive site (Sec. III B 2); in Sec. III C we introduce the problem of the gas-liquid coexistence; in Sec. III D we comment on the relevance of the pair-potential microscopic level of description; in Sec. IV we summarize some results obtained applying Wertheim theory to specific fluids with identical sites and sites of two different kinds; in Sec. V we apply the two theories to two simple dimerizing associating fluids (a binary mixture (Sec. V A 1) and a one-component fluid (Sec. V A 2)) and compare them with our Monte Carlo simulation results; in Sec. V B we consider again the problem of infinite clusters for the Bjerrum-Tani-Henderson theory; Sec. VI summarizes the main results and contains a few final remarks.

II. THERMODYNAMICS

Consider a one-component fluid of N associating particles in a volume V at an absolute temperature $T = 1/\beta k_B$ with k_B Boltzmann constant. The inter-particle interaction is assumed to include a hard sphere (HS) part, an isotropic attraction, and localized bonding interaction, in general anisotropic.

The Helmholtz free energy A of a hard-sphere associating fluid can be written as a sum of separate contributions[24]

$$A = A_{HS} + A_{bond}, \tag{2.1}$$

where A_{HS} is the free energy due to the hard-sphere repulsive cores and A_{bond} is the change in the free energy due to the bonding interaction responsible for association. We will gen-

erally use the notation $a(\rho, T) = a = A/N$ for the free energy per particle, where $\rho = N/V$ is the density of the fluid.

The excess hard-sphere free energy per particle can be modeled by the Carnahan and Starling[23]

$$\beta a_{HS}^{ex} = \frac{4\eta - 3\eta^2}{(1-\eta)^2}, \tag{2.2}$$

where $\eta = (\pi/6)\rho\sigma^3$ is the packing fraction of the hard-spheres of diameter σ. So that adding the ideal gas contribution $\beta a_{id} = \ln(\rho\Lambda^3/e)$, with Λ the de Broglie thermal wavelength, we obtain $a_{HS} = a_{id} + a_{HS}^{ex}$.

We can always define a unit of length, $\mathcal{S}$, and a unit of energy, $\mathcal{E}$, so that we can introduce a reduced density, $\rho^* = \rho\mathcal{S}^3$, and a reduced temperature, $T^* = k_B T/\mathcal{E}$.

The association contribution A_{bond} will be discussed in Sec. III.

III. BJERRUM-TANI-HENDERSON VS WERTHEIM

We present now the two association theories of BTH[3] and of Wertheim (W).[5] We derive in each case the bond free energy per particle a_{bond} such that the full free energy per particle of the associating fluid can be written as $a = a_0 + a_{bond}$, where $a_0 = a_{id} + a_0^{ex}$ is the contribution of the reference fluid, the one obtained from the associating fluid setting to zero all the bonding localized attractions.

A. Bjerrum-Tani-Henderson thermodynamic theory

We assume that our fluid is composed of n_c species of clusters. The species i contains N_i clusters each made of i particles. Tani and Henderson[3, 15–19] assumed that the total partition function of the fluid can be written factorizing the n_c intra-cluster partition functions of the single clusters known *a priori* as functions of the temperature T alone. Moreover, assuming that the inter-cluster partition function can be approximated treating the (weakly interacting) clusters as hard-spheres of diameter σ_c, they find the following solution as a result of an extremum procedure,

$$N_1 = N\lambda z_1/\rho G(\eta_c), \tag{3.1}$$

$$N_i = N_1 \lambda^{i-1} z_i/z_1, \quad i = 1, 2, \dots, n_c \tag{3.2}$$

with

$$N = \sum_{i=1}^{n_c} i N_i, \tag{3.3}$$

$$N_c = \sum_{i=1}^{n_c} N_i < N, \tag{3.4}$$

where N is the total number of particles, $\rho = N/V$ is the density of the fluid, N_c the total number of clusters, $\rho_c = N_c/V$ is the density of the clusters, $\eta_c = (\pi/6)\rho_c\sigma_c^3$ is the packing fraction of the clusters of diameter σ_c, $z_i > 0$ the intra-cluster configuration partition function for the species i ($z_1 = 1$ by definition), and $\lambda > 0$ is determined through the constraint of

Eq. (3.3),

$$0 = \sum_{i=1}^{n_c} i\lambda^i z_i - \rho G(\eta_c), \qquad (3.5)$$

$$G(x) = \exp\left[\frac{d(x\beta a_0^{ex}(x))}{dx}\right] = \exp\left[\frac{x(8 - 9x + 3x^2)}{(1-x)^3}\right], \qquad (3.6)$$

where $a_0^{ex}(\eta) = a_{HS}^{ex}$. This equation for the unknown parameter λ always admits a unique solution. In fact, $G(x)$ is a strictly monotonous increasing function of $0 \le x < 1$ with $G(0) = 1$ and $\lim_{x \to 1^-} G(x) = +\infty$. We introduce the concentration of clusters of species i, the i-mers, as $x_i = N_i/N$, and the total concentration of clusters $x_c = N_c/N = \sum_{i=1}^{n_c} x_i = \sum_{i=1}^{n_c} \lambda^i z_i / \sum_{i=1}^{n_c} i\lambda^i z_i$. Then we notice that $\lim_{\lambda \to 0} x_c = 1$, $\lim_{\lambda \to \infty} x_c = 1/n_c < 1$, and x_c is a strictly monotonous decreasing function of λ.[25] So $G(\eta_c)$ is a strictly monotonous decreasing function of λ with $\lim_{\lambda \to 0} G(\eta_c) = G[(\pi/6)\rho\sigma_c^3]$ and $\lim_{\lambda \to \infty} G(\eta_c) = G[(\pi/6n_c)\rho\sigma_c^3]$. We also notice that we must require $(\pi/6)\rho\sigma_c^3 < 1$. Observing next that $\sum_{i=1}^{n_c} i\lambda^i z_i$ is a strictly monotonous increasing function of λ which is zero at $\lambda = 0$, we conclude that Eq. (3.5) must admit always only one solution $\lambda > 0$ such that $\lim_{\rho \to 0} \lambda = 0$ and $\lim_{\rho \to 0} x_1 = 1$.

The total partition function Q_{tot} of the fluid is given then by

$$\ln Q_{tot} = \sum_i [N_i \ln z_i - (N_i \ln N_i - N_i)] + \ln Z_c$$
$$= N_c - N_c \ln N_1 - (N - N_c)\ln\lambda + \ln Z_c, \quad (3.7)$$

where Z_c is the inter-cluster configurational partition function and $\beta A_c^{ex} = -\ln(Z_c/V^{N_c})$ is the inter-cluster excess free energy.

Introducing the concentration of monomers $x_1 = N_1/N$ and the concentration of clusters $x_1 < x_c = N_c/N < 1$ (note that $1/x_c$ can be considered as a measure of the average cluster size), we can rewrite

$$\beta a_{bond}^{BTH} = \beta[a - (a^{id} + a_0^{ex})]$$
$$= x_c \ln x_1 + (1 - x_c)\ln(\lambda e/\rho)$$
$$+ \beta(a_c^{ex} - a_0^{ex}) + constants, \qquad (3.8)$$

where $\beta a = -(\ln Q_{tot})/N$ is the associating fluid total free energy per particle and $a_0^{ex} + a^{id}$ is the reference system total free energy per particle. Note that, in the absence of attractions and therefore in the presence of monomers only $x_1 = x_c = 1$, in order to have $a_{bond}^{BTH} = 0$ we must have $a_0^{ex} = \lim_{x_c \to 1} a_c^{ex}$. Only for $\sigma_c = \sigma$ this condition is satisfied by the Carnahan-Starling reference system, a_{HS}^{ex} of Eq. (2.2). In the most general case we may think at σ_c as a function of the thermodynamic state of the associating fluid. In the present work we will always restrict to the case of a constant σ_c.

At high temperatures all $z_i \to 0$ for $i > 1$ and $x_1 \to x_c \to 1$ or $\lambda \to \rho G[(\pi/6)\rho\sigma_c^3]/z_1$, which means we have complete dissociation. At low temperatures all $z_i \to \infty$ for $i > 1$ and $x_1 \to 0$ or $\lambda \to 0$, which means that we have association.

B. Wertheim thermodynamic theory

In Wertheim theory[5] one assumes that each hard-sphere of the one-component fluid (the case of a mixture will be considered in detail in Sec. V A) is decorated with a set Γ of M attractive sites. Under the assumptions of (i) a single bond per site, (ii) no more than one bond between any two particles, and (iii) no closed loop of bonds, one can write in a first order thermodynamic perturbation theory framework, valid at reasonably high temperatures,

$$\beta a_{bond}^W = \sum_{\alpha \in \Gamma}\left(\ln x_\alpha - \frac{x_\alpha}{2}\right) + \frac{M}{2}, \qquad (3.9)$$

where $x_\alpha = N_\alpha/N$ is the fraction of sites α that are not bonded (not to be confused with x_i the concentration of clusters made of a number i of particles. We will always use a Greek index to denote a specific site) and can be solved by the "law of mass action,"

$$x_\alpha = \frac{1}{1 + \rho\sum_{\beta \in \Gamma} x_\beta \Delta_{\alpha\beta}}, \quad \alpha \in \Gamma, \qquad (3.10)$$

where the probability to form a bond, once the available sites of the two particles are chosen, is given by $\rho\Delta_{\alpha\beta} = \rho\Delta_{\beta\alpha}$ and approximated as

$$\Delta_{\alpha\beta} = \int_{v_{\alpha\beta}} g_0(r_{12})\langle f_{\alpha\beta}(12)\rangle_{\Omega_1,\Omega_2} d\mathbf{r}_{12}. \qquad (3.11)$$

Here the integral is over the volume $v_{\alpha\beta}$ of the bond $\alpha\beta$, g_0 is the radial distribution function of the reference system, $f_{\alpha\beta}$ is the Mayer function between site α on particle 1 and site β on particle 2 (see Sec. III D), and $\langle\ldots\rangle_{\Omega_1,\Omega_2}$ denotes an angular average over all orientations of particles 1 and 2 at a fixed relative distance r_{12}. Equation (3.10) should be solved for the real physically relevant solution such that $\lim_{\rho \to 0} x_\alpha = 1$.

At high temperatures $\Delta_{\alpha\beta} \to 0$ and $x_\alpha \to 1$, which means we have complete dissociation. At low temperatures (Wertheim theory is a high temperature expansion but here we just mean the formal low T limit of the first order Wertheim results) $\Delta_{\alpha\beta} \to \infty$ and $x_\alpha \to 0$, which means that we have complete association.

The number of attractive sites controls the physical behavior. Models with one site allow only dimerization. The presence of two sites permits the formation of chain and ring polymers. Additional sites allow formation of branched polymers and amorphous systems.

1. Finite vs infinite clusters

Wertheim theory, unlike BTH one, allows for the existence of infinite clusters in the fluid: The percolation phenomenon. In particular, in Wertheim theory one can define[10] $P_s = \sum_i i x_i$ as the probability to have a particle in a finite cluster (in BTH theory $P_s = 1$ by construction). One can then define the mean cluster size, or number averaged size of the finite clusters, $N_n = \sum_i i x_i / \sum_i x_i$, the mean size of a cluster to which a randomly chosen particle belongs, or weight averaged cluster size, $N_w = \sum_i i^2 x_i / \sum_i i x_i$, or higher moments of the cluster size distribution x_i.

The interplay between condensation and clustering in associating fluids has been the subject of many studies.[10] In particular, Coniglio *et al.*[22] proposed a general theory of the equilibrium distribution of clusters, establishing a relation between percolation and condensation. Percolation is generally believed to be a prerequisite for condensation. As a matter of fact in Sec. V B we will show explicitly that BTH theory is unable to account for condensation.

2. One attractive site

The simplest case we can consider in Wertheim theory is the one with a single site α, $M = 1$. In this case only monomers and dimers can ever form. Solving the law of mass action for $x = x_\alpha$, the fraction of non-bonded sites α which coincides with the concentration of monomers x_1, we find

$$x = \frac{2}{1 + \sqrt{1 + 4\rho\Delta}}, \qquad (3.12)$$

with $\Delta = \Delta_{AA}$, which has the correct low density limit $\lim_{\rho \to 0} x = 1$.

Analogously we can solve this simple case in BTH theory allowing only for monomers and dimers, $n_c = 2$, and choosing the ideal gas approximation for the inter-cluster configurational partition function, $G = 1$ (the $\sigma_c \to 0$ limit of Eq. (3.6)). Then we should solve for $\lambda > 0$ in the following quadratic equation:

$$x_1 = \lambda z_1/\rho, \qquad (3.13)$$

$$x_2 = \lambda^2 z_2/\rho, \qquad (3.14)$$

$$1 = x_1 + 2x_2. \qquad (3.15)$$

The solution for the monomers concentration is

$$x_1 = \frac{2}{1 + \sqrt{1 + 8\rho z_2/z_1^2}}. \qquad (3.16)$$

We then see that we have agreement between the two theories if we choose

$$\Delta = 2z_2/z_1^2 = 2z_2. \qquad (3.17)$$

Already for this simple case we see that the bond contribution to the free energy predicted by the two theories, Eqs. (3.9) and (3.8), coincide. In fact, from BTH theory of Eq. (3.8), since the excess free energy of the reference system and the inter-cluster excess free energy are both zero, we find, up to an additive constant,

$$
\begin{aligned}
\beta a_{bond}^{BTH} &= x_c \ln x_1 + (1 - x_c) \ln(\lambda e/\rho) \\
&= \ln x_1 + (1 - x_c) \\
&= \ln x_1 - x_1/2 + 1/2 = \beta a_{bond}^W, \qquad (3.18)
\end{aligned}
$$

where the second equality follows from Eq. (3.13), the third one from observing that $x_2 = (1 - x_1)/2$, and the last one from Eq. (3.9).

BTH theory, on the other hand, allows to be more accurate and to treat the fluid of clusters instead of just as an ideal

gas as a fluid of hard-spheres of diameter σ_c. In this case one should solve numerically Eqs. (3.1), (3.2), and (3.5) with G given by Eq. (3.6). And the inter-cluster excess free energy will be given by

$$\beta a_c^{ex} = \frac{4\eta_c - 3\eta_c^2}{(1 - \eta_c)^2}, \qquad (3.19)$$

whereas the excess free energy per particle of the reference system will be the usual Carnahan-Starling one of Eq. (2.2).[26]

Taking $a = a_{HS} + a_{bond}$ and choosing $z_2 = \Delta/2$ we compared the behavior of the two theories. Following Ref. 7 and approximating the radial distribution function of the reference system, in Eq. (3.31) which appears next in the text, with its zero density limit, we choose $\Delta = K^0[\exp(\beta\epsilon) - 1]$ with $K^0 = \pi d^4(15\sigma + 4d)/30\sigma^2 \approx 0.332 \times 10^{-3}\sigma^3$. This choice is dictated by the fact that Wertheim theory gives only a semi-quantitative agreement with simulation data and we did not find any substantial improvement, at least in the density ranges we considered, by choosing a better refined low density approximation, as is done in other works.[7,12] In Fig. 1 we show the comparison of the behavior of the pressure (from Eq. (3.20) which appears next in the text) and dimers concentration as functions of density calculated analytically in Wertheim theory and numerically in BTH theory with $\sigma_c = \sigma$, on several isotherms. As expected even at very small
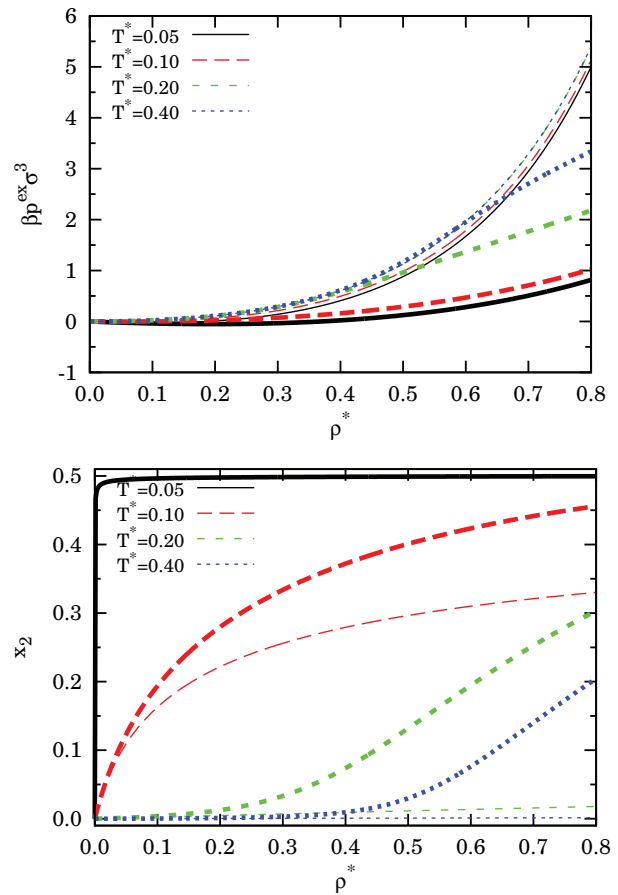

FIG. 1. Comparison of the behavior of the excess pressure, $\beta p^{ex} = \beta p - \rho$ (top panel) and dimers concentration (bottom panel) as functions of density for the BTH theory (thick lines), for $\sigma_c = \sigma$, and the W theory (thin lines), on several isotherms.

temperatures there is no sign of a gas-liquid coexistence, the pressure being a monotonously increasing function of density. We have just shown that at low density the two theories must coincide since $\lim_{\rho \to 0} G = 1$, but from the figure we see that the interval of densities over which the two theories agree increases of width as T increases. The figure shows how at high temperatures the two theories tend to become coincident but at low temperatures they differ strongly. This raises the question of which one of the two theories is a better approximation when compared to the exact Monte Carlo results. We will delay the answer to this legitimate question until Sec. V A 2. BTH theory naturally demands an approximation for the intra-cluster partition functions. In this work, unlike previous ones,[3,15–19] we will always use the relation (3.17) when comparing the two theories.

Nonetheless we expect Wertheim theory to become more simple and elegant than BTH theory for $M > 1$. As a matter of fact we expect in these cases the presence in the fluid of i-mers of any size i. So that using BTH theory we will necessarily introduce the additional approximation of the maximum number of cluster species $i \leq n_c$, an artificial cutoff not needed in Wertheim theory.

C. The gas-liquid coexistence

In order to determine the gas-liquid coexistence line (the binodal) one needs to find the compressibility factor $z = \beta p/\rho$, with p the pressure, and the chemical potential μ of the associating fluid according to the thermodynamic relations

$$z(\rho, T) = \rho \left(\frac{\partial \beta a}{\partial \rho} \right)_{T,N}, \tag{3.20}$$

$$\beta\mu(\rho, T) = \left(\frac{\partial \beta a \rho}{\partial \rho} \right)_{T,V} = z + \beta a. \tag{3.21}$$

The coexistence line is then given by the Gibbs equilibrium condition of equality of the pressures and chemical potentials of the two phases

$$\rho_g z(\rho_g, T) = \rho_l z(\rho_l, T), \tag{3.22}$$

$$\beta\mu(\rho_g, T) = \beta\mu(\rho_l, T), \tag{3.23}$$

from which one can find the coexistence density of the gas $\rho_g(T)$ and of the liquid $\rho_l(T)$ phases.

The critical point (ρ_c, T_c) is determined by solving the following system of equations:

$$\left. \frac{\partial z\rho}{\partial \rho} \right|_{\rho_c, T_c} = 0, \tag{3.24}$$

$$\left. \frac{\partial^2 z\rho}{\partial \rho^2} \right|_{\rho_c, T_c} = 0. \tag{3.25}$$

D. Microscopic description: Importance of the pair potential

The fluid is assumed to be made of particles interacting only through a pair-potential $\phi(12) = \phi(\mathbf{r}_1, \Omega_1, \mathbf{r}_2, \Omega_2)$,

where $\mathbf{r}_i$ and Ω_i are the position vector of the center of particle i and the orientation of particle i, respectively.

To give structure to the fluid we further assume that the particles have an isotropic hard-core of diameter σ with

$$\phi(12) = \phi_{HS}(r_{12}) + \Phi(12), \tag{3.26}$$

where $r_{12} = |\mathbf{r}_{12}| = |\mathbf{r}_2 - \mathbf{r}_1|$ is the separation between the two particles 1 and 2 and

$$\phi_{HS}(r) = \begin{cases} +\infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}. \tag{3.27}$$

The anisotropic part $\Phi(12)$ in Wertheim theory is generally chosen as

$$\Phi(12) = \sum_{\alpha \in \Gamma} \sum_{\beta \in \Gamma} \psi_{\alpha\beta}(r_{\alpha\beta}), \tag{3.28}$$

where

$$\mathbf{r}_{\alpha\beta} = \mathbf{r}_2 + \mathbf{d}_\beta(\Omega_2) - \mathbf{r}_1 - \mathbf{d}_\alpha(\Omega_1) \tag{3.29}$$

is the vector connecting site α on particle 1 with site β on particle 2. Here $\mathbf{d}_\alpha$ is the vector from the particle center to site α with $d_\alpha < \sigma/2$. The site-site interactions $\psi_{\alpha\beta} \leq 0$ are assumed to be purely attractive. The Mayer functions introduced in Sec. III B are then defined as $f_{\alpha\beta}(12) = \exp\left[-\beta\psi_{\alpha\beta}(r_{\alpha\beta})\right] - 1$.

Wertheim theory depends on the specific form of the site-site potential only through the quantity $\Delta_{\alpha,\beta}$ of Eq. (3.11), as long as the three conditions of a single bond per site, no more than one bond between any two particles, and no closed loop of bonds, are satisfied. A common choice, for example, is a square-well form

$$\psi_{\alpha\beta}(r) = \begin{cases} -\epsilon_{\alpha\beta} & r \leq d_{\alpha\beta} \\ 0 & r > d_{\alpha\beta} \end{cases}, \tag{3.30}$$

where $\epsilon_{\alpha\beta} > 0$ are site-site energy scales, the wells depths, and $d_{\alpha\beta}$ are the wells widths. In this case we must have $d_\alpha + d_\beta > \sigma - d_{\alpha\beta}$ moreover we will have

$$\Delta_{\alpha\beta} = K_{\alpha\beta}(\sigma, d_{\alpha\beta}, \eta)(e^{\beta\epsilon_{\alpha\beta}} - 1). \tag{3.31}$$

We will also call $\lim_{\rho \to 0} K_{\alpha\beta} = K^0_{\alpha\beta}$ some purely geometric factors. Remember that $\lim_{\rho \to 0} g_0(r) = \Theta(r - \sigma)$ with Θ the Heaviside step function. Another common choice is the Kern-Frenkel patch-patch pair-potential model.[27]

In BTH theory on the other hand, we are allowed to relax these conditions and the choice of the pair-potential is more flexible as long as it includes some attractive component responsible for the association.

IV. SOME RESULTS FROM WERTHEIM THEORY

Wertheim theory of associating fluids has been recently tested extensively by Sciortino and co-workers. In a series of papers, they have studied fluids of hard-spheres with identical sites allowing for "chaining"[6–9] and with sites of two different kinds allowing for "branching"[10–12] and for

"rings" formation.[13,14] They showed how the parameter-free Wertheim theory is flexible enough to accommodate a vast number of different microscopic pair-potentials descriptions and nonetheless pointed out some relevant classes of microscopic features giving rise to specific macroscopic behaviors at the level of the clustering, the percolation threshold, and the gas-liquid coexistence.

In all these cases $n_c \to \infty$ so they cannot be treated with the BTH theory which as we will see in Sec. V B is unable to account for the gas-liquid coexistence. Thus, in order to compare the two theories we have to choose different systems.

V. COMPARISON BETWEEN WERTHEIM THEORY AND BJERRUM-TANI-HENDERSON THEORY

In order to test the accuracy of the Wertheim and BTH theories we carried out some Monte Carlo (MC) simulations on simple models of associating fluids.

A. One attractive site, $n_c = 2$

We limit ourselves to the case $n_c = 2$ and we consider two different realizations of this scenario: A binary mixture and a one-component fluid.

1. A binary mixture

To test the single site case we considered a symmetric binary mixture of particles with the following pair-potential between a particle of species $\bar{\alpha}$ (in this section a Greek index with an over-bar labels the particle species) and one of species $\bar{\beta}$ a center-to-center distance r apart

$$\phi_{\bar{\alpha}\bar{\beta}}(r) = \begin{cases} +\infty & r \leq \sigma_{\bar{\alpha}\bar{\beta}} \\ -(1 - \delta_{\bar{\alpha}\bar{\beta}})\epsilon & \sigma_{\bar{\alpha}\bar{\beta}} < r \leq \sigma_{\bar{\alpha}\bar{\beta}} + \mathcal{W} \\ 0 & r > \sigma_{\bar{\alpha}\bar{\beta}} + \mathcal{W} \end{cases} , \quad (5.1)$$

where $\sigma_{\bar{\alpha}\bar{\beta}} = (1/2)(\sigma_{\bar{\alpha}} + \sigma_{\bar{\beta}})(1 + \mathcal{D}_{\bar{\alpha}\bar{\beta}})$ with $\sigma_{\bar{\alpha}} = \sigma$ and $\mathcal{D}_{\bar{\alpha}\bar{\beta}} = -(1 - \delta_{\bar{\alpha}\bar{\beta}})$ with $\bar{\alpha}$ and $\bar{\beta}$ equal to 1, 2 and δ the Kronecker delta. So that $\sigma_{\bar{\alpha}\bar{\beta}} = \sigma \delta_{\bar{\alpha}\bar{\beta}}$. $\epsilon > 0$ and $\mathcal{W} > 0$ are, respectively, the square well depth and width for the attraction of unlike particles. Also we choose the symmetric case where the concentrations of particles of species $\bar{\alpha}$, $\mathcal{X}_{\bar{\alpha}} = 1/2$ for $\bar{\alpha} = 1, 2$. In this case the ideal part of the free energy will be given by $\beta a_{id} = \ln(\rho \Lambda^3/e) + \mathcal{X}_1 \ln \mathcal{X}_1 + \mathcal{X}_2 \ln \mathcal{X}_2$, where the entropy of mixing, the last two terms, is just an additive constant.

It is then clear that, for $\mathcal{W} < \sigma/2$, this model fluid allows for dimerization only, just as the $M = 1$ case of Wertheim. In fact, whenever two unlike particles bind, a third particle can never bind to the formed dimer because of the hard-core repulsion between like particles. Moreover by choosing $\mathcal{W}$ small at will we may reach the ideal condition of $\sigma_c = \sigma$ with σ_c the diameter of the dimers in the BTH theory. The reference fluid, the one with $\epsilon = 0$, is a symmetric non-additive-hard-sphere (NAHS) mixture with non-additivity $\mathcal{D}_{12} = -1$.

We will then take

$$\beta a_0^{ex} = \frac{2\eta - (3/4)\eta^2}{[1 - (1/2)\eta]^2}. \quad (5.2)$$

Wertheim theory has been extended to multicomponent mixtures by Chapman *et al.*[28] For a mixture with a number n_s of species and $N_{\bar{\alpha}} = N\mathcal{X}_{\bar{\alpha}}$ particles of species $\bar{\alpha} = 1, 2, \ldots, n_s$, we have

$$\beta a_{bond}^W = \sum_{\bar{\alpha}=1}^{n_s} \mathcal{X}_{\bar{\alpha}}[\ln x_{\bar{\alpha}} - x_{\bar{\alpha}}/2 + 1/2], \quad (5.3)$$

where $x_{\bar{\alpha}} = N_1^{\bar{\alpha}}/N_{\bar{\alpha}}$ is the monomer fraction of species $\bar{\alpha}$, with $N_1^{\bar{\alpha}}$ the number of monomers of species $\bar{\alpha}$, and is determined by the following law of mass action,

$$x_{\bar{\alpha}} = \frac{1}{1 + \rho \sum_{\bar{\beta}=1}^{n_s} \mathcal{X}_{\bar{\beta}} x_{\bar{\beta}} \Delta_{\bar{\alpha}\bar{\beta}}}, \quad (5.4)$$

where

$$\Delta_{\bar{\alpha}\bar{\beta}} = \Delta_{\bar{\beta}\bar{\alpha}} = \int_{v_{\bar{\alpha}\bar{\beta}}} g_{\bar{\alpha}\bar{\beta}}^0(r_{12}) \langle f_{\bar{\alpha}\bar{\beta}}(12) \rangle_{\Omega_1, \Omega_2} d\mathbf{r}_{12}, \quad (5.5)$$

with $g_{\bar{\alpha}\bar{\beta}}^0$ the partial radial distribution of the reference fluid and $f_{\bar{\alpha}\bar{\beta}}(12) = e^{-\beta[\phi_{\bar{\alpha}\bar{\beta}}(r_{12}) - \phi_{\bar{\alpha}\bar{\beta}}^0(r_{12})]} - 1$ the Mayer function between particle 1 of species $\bar{\alpha}$ and particle 2 of species $\bar{\beta}$, with $\phi_{\bar{\alpha}\bar{\beta}}^0$ the pair-potential of the reference fluid.

In our symmetric binary case $x_{\bar{\alpha}=1} = x_{\bar{\alpha}=2} = x$ and $\Delta = \Delta_{12} = K_{12}(e^{\beta\epsilon} - 1)$ (with $\Delta_{\bar{\alpha}\bar{\alpha}} = 0$ for $\bar{\alpha} = 1, 2$), where, since the unlike radial distribution function of the reference system is the one of the ideal gas, equal to one everywhere, we have exactly $K_{12} = (4/3)\pi \mathcal{W}^3$. The solution of Eq. (5.4) is

$$x = \frac{2}{1 + \sqrt{1 + 2\rho\Delta}}. \quad (5.6)$$

Here we will choose $\mathcal{W} = 0.1\sigma$.

On the other hand BTH theory continues to hold just as in its one component fluid formulation given in Sec. III A. We expect the cluster diameter to vary within the interval $\sigma \leq \sigma_c \leq \sigma + \mathcal{W}$ even if for the comparison with the simulation data we will need to consider $\sigma_c < \sigma$. We will now choose $z_2 = \Delta/4$.

At high temperatures $z_2 = \Delta/4 \to 0$ and $x_1 \to 1$, $x_c \to 1$ so $\beta a^W = \beta a_{id} + [2\eta - (3/4)\eta^2]/[1 - (1/2)\eta]^2$, whereas $\beta a^{BTH} = \beta a_{id} + [4\eta_c - 3\eta_c^2]/[1 - \eta_c]^2$. Then for $\sigma_c \neq \sigma/2^{1/3}$ the parameter free Wertheim theory is certainly a better approximation than BTH. At low temperatures $z_2 = \Delta/4 \to \infty$ and $x_1 \to 0$, $x_c \to 1/2$, and the two theories become equivalent for $\sigma_c = \sigma$ (see the Appendix). Within BTH one is free to choose σ_c in such way to get more accurate results.

The opposite behavior was observed for the one-component case of Sec. III B 2 where the two theories, for $\sigma_c = \sigma$, become equivalent at high temperature and at low temperature they differ and BTH is expected to become better than W.

We carried out MC simulations of this mixture in the canonical ensemble using a total number $N = 500$ of particles. In the simulation we measure the pressure from the virial

theorem as[29]

$$z^{MC} = 1 + \frac{1}{3}\pi\rho\left[\sigma^3 g_{11}(\sigma^+) - (e^{\beta\epsilon} - 1)\mathcal{W}^3 g_{12}(\mathcal{W}^+)\right], \quad (5.7)$$

where $g_{\bar{\alpha}\bar{\beta}}$ are the partial radial distribution functions. In the simulation we define a dimer as any two particles for which the pair-potential equals $-\epsilon$. So, we measure the dimers concentration $x_2^{MC} = -u^{ex}/\epsilon$, where u^{ex} is the excess internal energy per particle of the fluid. As usual we choose σ as the unit of length and ϵ as the unit of energy. At the lowest temperature studied, $T^* = 0.1$, the probability of breaking a bond is of the order of $\exp(1/0.1)$, thus requiring 2×10^4 MC attempts to break such a bond. Our simulations were of the order of 4×10^5 MC steps long, with a MC step made by N single particle moves.

We compare the simulation data with the dimers concentrations, x_2^W and x_2^{BTH}, and pressures, ρz^W and ρz^{BTH}, predicted by Wertheim and BTH theories, where

$$z^W = 1 + \rho\frac{\partial\beta\left(a_0^{ex} + a_{bond}^W\right)}{\partial\rho}, \quad (5.8)$$

$$z^{BTH} = 1 + \rho\frac{\partial\beta\left(a_0^{ex} + a_{bond}^{BTH}\right)}{\partial\rho}, \quad (5.9)$$

with a_0^{ex} given by Eq. (5.2), a_{bond}^W given by Eq. (5.3), and a_{bond}^{BTH} given by Eq. (3.8) with $n_c = 2$ and $z_2 = \Delta/4$.

In Fig. 2 we compare the equation of state and the dimers concentration as a function of density predicted by Wertheim and BTH theories with the MC results at a low reduced temperature $T^* = 0.1$. We see that by choosing the cluster diameter opportunely, $\sigma_c < \sigma$, one can get the BTH results for the pressure to overlap with MC data over a wide range of densities. Fig. 3 shows the same comparison at the high temperature $T^* = 0.4$ for the optimal $\sigma_c = \sigma/2^{1/3}$. From the figures we conclude that BTH theory, with the optimal σ_c for the equation of state, improves at low temperatures, where it becomes more accurate than Wertheim theory, but fails a correct descriptions of the clusters concentration at high temperatures and high densities. By appropriately tuning the cluster diameter σ_c it is possible to get better agreement for the dimer concentration but then the theory would fail to reproduce the pressure correctly. So it is never possible to get good agreement for both the pressure and the dimer concentration.

In Fig. 4 we compare the pressure and the dimers concentration as functions of temperature predicted by the two theories, when $\sigma_c = \sigma/2^{1/3}$ in BTH, with the MC results at a low reduced density $\rho^* = 0.6$. The figure shows how in this case the Wertheim theory is better than BTH.

2. A one-component fluid

As a one-component fluid we chose the single patch Kern-Frenkel model[15,27] where the particles interact with the following pair-potential

$$\phi(r_{12}) = \phi_{HS}(r_{12}) + \phi_{SW}(r_{12})\gamma(\hat{\mathbf{n}}_1, \hat{\mathbf{n}}_2, \hat{\mathbf{r}}_{12}), \quad (5.10)$$
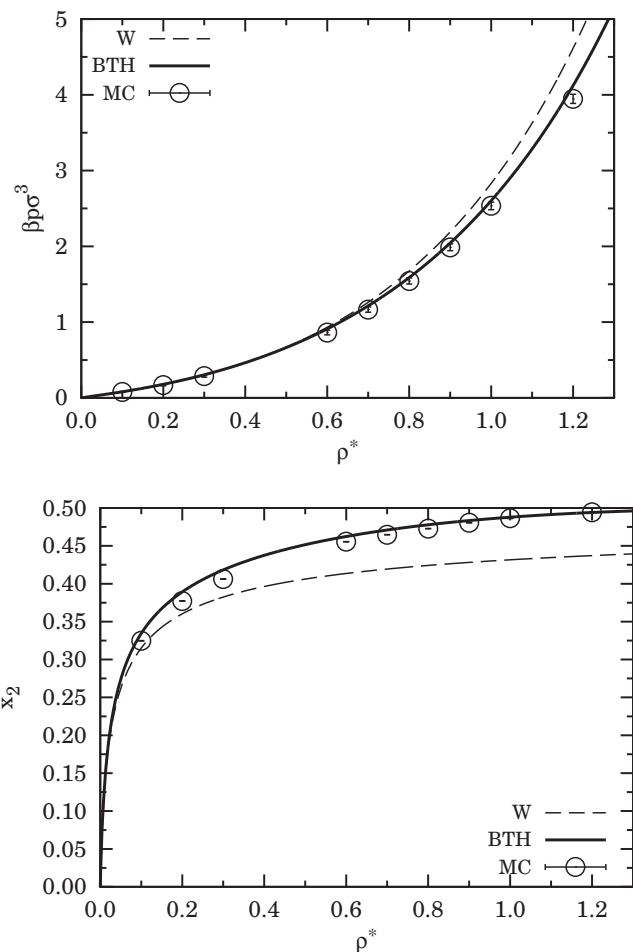

FIG. 2. Pressure (top panel) and dimers concentration (bottom panel) as a function of density on the $T^* = 0.1$ isotherm for $\mathcal{W} = 0.1\sigma$. The broken line is the prediction of W theory, the continuous line the one of BTH theory with $\sigma_c = 0.98\sigma$, and the points are the exact MC data.

where

$$\phi_{SW}(r) = \begin{cases} -\epsilon & \sigma < r \leq \sigma + \mathcal{W} \\ 0 & \text{else} \end{cases}, \quad (5.11)$$

and

$$\gamma(\hat{\mathbf{n}}_1, \hat{\mathbf{n}}_2, \hat{\mathbf{r}}_{12})$$
$$= \begin{cases} 1 & \hat{\mathbf{n}}_1 \cdot \hat{\mathbf{r}}_{12} \geq \cos\theta_0 \quad \text{and} \quad -\hat{\mathbf{n}}_2 \cdot \hat{\mathbf{r}}_{12} \geq \cos\theta_0 \\ 0 & \text{else} \end{cases}, \quad (5.12)$$

here $\hat{\mathbf{n}}_i$ is a unit vector pointing from the center of particle i towards the center of her attractive patch and θ_0 is the angular semi-amplitude of the patch. The fraction of the particle surface covered by the attractive patch will then be $\chi = \sqrt{\langle\gamma\rangle_{\Omega_1,\Omega_2}} = \sin^2(\theta_0/2)$.

In order to have $n_c = 2$ we must choose $\theta_0 < \pi/6$ or $\chi < (\sqrt{3}-1)^2/8 \approx 0.0670$ in the sticky limit $\mathcal{W} \to 0$ and

$$\cos 2\theta_0 > \frac{1}{2} + \frac{1}{2\sigma(\sigma + \mathcal{W})}$$
$$\times \sqrt{6\sigma^3\mathcal{W} - \sigma^2\mathcal{W}^2 - 4\sigma\mathcal{W}^3 - \mathcal{W}^4}, \quad (5.13)$$
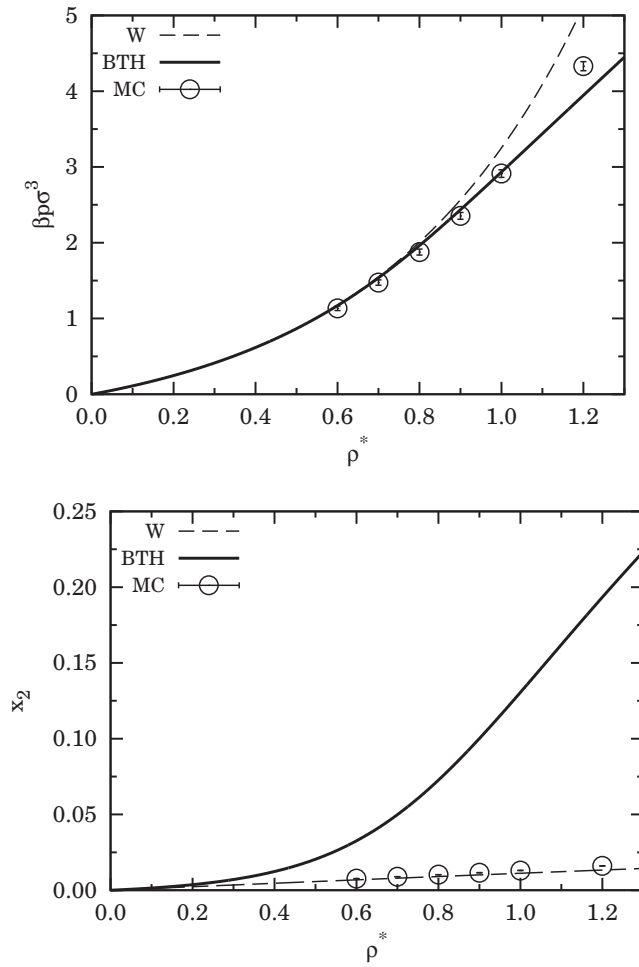
FIG. 3. Pressure (top panel) and dimers concentration (bottom panel) as a function of density on the $T^* = 0.4$ isotherm for $\mathcal{W} = 0.1\sigma$. The broken line is the prediction of W theory, the continuous line the one of BTH theory with $\sigma_c = \sigma/2^{1/3}$, and the points are the exact MC data.
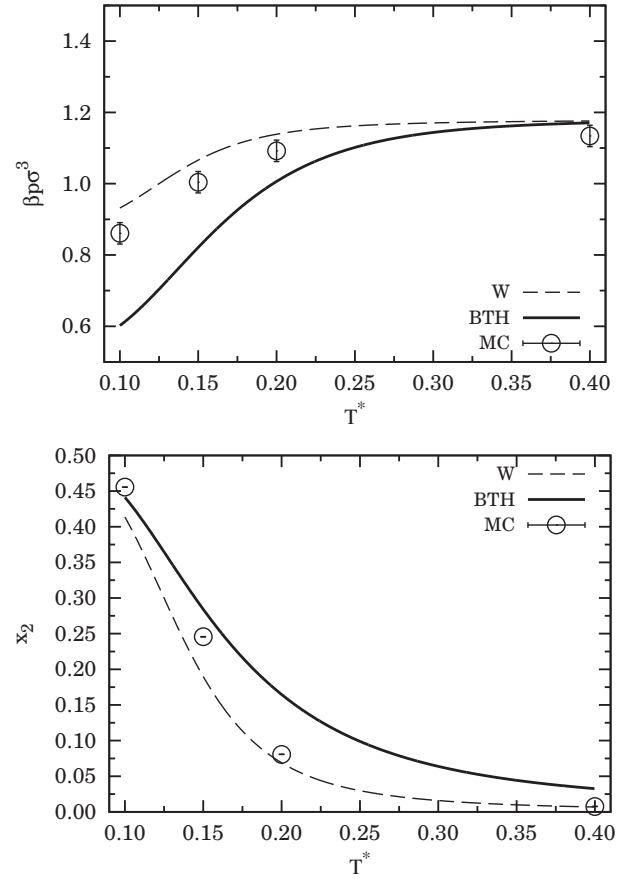

FIG. 4. Pressure (top panel) and dimers concentration (bottom panel) as a function of temperature on the $\rho^* = 0.6$ isochore for $\mathcal{W} = 0.1\sigma$. The broken line is the prediction of W theory, the continuous line the one of BTH theory with $\sigma_c = \sigma/2^{1/3}$, and the points are the exact MC data.

more generally, for small $\mathcal{W}$. As before we choose $\mathcal{W} = 0.1\sigma$ and in order to fulfill the single bond per patch condition (5.13) we take $\theta_0 = \pi/12$ or $\chi = 0.0170$. This choice corresponds to a patch-patch bonding volume $v_{pp} = (\pi/3)[(\sigma + \mathcal{W})^3 - \sigma^3](1 - \cos\theta_0)^2 \approx 0.402 \times 10^{-3}\sigma^3$. We then choose for Δ its zero density limit approximation $\Delta = v_{pp}(e^{\beta\epsilon} - 1)$.

We carried out MC simulations of this one-component fluid in the canonical ensemble using a number $N = 500$ of particles. The pressure is calculated during the simulation from the virial theorem as follows,[27]

$$z^{MC} = 1 + \frac{2\pi}{3}\rho\sigma^3[g(\sigma^+) - (1 + \mathcal{W}/\sigma)^3\{g_{pp}[(\sigma + \mathcal{W})^-]$$
$$- g_{pp}[(\sigma + \mathcal{W})^+]\}], \tag{5.14}$$

where $g_{pp}(r)$ is the radial patch-patch distribution function: The partial radial distribution function which considers only particles with facing patches. Again, we measure the dimers concentration as $x_2^{MC} = -u^{ex}/\epsilon$. As usual we choose σ as the unit of length and ϵ as the unit of energy. A MC move here consisted of both a random displacement of the center of the particle and a random rotation of the particle (according to the Marsaglia algorithm[30]).

In Figs. 5 and 6 we compare the simulation data on two different isotherms, at low temperature $T^* = 0.1$ and high temperature $T^* = 0.4$, with the dimers concentrations, x_2^W and x_2^{BTH}, and pressures, ρz^W and ρz^{BTH}, predicted by Wertheim and BTH theories as shown in Sec. III B 2. From the comparison emerges that at low temperatures one can adjust σ_c in the BTH theory to obtain good agreement either with the pressure or with the dimers concentration data, but not with both simultaneously. In the high temperature limit the two theories coincide for $\sigma_c = \sigma$, but again BTH fails at high densities at large but finite temperature.

For this system we also tried to use in the BTH theory an intercluster partition function derived from the Freasier et al.[31] equation of state for dumbbells with a center-to-center distance equal to σ. But we soon discovered that such an equation of state is very similar to a Carnahan-Starling with a $\sigma_c \approx 2.5\sigma$. This implied that we could study only a density range $\rho^* < 6\sigma^3/(\pi\sigma_c^3) \approx 0.1222$. At such low densities the fluid tends to dissociate into monomers and as a consequence such refined BTH becomes worst than the usual BTH with a Carnahan-Starling intercluster partition function with σ_c close to σ.
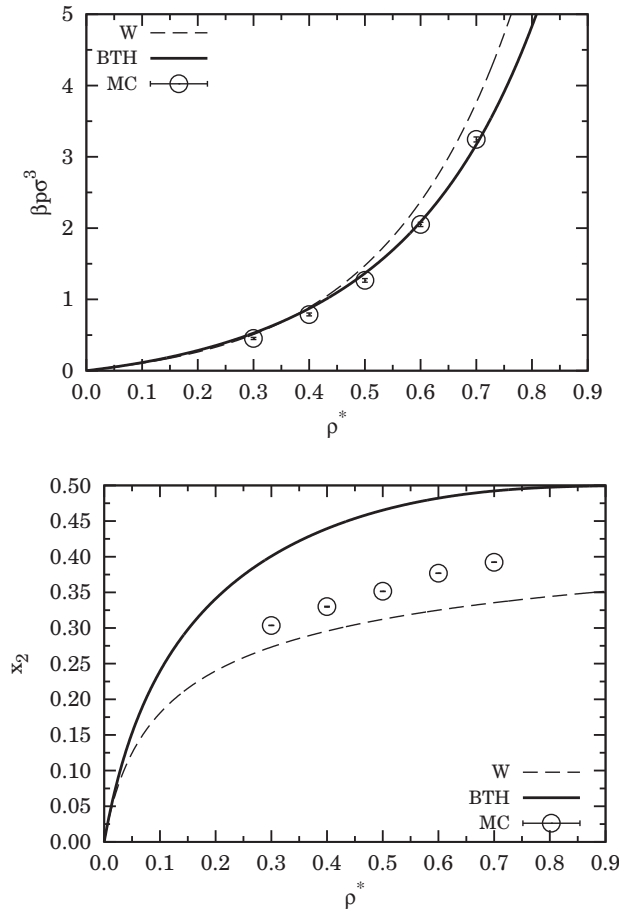
FIG. 5. Pressure (top panel) and dimers concentration (bottom panel) as a function of density on the $T^* = 0.1$ isotherm for $\mathcal{W} = 0.1\sigma$ and $\theta_0 = \pi/12$. The broken line is the prediction of W theory, the continuous line the one of BTH theory with $\sigma_c = 1.23\sigma$, and the points are the exact MC data.
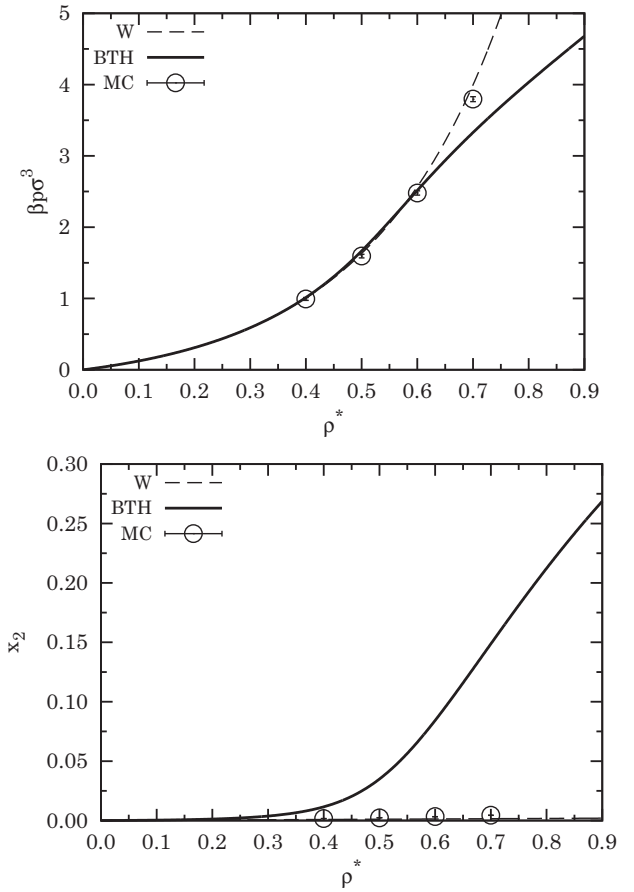

FIG. 6. Pressure (top panel) and dimers concentration (bottom panel) as a function of density on the $T^* = 0.4$ isotherm for $\mathcal{W} = 0.1\sigma$ and $\theta_0 = \pi/12$. The broken line is the prediction of W theory, the continuous line the one of BTH theory with $\sigma_c = \sigma$, and the points are the exact MC data.

B. Number of cluster species $n_c > 2$

We have seen in various ways that as long as $n_c \leq 2$ we expect, either from the Wertheim theory or from the BTH theory, the absence of the liquid phase. So now we want to understand if there exists a critical n_c, $\bar{n}_c$, such that for $n_c > \bar{n}_c$ we may have the appearance of the liquid in the associating fluid.

According to Wertheim:[5] "*As long as [n_c] is finite, or at least a reasonably small number, we would expect increasing association with decreasing T, but no gas-liquid transition. On this basis one may conjecture that the gas-liquid transition is related to the catastrophic increase with s of allowed s-mer[s] [...] when no cutoff [...] is provided.*"

Wertheim also suggests that, releasing the single bond per site condition, a pair-potential of the form given by Eqs. (3.26)–(3.30) allows to have fluids with $n_c > 2$ finite. If Wertheim is correct we would be unable to predict the liquid phase within the BTH theory.

In order to understand better this point we looked if it is possible to have the appearance of a van der Waals loop in $\beta p^{BTH} = \rho z^{BTH} = \rho^2 \partial \beta a^{BTH}/\partial \rho$ for $n_c > 2$. We looked then at the low temperature $T \to 0$ and large number of cluster species $n_c \to \infty$ limit. We choose the $z_i \to \infty$ for $i > 1$ in the low temperature limit, in such a way to fulfill complete

association, i.e., $\lim_{T \to 0} x_{n_c} = 1/n_c$. Specifically we realized this by the choice $z_i = (z_2)^{i-1}$, which can be justified from the extensive property of the intra-cluster excess free energy. Then, due to the complete association, we have

$$x_c \xrightarrow{T \to 0} \frac{1}{n_c} \xrightarrow{n_c \to \infty} 0, \qquad (5.15)$$

so $a_c^{ex} \to 0$. Moreover, it is easy to see, either from a numerical analysis or analytically, that

$$-\rho < \alpha(n_c) = \lim_{T \to 0} \rho^2 \frac{\partial [x_c \ln x_1 + (1 - x_c) \ln(\lambda e/\rho)]}{\partial \rho}$$
$$\leq -\frac{\rho}{2}, \qquad (5.16)$$

with $\alpha(n_c) = (1/n_c - 1)\rho$ (remember that $\lim_{T \to 0} \lambda = 0$ and temperature and density are two independent variables) and $\lim_{n_c \to \infty} \alpha(n_c) = -\rho$ and $\alpha(2) = -\rho/2$ (see the Appendix). So that, in particular,

$$\lim_{n_c \to \infty} \lim_{T \to 0} p^{BTH} = 0. \qquad (5.17)$$

This result strongly suggests that BTH will never be able to account for the liquid phase, contrary to the Wertheim theory.[6, 11, 14]

VI. CONCLUSIONS

We compared Wertheim and BTH association theories. Whereas Wertheim theory is able to account for fluids with an infinite number of cluster species, BTH is not. As a result, only Wertheim's approach is able to account for the percolation and the condensation phenomena.

For the special case of fluids allowing for dimerization only, Wertheim theory becomes equivalent to BTH provided an ideal gas description of the inter-cluster partition function is used. For the Bjerrum-Tani-Henderson theory we also rigorously proved the uniqueness of the solution for the cluster's concentrations and the reduction of the system of equations to a single one for a single unknown.

To assess the accuracy of Wertheim and the full BTH using a hard-sphere (Carnahan-Starling) description of the inter-cluster partition function, we performed some MC simulations of two dimerizing systems: a binary mixture of associating non-additive hard-spheres and a one component single patch Kern-Frenkel fluid. Our results show that the parameter free Wertheim's theory captures well, at low density, the behavior of the MC data, both for the pressure and the concentration of dimers, and the range of densities where it is valid increases with increasing temperature. BTH, on the other hand, has the dimer diameter as a free parameter which can be adjusted to find more accurate agreement with the simulation data, even if the breakdown of its validity at high density still remains.

ACKNOWLEDGMENTS

APPENDIX: LOW TEMPERATURE LIMIT OF BTH AND W THEORIES

For the case studied in Sec. V A, from W theory we find, for the compressibility factor,

$$z_{bond}^{W} = \rho \frac{\partial \beta a_{bond}^{W}}{\partial \rho} = -\frac{\Delta \rho}{\left(1 + \sqrt{1 + 2\Delta \rho}\right)^2}, \quad \text{(A1)}$$

so, in the low temperature limit, we have

$$\lim_{\Delta \to \infty} z_{bond}^{W} = -1/2. \quad \text{(A2)}$$

In BTH theory instead

$$z_{bond}^{BTH} = \rho \frac{\partial \beta a_{bond}^{BTH}}{\partial \rho}. \quad \text{(A3)}$$

Recalling that $x_c = (1 + \lambda z_2)/(1 + 2\lambda z_2)$, we find, in the low temperature limit, $\lim_{z_2 \to \infty} x_c = 1/2$. Then, for $\sigma_c = \sigma$, we have $a_c^{ex} \to a_0^{ex}$. So, since z_2 and ρ are independent variables,

we find

$$\lim_{z_2 \to \infty} z_{bond}^{BTH} = \lim_{z_2 \to \infty} \rho \frac{\partial [x_c \ln x_1 + (1 - x_c) \ln(\lambda e/\rho)]}{\partial \rho}. \quad \text{(A4)}$$

Observing further that $\lim_{z_1 \to \infty} \lambda = 0$ we then find $\lim_{z_2 \to \infty} z_{bond}^{BTH} = -1/2$ as for Wertheim.

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[25] In fact $dx_c/d\lambda < 0$ if $\sum_{ij} ij\lambda^{i+j-1} z_i z_j < \sum_{ij} i^2 \lambda^{i+j-1} z_i z_j$. This can be proven observing that for $i \neq j$ we have $(i - j)^2 > 0$ or $2ij < ii + jj$ or $ija_{ij} + jia_{ji} < iia_{ij} + jja_{ij}$ for any $a_{ij} = a_{ji}$. Then we must also have $\sum_{ij} ija_{ij} < \sum_{ij} iia_{ij}$.

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