Structure and thermodynamics of a mixture of patchy and spherical colloids: A multi-body association theory with complete reference fluid information

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A mixture of solvent particles with short-range, directional interactions and solute particles with short-range, isotropic interactions that can bond multiple times is of fundamental interest in understanding liquids and colloidal mixtures. Because of multi-body correlations, predicting the structure and thermodynamics of such systems remains a challenge. Earlier Marshall and Chapman [J. Chem. Phys. **139**, 104904 (2013)] developed a theory wherein association effects due to interactions multiply the partition function for clustering of particles in a reference hard-sphere system. The multi-body effects are incorporated in the clustering process, which in their work was obtained in the absence of the bulk medium. The bulk solvent effects were then modeled approximately within a second order perturbation approach. However, their approach is inadequate at high densities and for large association strengths. Based on the idea that the clustering of solvent in a defined coordination volume around the solute is related to occupancy statistics in that defined coordination volume, we develop an approach to incorporate the complete information about hard-sphere clustering in a bulk solvent at the density of interest. The occupancy probabilities are obtained from enhanced sampling simulations but we also develop a concise parametric form to model these probabilities using the quasichemical theory of solutions. We show that incorporating the complete reference information results in an approach that can predict the bonding state and thermodynamics of the colloidal solute for a wide range of system conditions. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4960985]

I. INTRODUCTION

The physical mechanisms governing the structure and dynamics of particles interacting with short-range anisotropic interactions are of fundamental interest in the quest to understand how inter-molecular interactions dictate macroscopic structural and functional organization.[1–5] Patchy colloids, particles with engineered directional interactions, are archetypes of such systems, with numerous emerging applications in designing materials from the nanoscale level.[6–10] Experiments on patchy colloidal systems have focused on the synthesis of different kinds of self assembling units and their consequence for the emergent structure.[11–18] Complementing these experimental studies, molecular simulations have also sought to understand how the anisotropy of interactions determines the emergent structure[19–22] and the phase behavior.[23–28] But, despite the simplicity in describing and engineering the inter-molecular interactions, a general theory to predict the phase behavior is not yet available. The present article addresses this challenge.

Wertheim's theory in the form of the statistical associating fluid theory (SAFT)[1,24,29–35] has proven effective in describing systems with short range, directional (i.e., specific) interactions and is thus of natural interest in describing patchy colloids. In Wertheim's approach, association due to specific interaction is described within a chemical equilibrium framework, with inter-particle correlations obtained using a non-associating reference fluid (typically a hard-sphere fluid).

The nature of information from the reference determines the order of the theory. In the first order (TPT1) theory, pair-correlation information, and in the second order (TPT2) approach, three-body correlation from the reference are included in the theory.

Wertheim's approach forms the basis of several recent studies that reveal the importance of multi-body effects. Recognizing that patchiness broadens the vapor-liquid coexistence relative to a system with isotropic interactions, Liu *et al.*[27] incorporated a square well reference in Wertheim's first order (TPT1) perturbation theory. This model could qualitatively capture the increasing critical temperature with increasing number of patches but quantitative accuracy was limited. Within an integral equation approach, Kalyuzhnyi and Stell[36] reformulated Wertheim's multi-density formalism[37] to incorporate spherically symmetric interactions. However, the solution becomes complex for large values of bonding states. Using TPT2 Phan *et al.*[38] developed an equation of state for hard chain molecules and obtained numerical solution for mixtures of chain and star-like molecules. Based on Phan *et al.*'s[38] equation for linear chains, Marshall and Chapman[39] obtained analytical solutions for branched chain and star-molecules and their results matched with the numerical results of Phan *et al.*[38] for star-like molecules.

However there are numerous cases where multibody effects must be incorporated from the very foundations of the modeling effort. A specific example is the problem of modeling short-range association in a concentrated electrolyte (brine), a problem of interest in describing phase equilibria in oil-water-brine systems. In this case, the ion can be

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envisioned as a sticky particle that interacts isotropically with the solvent water. The water molecule here is analogous to a patchy particle and interacts along specific directional bonds. Since the ion can bind with multiple water molecules, the usual constraint of single bonding at a site (now the entire ion) used in Wertheim's original theory does not hold. The multiple bonding per site also sharply highlights the need to acknowledge multibody correlations.

To incorporate multiple bonding per site for solute molecules to describe multi-body effects within SAFT, Marshall and Chapman[40,41] extended Wertheim's multi-density formalism to multi-site associating fluids.[37] This theory generalizes the single chain approximation of Wertheim[42] for a site bonding multiple times, but it requires the multi-body correlation function for solvent around the solute in the non-associating reference fluid. These multi-body correlations for the reference fluid were sought by characterizing the distribution of gas-phase solute-solvent clusters. The effect of the bulk solvent is subsequently incorporated at the TPT2 level by using the linear superposition of the pair correlation function plus a three body correction. This approximation works well for systems at low solvent densities or higher concentration of solute, i.e., conditions when low order correlations are important. However, this approach fails at high solvent densities and for low concentrations of solutes. In this work, we address these limitations and present a way to accurately incorporate multi-body correlations in the hard sphere reference.

Following Marshall and Chapman,[40,41] we model sticky solute and patchy solvent molecules as hard spheres of equal diameter (σ) and short range association sites. For the hard-sphere reference, we show how coordination distribution around a distinguished solute obtained from particle simulations can be used to incorporate multi-body correlations in the cluster integrals that appear in the theory. The link between coordination distribution and multi-body correlations is inspired by quasichemical theory[43,44] and ultimately draws upon seminal investigation of hard-sphere packing of Reiss and coworker.[45] In the present framework, all contributions from orientation-dependent attractive interactions are transparently decoupled from multi-body packing effects that are obtained for the reference fluid.

The rest of the paper is organized in the following way. In Section II A, we discuss the Marshall-Chapman[41] theory, their gas-phase cluster approximation, and highlight the need for improvement suggested by comparing the results of the theory with Monte Carlo simulations. In Section II B we present our approach for better describing the reference. To aid concision, the development based on the quasichemical theory of hard-sphere solutions is presented in Appendix B. Section IV collects the results and discussions of this study.

II. THEORY

Consider a mixture of solvent molecules, p, with two directional sites (labeled A and B) and isotropically sticky, solute molecules, s. For solvent-solvent association, only
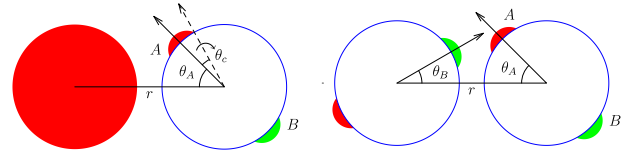

FIG. 1. Association between solute and solvent (left) and solvent molecules (right). Association potential of the sticky solute is isotropic (indicated by a uniform red color) and the solvent has directional interaction represented by A and B patches on the surface of the sphere. The solid angle subtended by the patch at the center of the sphere is $2 \cdot \pi \cdot [1 - \cos(\theta_c)]$. r is the center-to-center distance and θ_A and θ_B are the orientation of the attractive patches A and B relative to line connecting the centers. Note the sticky solute can only interact with the patch A (colored red).

bonding between A and B is allowed and the size of sites is such that single bonding condition holds (Fig. 1). The solute molecule can bond with site A of the solvent; the isotropic attraction ensures that the solute can bond multiple solvent molecules (Fig. 1). In the infinitely dilute regime considered here, we ignore the association between the solutes themselves.

The association potential for solvent-solvent (p, p) and solute-solvent (s, p) molecules is given by

$$u_{AB}^{(p,p)}(r) = \begin{cases} -\epsilon_{AB}^{(p,p)}, & r < r_c \text{ and } \theta_A \leq \theta_c^{(A)} \text{ and } \theta_B \leq \theta_c^{(B)} \\ 0 & \text{otherwise} \end{cases},$$

(1)

$$u_A^{(s,p)}(r) = \begin{cases} \epsilon_A^{(s,p)}, & r < r_c \text{ and } \theta_A \leq \theta_c^{(A)} \\ 0 & \text{otherwise} \end{cases},$$

(2)

where subscripts A and B represent the type of site and ϵ is the association energy. r is the distance between the particles and θ_A is the angle between the vector connecting the centers of two molecules and the vector connecting association site A to the center of that molecule (Fig. 1). The critical distance beyond which particles do not interact is r_c and θ_c is the solid angle beyond which sites cannot bond.

In the Wertheim's multi-density formalism,[37,46] the free energy due to association can be expressed as

$$\frac{A^{AS}}{Vk_BT} = \sum \left(\rho^{(k)} \ln \frac{\rho_0^{(k)}}{\rho^{(k)}} + Q^{(k)} + \rho^{(k)} \right) - \frac{\Delta c^{(0)}}{V},$$

(3)

where k_B is the Boltzmann constant, T is the temperature, the summation is over the species ($k = s, p$), ρ is the number density, ρ_0 is the monomer density, $Q^{(k)}$ is obtained from the work of Marshall-Chapman[41] and $\Delta c^{(0)}$ is the contribution to the graph sum due to association between the solvent-solvent (p, p) and solute-solvent (s, p) molecules, i.e.,

$$\Delta c^{(0)} = \Delta c_{pp}^{(0)} + \Delta c_{sp}^{(0)}.$$

(4)

A. Marshall-Chapman theory

In the work of Marshall-Chapman[40,41], the role of attractions between solvent, p, molecules is accounted by standard first order thermodynamic perturbation theory[1] (TPT1). For the association contribution to intermolecular interactions between the solute (s molecules) and solvent
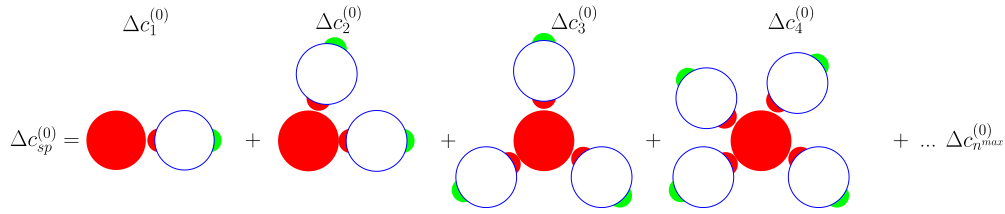
FIG. 2. Representation of graph sums for all the possible arrangements due to association of the solvent around a solute. Note that, for example, the graph for $\Delta c_3^{(0)}$ will include other higher occupancy states and is thus a measure of the effective association with 3 solvent particles.

(p molecules), Marshall and Chapman[40,41] developed a theory based on generalization of Wertheim's single chain approximation.[37,42] By including graph sums for all the possible arrangements of the solvent around the solute, i.e., one solvent around solute, two solvents around solute, etc., (Fig. 2), Marshall and Chapman obtained the free energy expression for the mixture as

$$\Delta c_{sp}^{(0)} = \sum_{n=1}^{n^{\max}} \Delta c_n^{(0)}, \tag{5}$$

where

$$\Delta c_n^{(0)} = \frac{\rho_0^{(s)}(\rho^{(p)} X_A^{(p)})^n}{\tilde{\Omega}^{n+1} n!} \int d(1) \cdots \int d(n+1)\, g_{HS}(1\cdots n+1) \cdot \prod_{k=2}^{n+1}(f_A^{(s,p)}(1,k)). \tag{6}$$

In Eq. (6), $\rho^{(p)}(= \rho \cdot x^{(p)})$ is the density of solvent molecules obtained from the mole fraction of solvent($x^{(p)}$) and the total density(ρ), $X_A^{(p)}$ is the fraction of solvent molecules not bonded at site A, $\tilde{\Omega}(= 4\pi)$ is the total number of orientations, $f_A^{(s,p)}(1,k)(= \exp(\varepsilon_A^{(s,p)}/k_B T) - 1)$ is the Mayer function for association between p and s molecules corresponding to the potential in Eq. (2), and the integral is over all the orientations and positions of the $n+1$ particles. If the spherical particle is fixed at the origin, the above integral can be written as

$$\frac{\Delta c_n^{(0)}}{V} = \frac{\rho_0^{(s)}(\rho^{(p)} X_A^{(p)})^n}{\tilde{\Omega}^n n!} \int d\vec{r}_1 d\omega_1 \cdots \int d\vec{r}_n d\omega_n\, g_{HS}(\vec{r}_1 \cdots \vec{r}_n | 0) \cdot \prod_{k=1}^{n}(f_A^{(s,p)}(0,k)), \tag{7}$$

where $\vec{r}_i$ defines the location of the particle (relative to the origin) and ω_i defines its orientation.

As is usual in SAFT, the contribution due to association is given by an averaged f-bond and factored outside the integral. Integrating over the orientations and defining $\sqrt{\kappa_{AA}}(= (1 - \cos(\theta_c))/2)$ as the probability that molecule p is oriented such that patch A on p bonds to s, we get

$$\frac{\Delta c_n^{(0)}}{V} = \frac{\rho_0^{(s)}(\rho^{(p)} X_A^{(p)} f_A^{(s,p)} \sqrt{\kappa_{AA}})^n}{n!} \int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n\, g_{HS}(\vec{r}_1 \cdots \vec{r}_n | 0). \tag{8}$$

Since the Mayer f function is zero for $r > r_c$ and the multibody correlation is zero for any pair below $r < \sigma$, the integral in Eq. (7) reduces to that over the observation shell (v) defined by the region between σ and r_c. Due to the limited knowledge of the mth order correlation functions for $m > 2$ ($n = 1$ corresponds to pair correlation), the calculation of the integral in Eq. (8) is a daunting numerical challenge.

1. Marshall-Chapman approximation (MCA)

To simplify numerical calculations, Marshall and Chapman[40] developed an approximation for the cavity correlation function, $y_{HS}(\vec{r}_1 \cdots \vec{r}_n | 0)$, defined by

$$g_{HS}(\vec{r}_1 \cdots \vec{r}_n | 0) = y_{HS}(\vec{r}_1 \cdots \vec{r}_n | 0) \prod_{\{l,k\}} e_{HS}(r_{lk}). \tag{9}$$

As usual, $e_{HS}(r_{lk}) = \exp(-u_{HS}(r_{lk})/k_B T)$ are reference system e-bonds which serve to prevent hard sphere overlap in the cluster; $e_{HS}(r_{lk}) = 0$ for $r_{lk} = |\vec{r}_l - \vec{r}_k| < \sigma$. At the TPT2 level, Marshall-Chapman approximated the cavity correlation function by the first order superposition of pair cavity correlation function at contact corrected by a second order factor ($\delta^{(n)}$) to account for three body interactions,[39] i.e.,

$$y_{HS}(\vec{r}_1 \cdots \vec{r}_n | 0) \approx y_{HS}^n(\sigma)\delta^{(n)}. \quad (10)$$

This leads to

$$\int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n \, g_{HS}(\vec{r}_1 \cdots \vec{r}_n | 0) \approx y_{HS}^n(\sigma)\delta^{(n)}\Xi^{(n)}, \quad (11)$$

where

$$\Xi^{(n)} = \int_v d\vec{r}_1 \int_v d\vec{r}_2 \cdots \int_v d\vec{r}_n \prod_{j>i=1}^{n} e_{HS}(r_{ij}) \quad (12)$$

is the partition function for an isolated cluster with n solvent hard spheres around a hard sphere solute in the bonding volume, i.e., the spherical shell bounded by σ and r_c, within which particles can associate.

$\Xi^{(n)}$ can be obtained as

$$\Xi^{(n)} = v_b^n P^{(n)}, \quad (13)$$

where v_b is the bonding volume and $P^{(n)}$ is the probability that there is no hard sphere overlap for randomly generated p molecules in the bonding volume (or inner-shell) of s molecules. A hit-or-miss Monte Carlo[43,47] approach to calculate $P^{(n)}$ proves inaccurate for large values of n ($n > 8$). But since

$$P^{(n)} = P_{insert}^{(n)} P^{(n-1)}, \quad (14)$$

where $P_{insert}^{(n)}$ is the probability of inserting a *single* particle given $n-1$ particles are already in the bonding volume, an iterative procedure can be used to build the higher-order partition function from lower order one.[40] The one-particle insertion probability $P_{insert}^{(n)}$ is easily evaluated using hit-or-miss Monte Carlo. The maximum number of p molecules for which a non-zero insertion probability can be obtained defines n^{max}.

With the potential defined by Eq. (2) and the approximation made in Eq. (10), Eq. (8) reduces to

$$\frac{\Delta c_n^{(0)}}{V} = \frac{1}{n!}\rho_0^{(s)}\Delta^n\Xi^{(n)}\delta^{(n)}, \quad (15)$$

where for a two patch solvent,

$$\Delta = y_{HS}(\sigma) X_A^{(p)}\rho^{(p)}f_A^{(s,p)}\sqrt{\kappa_{AA}}. \quad (16)$$

The fraction of solute bonded n times is

$$X_n^{(s)} = \frac{\frac{1}{n!}\Delta^n\Xi^{(n)}\delta^{(n)}}{1 + \sum\limits_{n=1}^{n^{max}} \frac{1}{n!}\Delta^n\Xi^{(n)}\delta^{(n)}}, \quad n > 0, \quad (17)$$

and the fraction bonded zero times is

$$X_0^{(s)} = \frac{1}{1 + \sum\limits_{n=1}^{n^{max}} \frac{1}{n!}\Delta^n\Xi^{(n)}\delta^{(n)}}. \quad (18)$$

Finally, the average number of solvent associated with the solute is given by

$$n_{avg} = \sum_n n \cdot X_n^{(s)}. \quad (19)$$

The fraction of solvent not bonded at site A and site B can be obtained by simultaneous solution of the following equations:

$$X_A^{(p)} = \frac{1}{1 + \xi\kappa_{AB}f_{AB}^{(p,p)}\rho^{(p)}X_B^{(p)} + \frac{\rho^{(s)}}{\rho^{(p)}}\frac{n_{avg}}{X_A^{(p)}}}, \quad (20)$$

$$X_B^{(p)} = \frac{1}{1 + \xi\kappa_{AB}f_{AB}^{(p,p)}\rho^{(p)}X_A^{(p)}}, \quad (21)$$

where

$$\xi = 4\pi\sigma^2(r_c - \sigma)\,y_{HS}(\sigma),$$
$$\kappa_{AB} = [1 - \cos(\theta_c)]^2/4,$$
$$f_{AB}^{(p,p)} = \exp(\varepsilon_{AB}^{(p,p)}/k_B T) - 1.$$

As will be shown below, the approximation Eq. (11) works very well for low solvent densities ($\rho\sigma^3 < 0.6$) but is inadequate in modeling a dense system.

B. The complete reference approach

The integral appearing in Eq. (8) has a simple physical interpretation. It is related to the average number of n-solvent clusters (around the distinguished solute) in the hard sphere system,[45] $F^{(n)}$, by

$$F^{(n)} = \frac{\rho^n}{n!}\int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n g_{HS}(\vec{r}_1 \cdots \vec{r}_n | 0) = \sum_{m=n}^{n^{max}} C_n^m p_m, \quad (22)$$

where p_m is the probability of observing exactly m solvent molecules in the observation shell of the solute in the reference system. C_n^m ($= m!/(m-n)! \cdot n!$) is the combinatorial term which defines the weight for a given coordination state. The association contribution (Eq. (8)) is then simply

$$\frac{\Delta c_n^{(0)}}{V} = \rho_0^{(s)}(x^{(p)}X_A^{(p)}f_A^{(s,p)}\sqrt{\kappa_{AA}})^n F^{(n)}. \quad (23)$$

Assuming the availability of $\{p_n\}$, the above approach amounts to including the complete hard-sphere occupancy (packing) information in the Marshall-Chapman framework. Henceforth, we will refer to this as the "complete reference" approach. As Figure 3 shows for an example of the $\Delta c_3^{(0)}$ term, observe that all occupancy states $m \geq n$ will contribute with combinatorial weights to the bonding state n. Thus errors in accounting for the occupancy of the coordination volume will have a substantial impact in capturing the bonding state.

Eq. (23) and the insight derived from it are the central contributions of this work. In the present work, in composing the sum (Eq. (22)), we use the occupancy probabilities $\{p_n\}$ obtained from Monte Carlo simulations using an ensemble reweighing approach (Table I; Appendix A). Anticipating future work, we also develop a concise parametric model for $\{p_n\}$ based on the quasichemical theory of solutions.
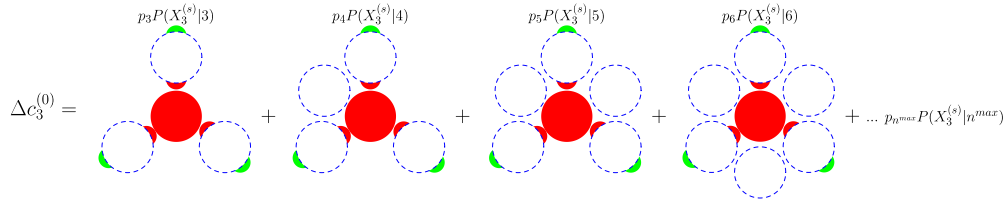
FIG. 3. Example graph sum to illustrate the joint role of occupancy and bonding. p_n is the probability of observing n-solvent around the solute without regard for their orientation. $P(X_i^{(s)}|n)$ is the conditional probability that given n-solvents occupy the bonding volume, $i(\leq n)$ of them are oriented correctly and bond with the solute. Patchy sites for only correctly oriented solvent are shown. Spheres are indicated by a dashed line to differentiate the graph from the effective association indicated in Fig. 2.

This development is presented in Appendix B. As an aside, approximating

$$F_{\text{MCA}}^{(n)} \approx \frac{\rho^n y_{HS}^n(\sigma)\delta^{(n)}\Xi^{(n)}}{n!}, \qquad (24)$$

leads to the Marshall-Chapman approximation.

Given $F^{(n)}$, the fraction of solute associated with n solvent molecules is given by

$$X_n^{(s)} = \frac{(x^{(p)}X_A^{(p)}f_A^{(s,p)}\sqrt{\kappa_{AA}})^n F^{(n)}}{1 + \sum\limits_{n=1}^{n^{\max}} (x^{(p)}X_A^{(p)}f_A^{(s,p)}\sqrt{\kappa_{AA}})^n F^{(n)}}, \qquad (25)$$

and the fraction of solute not bonded with any solvent molecule is

$$X_0^{(s)} = \frac{1}{1 + \sum\limits_{n=1}^{n^{\max}} (x^{(p)}X_A^{(p)}f_A^{(s,p)}\sqrt{\kappa_{AA}})^n F^{(n)}}. \qquad (26)$$

Using these distributions for associating mixture, average bonded state and fraction of solvent not bonded at sites can be obtained from Eqs. (19)-(21).

III. METHODS

A. Monte Carlo simulation of associating system

MC simulations were performed to evaluate the Marshall-Chapman approximation and test the Marshall-Chapman theory with improved representation of the multi-body cluster integrals (this work). The associating mixture comprises the sticky solute and the solvent with 2 diagonally opposed bonding sites. For all the simulations, the solvent-solvent and solute-solvent association is defined by the potentials in Eqs. (1) and (2), respectively, with $r_c = 1.1\sigma$ and $\theta_c^{(A)} = \theta_c^{(B)} = 27°$. Unless specifically stated, all simulations were based on 255 solvent particles and 1 solute. Each MC run comprised 1 million sweeps of equilibration, where a sweep is an attempted move for every particle. The translation/rotation factor was chosen to yield an acceptance ratio between 0.3–0.4. These parameters were kept constant in the production phase which also extended for 1 million sweeps.

The excess chemical potential of coupling the colloid with the solvent was obtained using thermodynamic integration,

$$\beta\mu^{Asso} = \epsilon \int_0^1 \langle\beta\psi\rangle_{\epsilon\cdot\lambda}d\lambda, \qquad (27)$$

where $\langle\beta\psi\rangle_{\epsilon\cdot\lambda}$ is the average binding energy of solute with the solvent as a function of the solute-solvent interaction strength scaled by λ and $\beta = 1/k_BT$. The integration was performed using a three-point Gauss-Legendre quadrature.[48] Binding strength data were collected every 100 sweeps for analysis. Statistical uncertainty in μ^{Asso} was obtained using the Friedberg-Cameron approach.[49,50] Simulations were performed at different densities for different interaction schemes and these are specifically noted in the results below. (μ^{Asso} calculations were based on 864 particles.)

To compare the predictions of the bonding state of the colloid ($X_i^{(s)}$) with simulations, from Bayes' rule we have

$$X_i^{(s)} = \sum_{n \geq i} p_n P(X_i^{(s)}|n), \qquad (28)$$

where $P(X_i^{(s)}|n)$ is the probability of observing the colloid in the i-bonded state given precisely n solvent particles are in the coordination volume. Knowing $X_i^{(s)}$, the average bonding state of the colloid is then

$$n_{avg} = \sum_n n \cdot X_n^{(s)}. \qquad (29)$$

To better reveal these low-X states, we used an ensemble reweighing approach.[51] Biases are calculated iteratively to sample n as uniformly as possible. The distribution $\{p_n\}$ is readily obtained from the reweighted probabilities $\{\bar{p}_n\}$ and the converged biases. For each n in the biased simulation, the distribution of $X_i^{(s)}$ is obtained and $P(X_i^{(s)}|n)$ constructed.

To study the effect of concentration of solute on n_{avg}, it was necessary to explore system with larger number of particles. Specifically, we performed simulations for various concentrations ($0 \leq x_s \leq 1$) by changing the number of solute molecules in a mixture with 864 number of particles. The hard-sphere $\{p_n\}$ distribution was obtained using the ensemble reweighing approach.[51]

B. Cluster partition function

To calculate P_{insert}^n (Eq. (14)), following Refs. 40 and 41, with the solute hard sphere at the center of coordinate system, trial position of the (inserted) solvent in the coordination volume is randomly generated. The position is accepted if there is no overlap with either the solute or the remaining $n-1$ particles. The insertion probability is based on similar trial placements averaged over $10^8–10^9$ insertions. For the
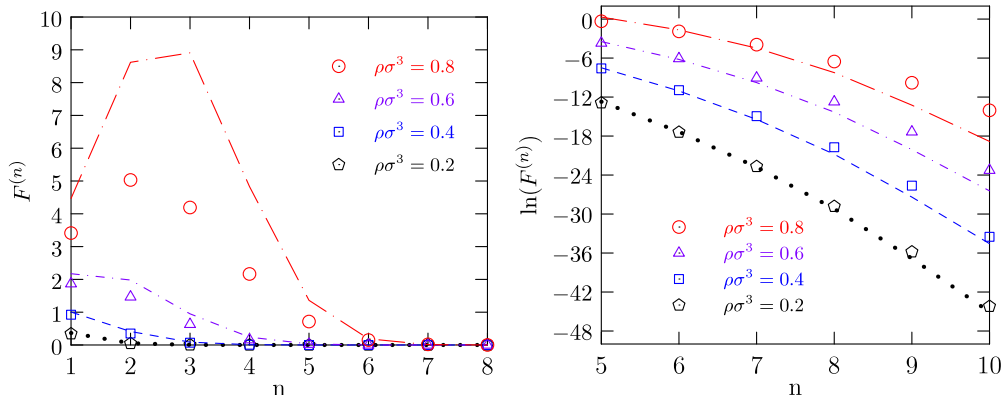
FIG. 4. Comparison of average number of n-mers ($F^{(n)}$) calculated from MC simulation (using Eq. (22), symbols) and Marshall-Chapman[40] approximation (using Eq. (24), lines) for different densities (right). n-mers are also presented in natural log scale to clearly show deviation for high coordination states (left).

present study involving solute and solvent of equal size, the radius of the coordination volume is the same as the cutoff radius of $r_c = 1.1\sigma$, where σ is the hard-sphere diameter.

IV. RESULTS AND DISCUSSIONS

A. Hard sphere reference

Table I (Appendix A) collects the reference $\{p_n\}$ obtained using reweighed sampling for various reduced densities $\rho\sigma^3$. Figure 4 shows the comparison of the prediction of $F^{(n)}$ based on the Marshall-Chapman approximation versus molecular simulations. Observe that for higher solvent densities that are of practical interest in modeling a dense solvent, the Marshall-Chapman approximation overestimates the population of lower n-mers and underestimates that of the higher n-mers, but somewhat fortuitously it captures n-mers in the range (6–7). Since the average number of n-mer is augmented by nth power of Mayer f-function (Eq. (8)), the Marshall-Chapman approximation is expected to be progressively inaccurate as the strength of solvent-solute association increases; thus a better account of $F^{(n)}$ is needed in securing quantitative accuracy. We next turn to the study of associating mixtures.

B. Associating mixture

1. Solute-solvent versus solvent-solvent association

Fig. 5 shows the distribution of the bonding states $\{X_n^{(s)}\}$ of the solute for a reduced density of $\rho\sigma^3 = 0.8$ for two cases, one with and the other without solvent-solvent interaction. In both cases, only one solute is present in the solvent bath and the solute-solvent interaction is 7 k_BT.

Fig. 5 reveals that for the same interaction energy, higher bonding states are more probable and hence multi-body effects are more important in the case when solvent-solvent association is absent. To understand this, note that when both solvent-solvent and solute-solvent interactions are present, there is a competition for patch A on solvent molecule (see Fig. 1) to associate with patch B on another solvent molecule or with the sticky solute. This competition is absent in the case when solvent-solvent association is absent and hence effectively more of the solvent patches are available to bond with the solute. Since the Marshall-Chapman approximation has a limitation in capturing the higher n-mer state (Fig. 4), it is seen that it is unable to capture the distribution of higher bonding states even qualitatively. However, the complete reference approach is able to describe the bonded fraction quite accurately.
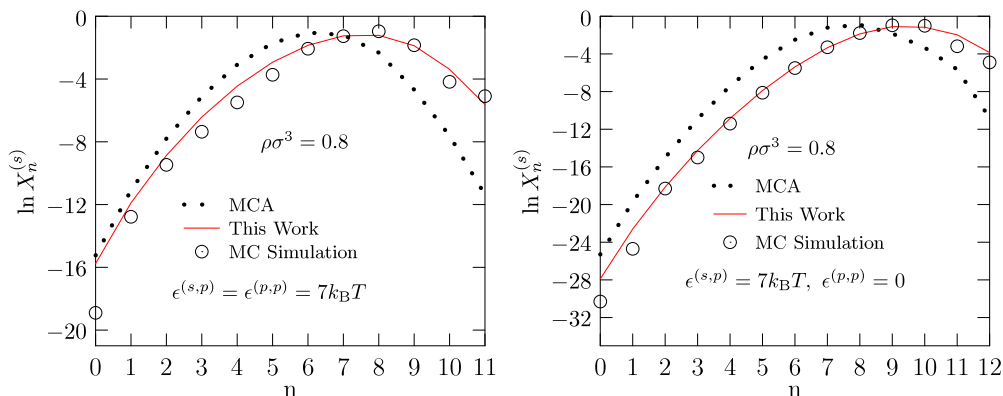

FIG. 5. Distribution of bonding states of the solute when the strength of solvent-solvent interaction is 7 k_BT (left) and zero (right). The reduced density $\rho\sigma^3 = 0.8$. $X_n^{(s)}$ is the fraction of solute bonded n-times to the patchy solvent molecules. The solute is infinitely dilute and association energy for interaction between solute and solvent is 7 k_BT.
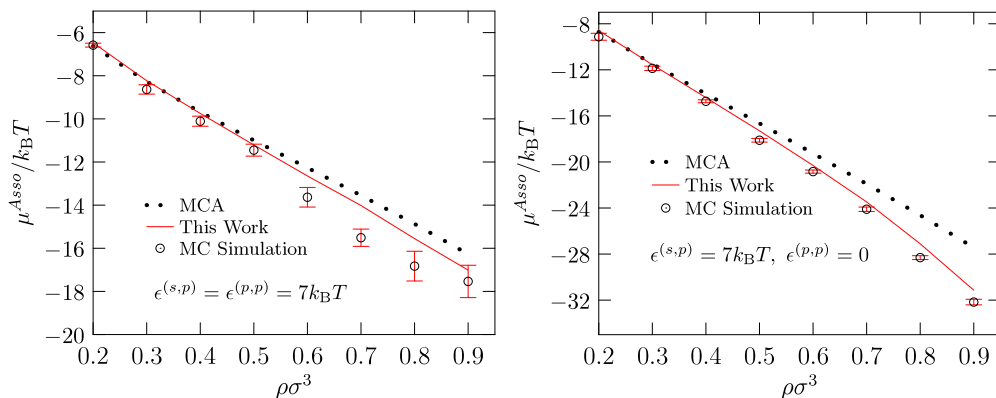
FIG. 6. Chemical potential for charging a solute molecule in a patchy solvent environment for different reduced densities. The solute is infinitely dilute and association energy for interactions between solute-solvent molecules is 7 k_BT. Solvent-solvent interaction energy is 7 k_BT (left) and zero (right).
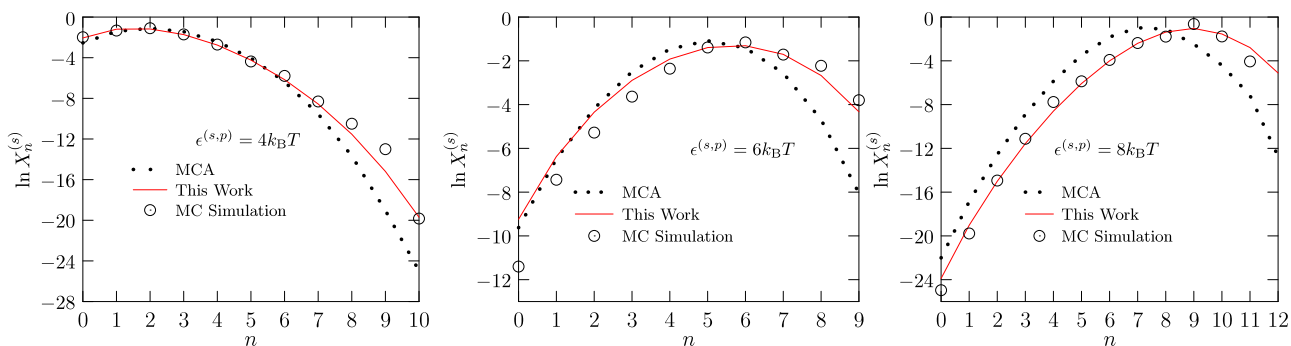

FIG. 7. Distribution of bonding states of solute at $\rho\sigma^3 = 0.8$ and different association energies between solute-solvent molecules; $\epsilon^{(s \cdot p)} = 4\ k_BT$ (left), $\epsilon^{(s \cdot p)} = 6\ k_BT$ (middle), $\epsilon^{(s \cdot p)} = 8\ k_BT$ (right). Solute is infinitely dilute and association energy for solvent-solvent interactions ($\epsilon^{(p \cdot p)}$) is 7 k_BT.

2. $\beta\mu^{Asso}$ of solute

The ability of the complete reference approach to capture the distribution of bonded states suggests that it should also better describe the association contribution to the chemical potential. Fig. 6 supports this suggestion, but for some densities, deviations as high as 1 k_BT are found. Somewhat surprisingly, when solvent-solvent interactions are comparable with solute-solvent interactions, μ^{Asso} calculated using Marshall-Chapman approximation is about as good as the result based with the revised reference (though deviations are larger than the complete reference approach).

Probing the basis for the surprisingly reasonable prediction for μ^{Asso} based on the Marshall-Chapman approximation reveals the importance of competitive solute-solvent and solvent-solvent interactions. When solvent-solvent association is comparable to solute-solvent association, specifically, $\epsilon^{(p,p)} \geq \epsilon^{(s,p)}$, the Marshall-Chapman approximation is able to capture the bonding states up to the most probable bonding state reasonably well (Fig. 7). However, when solute-solvent association strength is higher than solvent-solvent association, the Marshall-Chapman approximation is unable to capture neither the most probable bonding state nor the lower bonding states. Since in calculating μ^{Asso} we integrate the mean binding energy (Eq. (27)) over the regime where $\epsilon^{(p,p)} > \epsilon^{(s,p)}$, and since this is also the regime in which the Marshall-Chapman approximation is comparable to the revised theory, the final observed differences in the prediction of the chemical potential are not thus substantial.

We suspect that the entropic and enthalpic components of μ^{Asso} will be more sensitive to the description of the reference, an aspect that we are currently investigating. However, the chemical potential results do suggest a cautionary note, namely, that a metric based on μ^{Asso} may mask differences in underlying approximations.

3. Variation of average bonding with association energy

Fig. 8 shows the variation of average bonding numbers (n_{avg}) for the solute, when the solute-solvent and solvent-solvent association strengths are the same.
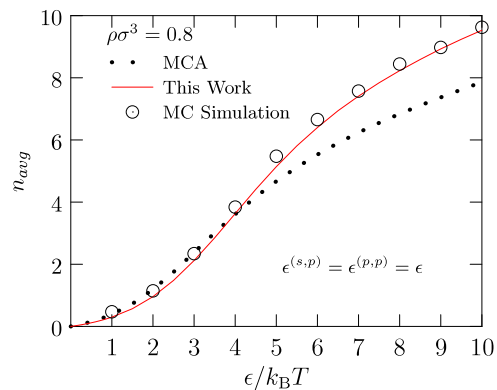

FIG. 8. Variation of average bonding number (n_{avg}) with the association energy between molecules (ϵ) for $\rho\sigma^3 = 0.8$. Solute is infinitely dilute.
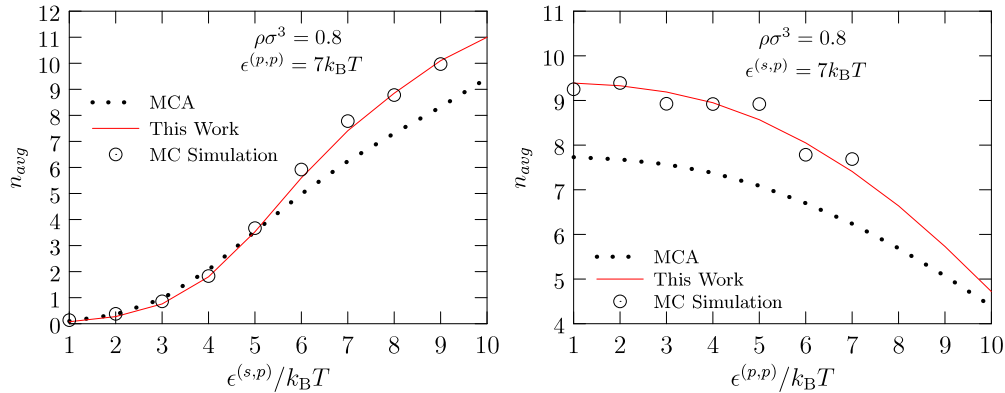
FIG. 9. Variation of average bonding number (n_{avg}) with the association energy between solute-solvent molecules($\epsilon^{(p,p)}$)(left) and solvent-solvent molecules ($\epsilon^{(s,p)}$)(right) for $\rho\sigma^3 = 0.8$. Solute is infinitely dilute.

It can be observed from Eq. (22) that at high densities, the contribution to $F^{(n)}$ from the higher-occupancy (higher p_n) state is non-negligible. For the association contribution, recall that $F^{(n)}$ is multiplied by n-factors of the Mayer f function which itself depends exponentially on strength of association. Thus for high density and high association strength, the TPT2 (Marshall-Chapman approximation) prediction is expected to underestimate n_{avg}. We find that this is indeed the case, but using the complete reference approach, we can capture n_{avg} accurately.

Fig. 9 further highlights the importance of the relative strengths of solute-solvent and solvent-solvent interactions on multi-body effects. As expected from the foregoing analysis, when the solute-solvent interactions are much stronger than solvent-solvent interactions, n_{avg} based on the Marshall-Chapman approximation deviates significantly from n_{avg} based on simulations.

4. Solute concentration effect

We also study the variation of average bonding number (n_{avg}) with the concentration of solute molecules (x_s) for a reduced density of $\rho\sigma^3 = 0.8$. (The solvent-solvent and solute-solvent interactions are all at the same level, $\epsilon = 7\ k_BT$.) For low concentration of solute, since more solvent molecules are
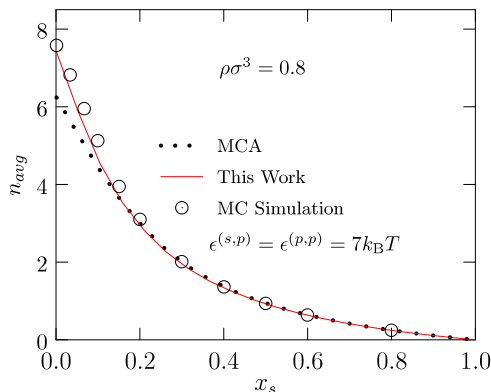
available to associate with the solute, higher bonding states are more probable. It is precisely in this limit that we expect larger deviations from the Marshall-Chapman approximation. As the concentration of sticky solute is increased, proportionately fewer solvent molecules are available to bond with the solute. In this limit, multi-body effects in solvation of the solute by patchy solvent molecules should be tempered and better agreement with the Marshall-Chapman approximation is expected. Fig. 10 confirms these expectations.

V. CONCLUSION

In this study, we have developed a simple and effective way to model multi-body effects in colloidal mixtures. Building on the Marshall and Chapman theory, we show that the challenge in describing the multi-body effects in associating mixtures can be handled by appreciating the importance of packing in the reference system. Importantly, we establish that the complex multi-body effects in the associating mixtures of different association geometries can be accurately determined if correct reference information is used. The present approach can elucidate the structure and thermodynamics of mixtures of patchy-solvent and sticky-solutes with size and interaction asymmetry as well as short-range ion-association phenomena in a dipolar solvent, cases where multi-body effects are potentially important.

In this work, we incorporate complete information from the hard-sphere reference fluid and present a modified expression for calculation of associative contribution to graph sums within the framework provided by Marshall-Chapman theory.[40,41] This modified expression is based on the analysis of physical clusters in the hard sphere and their representation in terms of occupancy distribution around a distinguished solute in the reference fluid. These occupancy distributions were obtained from enhanced sampling methods for hard sphere systems at different densities. Analysis of a wide range of association and concentration regimes shows that our approach incorporating complete hard sphere information accurately captures the behavior for bonding states, and the prediction of the chemical potential contribution due to association is within 1 k_BT of the reference Monte Carlo simulation results.

FIG. 10. Variation of average bonding number (n_{avg}) with the concentration of solute in the solution for $\rho\sigma^3 = 0.8$. Energy of association between molecules is 7 k_BT.

APPENDIX A: COORDINATION NUMBER DISTRIBUTION

Coordination number distribution from enhanced sampling[51] is given in Table I.

APPENDIX B: QUASI-CHEMICAL THEORY FOR SOLVATION OF HARD-SPHERE REFERENCE

Consider the equilibrium clustering reaction within some defined coordination volume of the solute A in a bath of solvent S molecules,
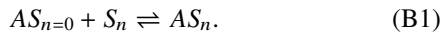
$$AS_{n=0} + S_n \rightleftharpoons AS_n. \tag{B1}$$

The equilibrium constant is

$$K_n = \frac{\rho_{AS_n}}{\rho_{AS_0}\rho_s^n}, \tag{B2}$$

where ρ_{AS_n} is the density of species AS_n and ρ_s is the density of the solvent. A mass balance then gives the fraction of n-coordinated solute as

$$p_n = \frac{K_n\rho_s^n}{1 + \sum\limits_{m \geq 1} K_m\rho_s^m}. \tag{B3}$$

The $n = 0$ term, p_0, is of special interest: $\ln p_0$ is free energy of allowing solvent molecules to populate a formerly empty coordination shell. In the language of quasichemical theory, $\ln p_0$ is called the chemical term.[52–54] Because the bulk medium pushes solvent into the coordination volume, an effective attraction exists between the solute and solvent even for a hard-sphere reference.

In the primitive quasichemical approximation,[55] the equilibrium constants are evaluated by neglecting the effect of the bulk medium, i.e., for an isolated cluster. Thus $K_n \approx K_n^{(0)}$,[43] where

$$n!K_n^{(0)} = \int\limits_v d\vec{r}_1 \cdots \int\limits_v d\vec{r}_n \prod_{j>i=1}^{n} e(i,j) \tag{B4}$$

with the integration restricted to the coordination volume (v). Comparing Eqs. (B4) and (12), clearly $n!K_n^{(0)} \equiv \Xi^{(n)}$, establishing a physical meaning for Eq. (12).

It is known that the primitive approximation leading to Eq. (B4) introduces errors in the estimation of $\ln p_0$,[43,44] especially for systems where the interaction of the solute with the solvent is not sufficiently stronger than the interaction amongst solvent particles.[55] For hard spheres, we must then expect the primitive approximation to fail outside the limit of low solvent densities.

One approach to improve the primitive approximation is to include an activity coefficient ζ_1, such that the predicted occupancy in the observation volume is equal to the occupancy, $\langle n \rangle$, expected in the dense reference,[43]

$$\sum_n nK_n^{(0)}\rho_S^n\zeta_1^n = \langle n \rangle \sum_n K_n^{(0)}\rho_S^n\zeta_1^n. \tag{B5}$$

Here the factor ζ_1 functions as a Lagrange multiplier to enforce the required occupancy constraint ($\langle n \rangle$). Physically, ζ_1 is an activity coefficient that serves to augment the solvent density in the observation volume over that predicted by the gas-phase equilibrium constant $K_n^{(0)}$.

Pratt and Ashbaugh[44] showed that ζ_1 alone is inadequate in modeling hard-sphere packing at high densities, but in addition, one needs a solvent coordinate-dependent molecular field to enforce uniformity of density inside the observation volume. With this additional molecular field, they showed that using the few-body cluster integrals (Eq. (B5)), they could predict hard-sphere packing in excellent agreement with the Carnahan-Starling[56] result up to high densities. Drawing inspiration from the work of Pratt and Ashbaugh,[44] we find that a two-parameter model

$$p_n = \frac{K_n^{(0)}[\zeta_1.\exp(\zeta_2.n)\rho_S]^n}{1 + \sum\limits_{m \geq 1} K_m^{(0)}[\zeta_1.\exp(\zeta_2.m)\rho_S]^m} \tag{B6}$$

with parameters reported in Table II is able to accurately reproduce both the free energy to evacuate the coordination volume around the reference solute and the average occupancy.

Interestingly, Eq. (B6) is identical in form with the model of Reiss and Merry[57] derived to describe the effects of clustering, medium and surface interactions simultaneously in hard-sphere packing in a cavity. Eq. (B6) can also be derived

TABLE I. $\ln(p_n)$ in hard sphere reference system obtained by reweighted sampling for different reduced densities ($\rho\sigma^3$).

n	$\rho\sigma^3 = 0.6$	$\rho\sigma^3 = 0.7$	$\rho\sigma^3 = 0.8$	$\rho\sigma^3 = 0.9$
0	−2.17	−3.22	−4.74	−6.74
1	−1.19	−1.78	−2.75	−4.29
2	−1.15	−1.22	−1.70	−2.75
3	−1.67	−1.28	−1.27	−1.79
4	−2.77	−1.87	−1.35	−1.33
5	−4.44	−2.98	−1.93	−1.35
6	−6.66	−4.60	−3.05	−1.84
7	−9.47	−6.85	−4.66	−2.83
8	−13.20	−9.80	−6.96	−4.39
9	−17.73	−13.62	−10.06	−6.71
10	−23.43	−18.64	−14.13	−9.79
11	−35.23	−25.35	−18.95	
12	−47.53	−32.85	−24.88	

TABLE II. Parameters for Eq. (B6) for different $\rho\sigma^3$.

$\rho\sigma^3$	ζ_1	ζ_2
0.2	1.2991	0.0175
0.6	3.1475	0.0361
0.7	4.1072	0.0457
0.8	5.5875	0.0609
0.9	7.5149	0.0829

using a MaxEnt procedure with the mean and variance of the occupancy as constraints.

Eq. (B6) can be used to obtain the average number of n-mer (Eq. (22)) in the coordination volume. It was also observed that based on the geometric effects involved in the surface interactions, $\{p_n\}$ can be determined by just one density dependent parameter along with a chemical potential. A detailed development of this idea will be presented later.

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