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A density functional theory for patchy colloids based on Wertheim's association theory: Beyond the single bonding condition

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In the framework of Wertheim's theory, we develop the first classical density functional theory for patchy colloids where the patch can bond more than once. To test the theory we perform new Monte Carlo simulations for the model system of patchy colloids in a planar slit pore. The theory is shown to be in excellent agreement with simulation for the density profiles and bonding fractions. It is also shown that the theory obeys the wall contact rule by accurately predicting bulk pressures from the wall contact density. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4776759>]

I. INTRODUCTION

Patchy colloids have attractive patches resulting in orientation dependent interactions between pairs of colloids. These interactions make patchy colloids an excellent model for network forming fluids¹ and empty liquids.² Patchy colloids are typically modeled using a primitive model of association first introduced by Bohl³ as a model for hydrogen bonding in molecular fluids. This potential treats a hydrogen bond as a square well interaction; if two molecules are within some critical radius of each other and are oriented correctly, they are considered bonded and the energy of the system is decreased by ε_A . The Bohl model was widely used to simulate the properties of model hydrogen bonding molecules based on hard spheres⁴ as well as Lennard-Jones spheres.⁵ It was later realized by Kern and Frenkel⁶ that this primitive model for associating fluids provided a good description of the interactions between patchy colloids. This potential has found widespread use in the modeling of patchy colloid systems.⁷

A well suited statistical mechanical framework to incorporate directional interactions is Wertheim's theory.^{8–12} In Wertheim's theory, statistical mechanics is written in a multi-density formalism which includes short range orientational interactions at an early point in the derivation allowing for accurate approximation techniques such as perturbation theory which treats association as a perturbation to a hard sphere reference fluid. Wertheim's first order perturbation theory (TPT1) forms the basis of the statistical associating fluid theory equation of state^{4,13,14} for associating fluids and TPT1 has been widely applied in the field of patchy colloids.⁷

An approximation in the development of TPT1 is the single bonding condition which restricts bonding such that each patch (or site for molecular fluids) can bond a maximum of once, that is, no double bonding of patches is allowed. This is an exact statement for small patch size, but as patch size increases multiple bonding of patches must be accounted for. This is a difficult problem due to the fact that blocking effects,

which involve more than two colloids must be accounted for. This was a problem first addressed by Kalyuzhnyi, Docherty, and Cummings¹⁵ (KDC) in the development of a homogeneous equation of state for one patch and multi-patch¹⁶ colloids where each patch can bond at most twice. In the original development¹⁵ of the theory, rings were not included in the theory and an empirical correction had to be added to the chain graph sum to correct for ring formation. The KDC approach has been shown to give accurate predictions of pressure over a wide range of temperatures; however, the theory predicts accurate bonding fractions and internal energies at high temperatures only.¹⁷ Recently, Marshall, Ballal, and Chapman (MBC)¹⁷ developed a theory in Wertheim's two density formalism^{8,9} for one patch colloids where the patch can bond at most twice. In the MBC approach, ring formation is treated in a rigorous way, which results in a theory that predicts accurate pressures, bonding fractions, and energies even at low temperatures. Both the KDC and MBC approaches lose validity for large patch coverage at low temperatures when the fraction of colloids bonded more than twice becomes significant.

In addition to homogeneous systems, Wertheim's theory has found wide application in the field of inhomogeneous associating fluids in the form of density functional theory (DFT).^{18–22} In DFT, the grand free energy which is a functional of density is minimized to obtain an equation for the positional dependant singlet density. DFTs based on Wertheim's theory have been shown to give good predictions of density profiles and monomer fractions of associating hard spheres (patchy colloids) in slit pores.^{20–22} Each application of Wertheim's theory for systems of patchy colloids has been for small patch size so the single bonding condition holds. Of course, it is easy to imagine a situation where this approach would prove inadequate; for instance, how do patchy colloids distribute near a solid surface when the patch size is such that multiple bonding per patch is allowed? None of the previous DFTs for associating spheres can address this problem.

The approach taken by MBC¹⁷ in the development of a bulk equation of state is generally valid for inhomogeneous systems. In the original work,¹⁷ the homogeneous limit of the

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theory was taken at an early point in the derivation, however, this was not a necessary step. Wertheim's theory is generally written in inhomogeneous form.^{23,24} In this work, we will apply the MBC free energy to develop the first density functional theory for one patch colloids where the patch can bond at most twice. As a test case, the theory is compared to new NVT (constant number of particles N , volume V , and temperature T) Monte Carlo simulation results for the classical case of a fluid in a planar slit pore. It is shown that the theory is in excellent agreement with the simulation results.

II. THEORY

In this section, the density functional theory for one patch colloids will be developed. We begin by defining the interaction potential between two colloids as the sum of a hard sphere potential and a short range directional attractive contribution

$$\phi(12) = \phi_{HS}(r_{12}) + \phi_A(12). \quad (1)$$

The notation $(1) \equiv (\vec{r}_1, \Omega_1)$ represents the position $\vec{r}_1$ and orientation Ω_1 of colloid 1, $\phi_R(r_{12})$ is the hard sphere potential

$$\phi_R(r_{12}) = \begin{cases} \infty & r_{12} < \sigma \\ 0 & \text{otherwise} \end{cases} \quad (2)$$

and $\phi_A(12)$ is the association potential of a conical site⁴

$$\phi_A(12) = \begin{cases} -\varepsilon_A, & r_{12} \leq r_c; \alpha_1 \leq \alpha_c; \alpha_2 \leq \alpha_c \\ 0 & \text{otherwise} \end{cases}. \quad (3)$$

The vector $\vec{r}_{12}$ connects the centers of two colloids, r_c is the maximum separation between two colloids for which association is allowed, α_1 is the angle between $\vec{r}_{12}$ and the orientation vector passing through the center of the patch on colloid 1 and α_c is the critical angle beyond which association is not allowed. A diagram of two colloids interacting through this potential can be found in Fig. 1.

The foundation of DFT is a minimum principle, which states that the grand free energy functional $\Theta[\rho]$ is minimized by the equilibrium density profile $\rho_{eq}(\vec{r})$

$$\left. \frac{\delta \Theta[\rho]}{\delta \rho(\vec{r})} \right|_{\rho=\rho_{eq}} = 0. \quad (4)$$

The grand free energy functional is given by

$$\Theta[\rho] = A[\rho] + \int \rho(\vec{r}) (V_{ext}(\vec{r}) - \mu) d\vec{r}. \quad (5)$$

FIG. 1. Diagram of interacting colloids.

Here, $A[\rho]$ is the Helmholtz free energy functional, $V_{ext}(\vec{r})$ is the external potential, and μ is the chemical potential. The Helmholtz free energy is split into ideal and excess terms

$$A[\rho] = k_B T \int \rho(\vec{r}) (\ln \rho(\vec{r}) - 1) d\vec{r} + A^{HS}[\rho] + A^{We}[\rho]. \quad (6)$$

The first term in Eq. (6) is the ideal contribution, the second term is the excess contribution due to hard sphere repulsion which is modeled using White Bear²⁵ fundamental measure theory^{26,27} and finally $A^{We}[\rho]$ is the association contribution for directional attractive patchy interactions based on Wertheim's two density formalism^{8,9} and is given by¹⁷

$$\frac{A^{We}[\rho]}{k_B T} = \int d\vec{r} \rho(\vec{r}) (\ln X_o(\vec{r}) + 1 - X_o(\vec{r}) - \frac{X_1(\vec{r})}{2} - \frac{X_{ring}(\vec{r})}{3}), \quad (7)$$

where X_o is the colloid monomer fraction, X_1 is the fraction of colloids bonded once, and X_{ring} is the fraction of colloids bonded twice in triatomic rings. Note that this is *not* a local density approximation; this is the free energy functional. In the development of Eq. (7), it was assumed that a colloid could bond a maximum of twice. It was shown¹⁷ that this assumption was generally accurate for critical angles of $\alpha_c < 40^\circ$; for larger α_c the accuracy of this assumption depends on density and temperature. To evaluate the bonding fractions it was further assumed that the probability of polymerization beyond triatomic chains was small and those contributions could be neglected. This is an excellent approximation for $\alpha_c < 40^\circ$ due to the fact that rings dominate at low temperatures. For a detailed discussion, the reader is referred to the original publication.¹⁷ With this assumption X_1 is given as the sum of the fraction of colloids bonded once in a dimer X_d and the fraction bonded once in a triatomic chain X_{1c}

$$X_1(\vec{r}) = X_d(\vec{r}) + X_{1c}(\vec{r}), \quad (8)$$

where

$$\frac{X_d(\vec{r}_1)}{X_o(\vec{r}_1)} = \frac{(1 - \cos \alpha_c)^2}{4} f_A \times \int d\vec{r}_2 \rho(\vec{r}_2) X_o(\vec{r}_2) y(\vec{r}_1, \vec{r}_2) \lambda(r_{12}), \quad (9)$$

where $f_A = \exp(\varepsilon_A/k_B T) - 1$, $y(\vec{r}_1, \vec{r}_2)$ is the hard sphere reference system inhomogeneous cavity correlation function, $r_{12} = |\vec{r}_2 - \vec{r}_1|$ and $\lambda(r_{12})$ is given by

$$\lambda(r_{12}) = \begin{cases} 1 & \sigma \leq r_{12} \leq r_c \\ 0 & \text{otherwise} \end{cases}. \quad (10)$$

The fraction bonded once in a triatomic chain is given by

$$\frac{X_{1c}(\vec{r}_1)}{X_o(\vec{r}_1)} = (f_A)^2 \int d\vec{r}_2 d\vec{r}_3 \rho(\vec{r}_2) \rho(\vec{r}_3) X_o(\vec{r}_2) X_o(\vec{r}_3) \times y(\vec{r}_1, \vec{r}_2, \vec{r}_3) \Gamma(\vec{r}_1, \vec{r}_2, \vec{r}_3). \quad (11)$$

The function $y(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is the inhomogeneous hard sphere reference system triplet cavity correlation function

and $\Gamma(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is a geometric quantity given by

$$\Gamma(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{\Omega^3} \int \lambda(r_{12}) \lambda(r_{23}) H(r_{13} - \sigma) \times U(\Omega_1, \Omega_2) U(\Omega_2, \Omega_3) d\Omega_1 d\Omega_2 d\Omega_3, \quad (12)$$

where $H(x)$ is the Heaviside step function, $\Omega = 4\pi$ and $U(\Omega_1, \Omega_2)$ is given by

$$U(\Omega_1, \Omega_2) = \begin{cases} 1 & \alpha_1 \leq \alpha_c \text{ and } \alpha_2 \leq \alpha_c \\ 0 & \text{otherwise} \end{cases}. \quad (13)$$

The fraction bonded twice X_2 is given as the sum of colloids bonded twice in a triatomic chain X_{2c} and twice in a ring X_{ring}

$$X_2(\vec{r}) = X_{2c}(\vec{r}) + X_{ring}(\vec{r}), \quad (14)$$

where

$$\frac{X_{2c}(\vec{r}_2)}{X_o(\vec{r}_2)} = \frac{(f_A)^2}{2} \int d\vec{r}_1 d\vec{r}_3 \rho(\vec{r}_1) \rho(\vec{r}_3) X_o(\vec{r}_1) X_o(\vec{r}_3) \times y(\vec{r}_1, \vec{r}_2, \vec{r}_3) \Gamma(\vec{r}_1, \vec{r}_2, \vec{r}_3) \quad (15)$$

and X_{ring} is given by

$$\frac{X_{ring}(\vec{r}_1)}{X_o(\vec{r}_1)} = \frac{(f_A)^3}{2} \int d\vec{r}_2 d\vec{r}_3 \rho(\vec{r}_2) \rho(\vec{r}_3) X_o(\vec{r}_2) X_o(\vec{r}_3) \times y(\vec{r}_1, \vec{r}_2, \vec{r}_3) \Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3). \quad (16)$$

The geometric integral $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is given by

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{\Omega^3} \int \lambda(r_{12}) \lambda(r_{23}) \lambda(r_{13}) U(\Omega_1, \Omega_2) \times U(\Omega_2, \Omega_3) U(\Omega_1, \Omega_3) d\Omega_1 d\Omega_2 d\Omega_3. \quad (17)$$

The monomer fractions are calculated by solving the equation

$$X_o(\vec{r}) + X_1(\vec{r}) + X_2(\vec{r}) = 1. \quad (18)$$

Now the inhomogeneous cavity correlation functions must be approximated. We note that when Eqs. (7) and (9) are combined the pair correlation function is embedded in an integral of the form $\int y(\vec{r}_1, \vec{r}_2) \lambda(r_{12}) Q(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$ where Q is some function. The function $\lambda(r_{12})$ given by Eq. (10) restricts the relative positions of particles 1 and 2 in this integral. It is reasonable to assume that when the location of a given particle in the integral is fixed and the other particle is integrated over the allowed volume that a coarse grained approximation of $y(\vec{r}_1, \vec{r}_2)$, which has been averaged over the integration domain, can be used. To construct this function, we first consider the coarse grained pair function $\overline{y}(\vec{r}_1)$

$$\overline{y}(\vec{r}_1) = \frac{\int d\vec{r}_2 y(\vec{r}_1, \vec{r}_2) \lambda(r_{12})}{\int d\vec{r}_2 \lambda(r_{12})}, \quad (19)$$

where we have averaged over a spherical shell of radius $r_c - \sigma$. We require the pair function to be symmetric $y(\vec{r}_1, \vec{r}_2) = y(\vec{r}_2, \vec{r}_1)$ since we could have also averaged over $\vec{r}_2$, a condition which can be satisfied by a geometric mean of the averages in Eq. (19). That is,

$$y(\vec{r}_1, \vec{r}_2) \approx (\overline{y}(\vec{r}_1) \times \overline{y}(\vec{r}_2))^{1/2}. \quad (20)$$

For homogeneous fluids, the product $r^2 y(r)$ is approximately constant throughout the bond volume.²³ We will assume that this is approximately true in the inhomogeneous regime also, giving $r_{12}^2 y(\vec{r}_1, \vec{r}_2) \approx (\sigma^2 \overline{y_c}(\vec{r}_1) \times \sigma^2 \overline{y_c}(\vec{r}_2))^{1/2}$ where $\overline{y_c}(\vec{r}_1)$ is the coarse grained pair function at contact which is obtained through Eq. (19) by the replacement $\lambda(r_{12}) \rightarrow \delta(r_{12} - \sigma)$ where $\delta(x)$ is the Dirac delta function. Finally, we assume the coarse grained pair function $\overline{y_c}(\vec{r}_1)$ can be evaluated as the bulk contact cavity correlation function $y_c = (1 - 0.5\eta)/(1 - \eta)^3$ evaluated with a coarse grained density, that is,

$$\overline{y_c}(\vec{r}_1) \approx y_c(\bar{\rho}(\vec{r}_1)), \quad (21)$$

where $\bar{\rho}(\vec{r}_1)$ is some coarse grained density. Here, we choose the average to be taken in a spherical volume of radius σ

$$\bar{\rho}(\vec{r}_1) = \frac{3}{4\pi\sigma^3} \int d\vec{r}_2 \rho(\vec{r}_2) H(\sigma - r_{12}). \quad (22)$$

Equations (19)–(22) constitute the approximation of the pair cavity correlation function. This approximation has proven to give accurate results in interfacial systems.²⁸ Now the triplet cavity correlation functions must be estimated. We write the triplet cavity correlation functions for the triplet chain and ring, respectively, as

$$y(\vec{r}_1, \vec{r}_2, \vec{r}_3)|_{chain} = y(\vec{r}_1, \vec{r}_2) y(\vec{r}_2, \vec{r}_3) y_o^c(\vec{r}_1, \vec{r}_2, \vec{r}_3), \quad (23)$$

$$y(\vec{r}_1, \vec{r}_2, \vec{r}_3)|_{ring} = y(\vec{r}_1, \vec{r}_2) y(\vec{r}_2, \vec{r}_3) y(\vec{r}_1, \vec{r}_3) \hat{y}_o^r(\vec{r}_1, \vec{r}_2, \vec{r}_3). \quad (24)$$

The term $y_o^c(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is a correction to a linear superposition of the triplet function in the chain, and $\hat{y}_o^r(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ is a correction to a Kirkwood superposition in the ring. In the homogenous theory,¹⁷ the correction to the linear superposition is evaluated using the fitting function of Müller and Gubbins²⁹ for three colloids in rolling contact $y_o^c(r_{12}, r_{23}, r_{13}) = y_o(\bar{\omega}_{chain})$ where in this work $\bar{\omega}_{chain}$ is the average angle when the first and third colloid in a triatomic chain are in contact with the second, see Fig. 2, and $y_o(\bar{\omega})$ is given by

$$y_o(\bar{\omega}) = \frac{1 + a\eta + b\eta^2}{(1 - \eta)^3}, \quad (25)$$

where a and b depend on bond angle (average angle $\bar{\omega}$ here) and are tabulated in Ref. 29. For the inhomogeneous function, we follow an averaging approach similar to that of the pair

FIG. 2. Diagram of three interacting colloids where colloid 1 and colloid 3 are both in contact with colloid 2.

function given above to obtain

$$\ln y_o^c(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{3} \ln[y_o(\vec{\rho}(\vec{r}_1), \vec{\omega}_{chain}) \times y_o(\vec{\rho}(\vec{r}_2), \vec{\omega}_{chain}) \times y_o(\vec{\rho}(\vec{r}_3), \vec{\omega}_{chain})]. \quad (26)$$

Similarly, in the triatomic ring triplet function

$$\ln \hat{y}_o^r(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{3} \ln[\hat{y}_o(\vec{\rho}(\vec{r}_1), \vec{\omega}_{ring}) \times \hat{y}_o(\vec{\rho}(\vec{r}_2), \vec{\omega}_{ring}) \times \hat{y}_o(\vec{\rho}(\vec{r}_3), \vec{\omega}_{ring})], \quad (27)$$

where $\hat{y}_o(\vec{\omega}_{ring}) = y_o(\vec{\omega}_{ring})/y_c$. The angles $\vec{\omega}_{ring}$ and $\vec{\omega}_{chain}$ are assumed to be that of the bulk system and are tabulated in our previous publication¹⁷ as a function of α_c .

Now that the Helmholtz free energy has been specified we evaluate Eq. (4) for the density profile

$$\rho(\vec{r}) = \exp\left(\frac{\mu}{k_B T} - \frac{\delta A^{We}[\rho]/k_B T}{\delta \rho(\vec{r})} - \frac{\delta A^{HS}[\rho]/k_B T}{\delta \rho(\vec{r})} - \frac{V_{ext}(\vec{r})}{k_B T}\right). \quad (28)$$

The association functional derivative is evaluated as

$$\begin{aligned} \frac{\delta A^{We}[\rho]/k_B T}{\delta \rho(\vec{r})} &= \ln X_o(\vec{r}) - \int d\vec{r}' \rho(\vec{r}') \left(1 - X_o(\vec{r}') - \frac{X_1(\vec{r}')}{2} - \frac{X_{ring}(\vec{r}')}{3}\right) \\ &\times \frac{\delta \ln y_c(\vec{\rho}(\vec{r}'))}{\delta \rho(\vec{r})} \\ &- \int d\vec{r}' \rho(\vec{r}') (X_2(\vec{r}') - X_{ring}(\vec{r}')) \frac{\delta \ln y_o(\vec{\rho}(\vec{r}'), \vec{\omega}_{chain})}{\delta \rho(\vec{r})} \\ &- \frac{1}{3} \int d\vec{r}' \rho(\vec{r}') X_{ring}(\vec{r}') \frac{\delta \ln y_o(\vec{\rho}(\vec{r}'), \vec{\omega}_{ring})}{\delta \rho(\vec{r})}. \end{aligned} \quad (29)$$

And the bulk chemical potential is (in rearranged form)¹⁷

$$\begin{aligned} \frac{\mu}{k_B T} &= \frac{\mu_R}{k_B T} + \ln X_o - \left(1 - X_o - \frac{X_1}{2} - \frac{X_{ring}}{3}\right) \eta \frac{\partial \ln y_c}{\partial \eta} \\ &- (X_2 - X_{ring}) \eta \frac{\partial \ln y_o(\vec{\omega}_{chain})}{\partial \eta} \\ &- \frac{X_{ring}}{3} \eta \frac{\partial \ln y_o(\vec{\omega}_{ring})}{\partial \eta}, \end{aligned} \quad (30)$$

where μ_R is the chemical potential of the hard sphere reference system. We have now completely specified the new density functional theory. We will also compare the new theory to predictions from TPT1. In TPT1, only 1 bond per patch is allowed yielding $X_{ring} = X_{2c} = X_{1c} = 0$ and $X_1 = X_d = 1 - X_o$ giving the following free energy and functional derivative

$$\left(\frac{A^{We}[\rho]}{k_B T}\right)_{TPT1} = \int d\vec{r} \rho(\vec{r}) \left(\ln X_o(\vec{r}) - \frac{X_o(\vec{r})}{2} + \frac{1}{2}\right), \quad (31)$$

$$\begin{aligned} \left(\frac{\delta A^{We}[\rho]/k_B T}{\delta \rho(\vec{r})}\right)_{TPT1} &= \ln X_o(\vec{r}) - \frac{1}{2} \int d\vec{r}' \rho(\vec{r}') (1 - X_o(\vec{r}')) \\ &\times \frac{\delta \ln y_c(\vec{\rho}(\vec{r}'))}{\delta \rho(\vec{r})}. \end{aligned} \quad (32)$$

In Secs. III and IV, theory and simulation will be compared for the case of a fluid in a planar slit pore. Specialization of the theory to systems with 1D planar inhomogeneities can be found in the Appendix.

III. SIMULATION

As a test of the DFT new NVT Monte Carlo simulations were performed for the case of a colloid fluid in a planar slit pore where the walls exert the external potential

$$V_{ext}(z) = \begin{cases} \infty & z < 0 \text{ or } z > H \\ 0 & \text{otherwise} \end{cases}. \quad (33)$$

The term H is the pore width. The colloids interact with each other through the intermolecular potential given by Eq. (1) with $r_c = 1.1\sigma$. The simulations were performed in the manner described previously,²¹ so the description here will be brief. Simulations were performed at the average pore densities $\rho_{av}^* = \rho_{av}\sigma^3 = 0.2, 0.5$, and 0.7 ; $N = 2744$ colloids were used in the simulation for densities $\rho_{av}^* = 0.5$ and 0.7 while $N = 784$ colloids were used for the density $\rho_{av}^* = 0.2$. The pore width H was chosen such that it was twice the simulation box length in the x and y dimension, L , yielding a simulation cell volume of $V = 2L^3$. Periodic boundary conditions were applied in the x and y dimensions. Each simulation was allowed to equilibrate for $1-4 \times 10^9$ trial moves and averages were taken over $1-12 \times 10^9$ trial moves. A trial move consists of an attempted displacement and reorientation of a colloid. Final reported quantities are averaged over both walls in the pore.

IV. RESULTS

In this section, DFT calculations will be compared to Monte Carlo simulations for the case of a single patch

FIG. 3. Comparison of theoretical (curves) and simulation (symbols) predictions of density profiles scaled by bulk density ρ_b at a pore density of $\rho_{av}^* = 0.2$ and critical angle of $\alpha_c = 35^\circ$. The variation of the bulk density from the average density is small in this case. The dashed line is the prediction of TPT1 and $\epsilon^* = \epsilon_A/k_B T$.

FIG. 4. Bulk bonding fractions, X_k^b ($k = 0, 1, 2$) for $\alpha_c = 35^\circ$ and $\rho_b^* = 0.2$.

colloid fluid in a slit pore. Here, we only show results for a single wall in the pore, the other wall is symmetric. We begin with a discussion of the layering of density profiles near the hard wall at a low density of $\rho_{av}^* = 0.2$ and critical angle of $\alpha_c = 35^\circ$. Figure 3 compares simulation and theoretical density profiles for association energies (temperatures) $\varepsilon^* = \varepsilon_A/k_B T = 4, 6, 8$, and 10. For comparison we have included results from TPT1 DFT (dashed lines). At energy $\varepsilon^* = 4$ the association is weak and density is enhanced at the wall in a wetting effect characteristic of hard sphere fluids. Increasing the energy further to $\varepsilon^* = 6$, the wall contact density $\rho_c = \rho(0)$ decreases, this decrease is the result of a combined energetic/entropic phenomena; on the entropic side, as more colloids associate into dimers, etc., there becomes less allowed configurations where the colloid can approach the wall, and energetically it is more difficult to form an association bond near wall contact. These effects combine to decrease ρ_c . At these high temperatures TPT1 still does a good job describing the structure of the fluid. Increasing the energy further to $\varepsilon^* = 8$, ρ_c decreases further nearing that of the bulk density, and finally at $\varepsilon^* = 10$ ρ_c becomes less than the bulk density and the fluid is depleted from the wall in a drying effect. At these energies TPT1 fails to accurately predict the fluid structure. The cause for this depletion can be seen in Fig. 4 which depicts the bulk bonding fractions at a bulk density of

FIG. 5. Position dependant bonding fractions, $X_k(z)$ for $\alpha_c = 35^\circ$ and an average pore density $\rho_{av}^* = 0.2$. Symbols give simulation results, solid curves give new DFT results and dashed lines give TPT1 DFT results. $\varepsilon^* = 4$ (green), $\varepsilon^* = 6$ (red), $\varepsilon^* = 8$ (black), $\varepsilon^* = 10$ (blue).

$\rho_b^* = 0.2$. For low energies X_1 dominates due to the fact that it is entropically unfavorable to associate into clusters larger than dimers; it is in this realm, where multiple bonding is not significant, that TPT1 is accurate. Increasing the energy further, the energetic benefit for a colloid to form multiple bonds overcomes this entropic penalty and larger cluster form with a corresponding increase in X_2 . At an energy $\varepsilon^* = 10$ the monomer fraction X_o is small and X_2 dominates, meaning the fluid is primarily composed of associated triatomic clusters, which results in a depletion at the wall characteristic of low

FIG. 6. Same as Fig. 3 except with $\rho_{av}^* = 0.5$ and $\rho_b^* \sim 0.493 \pm 0.002$.

FIG. 7. Same as Fig. 5 except with $\rho_{av}^* = 0.5$.

density polyatomic fluids. Figure 5 shows the position dependant bonding fractions of this low density fluid. For all cases X_0 is enhanced at the wall and X_2 is depleted. The fraction X_1 is depleted at the wall for all energies except $\epsilon^* = 10$ where it becomes enhanced at wall contact. This enhancement is the result of the antipathy X_2 shows the wall. At this energy X_2 is favored, however, near wall contact a colloid bonded twice pays a much higher entropic penalty than one bonded once; this results in the enhancement of X_1 . Overall the new theory is in excellent agreement with simulation. TPT1 is accurate at low energies but loses accuracy in the prediction of X_0 and X_1 at higher energies (lower temperatures) due to the fact that multiple bonding per patch is not accounted for; TPT1 cannot make a prediction for X_2 since only one bond per colloid is allowed.

Increasing the pore density further, Fig. 6 gives density profiles and Fig. 7 gives bonding fractions for an average pore density of $\rho_{av}^* = 0.5$ and $\alpha_c = 35^\circ$. Like the low density case increasing ϵ^* decreases ρ_c ; however, at no point does the fluid become depleted at the wall, at this higher density the hard sphere packing effect is too strong. Like the low density

FIG. 9. Effect of critical angle α_c on density profile at $\rho_{av}^* = 0.2$ and $\epsilon^* = 6$. Symbols give simulation results and curves give theoretical predictions. Inset shows the fraction of colloids bonded three times, X_3 . $\alpha_c = 35^\circ$ (black), $\alpha_c = 40^\circ$ (red), $\alpha_c = 45^\circ$ (green).

case X_1 is depleted at wall contact for low ϵ^* and enhanced at high ϵ^* . Again, TPT1 is reasonably accurate for $\epsilon^* \leq 6$ and loses accuracy at higher energy (lower T), while the new theory is accurate over the full temperature range. Finally, Fig. 8 gives density profiles for $\rho_{av}^* = 0.7$ and $\alpha_c = 35^\circ$. At this high density there is strong layering in the density profiles. Both TPT1 and the new theory are accurate at $\epsilon^* = 4$; for energy $\epsilon^* = 8$ the new theory is in excellent agreement with simulation while TPT1 overpredicts ρ_c .

Until now we have only considered critical angles of $\alpha_c = 35^\circ$. The new DFT does not account for colloids bonded more than twice, so it should be expected that the theory will lose accuracy as α_c is increased. For instance, Fig. 9 compares simulation and theoretical density profiles at critical angles $\alpha_c = 35^\circ, 40^\circ$, and 45° at a density $\rho_{av}^* = 0.2$ and association energy $\epsilon^* = 6$. As can be seen, the theory is in good agreement with simulation for 35° and 40° but loses accuracy at 45° ; at this α_c the fraction of colloids bonded three times becomes significant at this ϵ^* (see inset of figure).

Finally, we show that the new theory obeys the wall contact theorem, which states that the bulk pressure is related to the contact density through the relation $P = k_B T \rho_c$. Figure 10 compares DFT calculations to NPT simulations¹⁷ for the change in pressure due to association $\Delta P^* = (P - P^{HS})\sigma^3/k_B T = \rho_c^* - \rho_c^*(\epsilon^* = 0)$ at critical angles $\alpha_c = 35^\circ$ and 45° . At $\alpha_c = 35^\circ$ the theory is in excellent agreement with simulation over the full temperature range, while at $\alpha_c = 45^\circ$ the theory is only accurate for high temperatures due to the fact that the fraction of colloids bonded three times becomes significant at lower temperatures (higher ϵ^*).

FIG. 8. Same as Fig. 3 except with $\rho_{av}^* = 0.7$ and $\rho_b^* \sim 0.684 \pm 0.001$.

FIG. 10. Change in pressure due to association ΔP^* for $\alpha_c = 35^\circ$ (top) and $\alpha_c = 45^\circ$ (bottom). Symbols give NPT simulation results¹⁷ and curves give DFT predictions calculated through the wall contact theorem.

V. CONCLUSIONS

In the framework of Wertheim's theory, we have presented the first density functional theory for patchy colloids where the patch can bond more than once. The theory was extensively tested against new Monte Carlo simulations for the case of a fluid in a planar slit pore and found to be very accurate. Specifically, it was shown that the theory predicts accurate density profiles and bonding fractions over a wide range of temperatures when α_c is moderate. For larger α_c the accuracy of the theory will depend on density and temperature. Extension of the current approach to multiple patch colloids should be relatively straightforward; this will be the subject of a future publication.

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APPENDIX: SPECIALIZATION TO PLANAR INHOMOGENEITIES

In this section, we specialize Eqs. (9), (11), (15), and (16) to systems with planar inhomogeneities in the z dimension. In this case, we write Eq. (9) as

$$\frac{X_d(z_1)}{X_o(z_1)} = \frac{\pi}{2} \sigma^2 (1 - \cos \alpha_c)^2 (r_c - \sigma) f_A \times \int_{z_1/\sigma-1}^{z_1/\sigma+1} d\left(\frac{z_2}{\sigma}\right) \rho(z_2) X_o(z_2) y(z_1, z_2), \quad (\text{A1})$$

where $y(z_1, z_2) = \sqrt{y_c(\bar{\rho}(z_1)) \times y_c(\bar{\rho}(z_2))}$. We approximate $X_{1c}(z_1)$ as

$$\frac{X_{1c}(z_1)}{X_o(z_1)} = (f_A)^2 \int_{z_2-\tilde{r}}^{z_2+\tilde{r}} \int_{z_1-\tilde{r}}^{z_1+\tilde{r}} dz_2 dz_3 \rho(z_2) \rho(z_3) X_o(z_2) X_o(z_3) \times y^{\text{chain}}(z_1, z_2, z_3) \tilde{\Gamma}(\Delta z_{12}, \Delta z_{32}), \quad (\text{A2})$$

where

$$y^{\text{chain}}(z_1, z_2, z_3) = \sqrt{y_c(\bar{\rho}(z_1)) \times y_c(\bar{\rho}(z_2))} \times \sqrt{y_c(\bar{\rho}(z_2)) \times y_c(\bar{\rho}(z_3))} \times \sqrt[3]{y_o(\bar{\rho}(z_1), \bar{\omega}_{\text{chain}}) \times y_o(\bar{\rho}(z_2), \bar{\omega}_{\text{chain}}) \times y_o(\bar{\rho}(z_3), \bar{\omega}_{\text{chain}})} \quad (\text{A3})$$

and $\tilde{\Gamma}(\Delta z_{12}, \Delta z_{32})$ is a geometric integral and $\Delta z_{12} = z_1 - z_2$. $\tilde{\Gamma}$ is given as

$$\tilde{\Gamma}(\Delta z_{12}, \Delta z_{32}) = \frac{\sigma^4 (r_c - \sigma)^2}{\Omega^3 \tilde{r}^2} \int_{r_{12}=r_{32}=\tilde{r}} H(r_{13} - \sigma) U(\Omega_1, \Omega_2) \times U(\Omega_2, \Omega_3) d\Omega_1 d\Omega_2 d\Omega_3 d\phi_1 d\phi_3. \quad (\text{A4})$$

Here, ϕ_1 is the azimuthal angle of particle 1 in a spherical coordinate system centered on particle 2 (particle 2 is the one bonded twice), ϕ_3 is the azimuthal angle of particle 3 in a spherical coordinate system centered on particle 2, and $\tilde{r} = \sigma + (r_c - \sigma)/2$ is a fixed distance for particles 1 and 3 in relation to particle 2. $\tilde{\Gamma}$ is independent of density so, for a given α_c it only needs to be evaluated once. The only approximation introduced in the evaluation of the geometric integral was for the radial integration of colloids 1 and 3 in the reference frame of colloid 2 that the integral had the same value, on average, as when $r_{12} = r_{23} = \tilde{r} = 1.05\sigma$; this approximation introduces the factor $\delta(r_{12} - \tilde{r}) \delta(r_{23} - \tilde{r}) (r_c - \sigma)^2$ and allows the integral to be calculated as a function of z . Given the small range of r where bonding is allowed, 0.1σ , this approximation introduces little error.

Similarly, X_{2c} and X_{ring} are given by

$$\frac{X_{2c}(z_2)}{X_o(z_2)} = \frac{(f_A)^2}{2} \int_{z_2-\tilde{r}}^{z_2+\tilde{r}} \int_{z_2-\tilde{r}}^{z_2+\tilde{r}} dz_1 dz_3 \rho(z_1) \rho(z_3) X_o(z_1) X_o(z_3) \times y^{\text{chain}}(z_1, z_2, z_3) \tilde{\Gamma}(\Delta z_{12}, \Delta z_{32}), \quad (\text{A5})$$

$$\frac{X_{\text{ring}}(z_1)}{X_o(z_1)} = \frac{(f_A)^3}{2} \int_{z_1-\tilde{r}}^{z_1+\tilde{r}} \int_{z_1-\tilde{r}}^{z_1+\tilde{r}} dz_2 dz_3 \rho(z_2) \rho(z_3) X_o(z_2) X_o(z_3) \times y^{\text{ring}}(z_1, z_2, z_3) \tilde{\Psi}(\Delta z_{21}, \Delta z_{31}), \quad (\text{A6})$$

where

$$y^{\text{ring}}(z_1, z_2, z_3) = \sqrt{y_c(\bar{\rho}(z_1)) \times y_c(\bar{\rho}(z_2))} \times \sqrt{y_c(\bar{\rho}(z_2)) \times y_c(\bar{\rho}(z_3))} \times \sqrt{y_c(\bar{\rho}(z_1)) \times y_c(\bar{\rho}(z_3))} \times \sqrt[3]{\hat{y}_o(\bar{\rho}(z_1), \bar{\omega}_{\text{ring}}) \times \hat{y}_o(\bar{\rho}(z_2), \bar{\omega}_{\text{ring}}) \times \hat{y}_o(\bar{\rho}(z_3), \bar{\omega}_{\text{ring}})} \quad (\text{A7})$$

and $\tilde{\Psi}(\Delta z_{21}, \Delta z_{31})$ is the ring geometric integral given by

$$\tilde{\Psi}(\Delta z_{21}, \Delta z_{31}) = \frac{\sigma^4 (r_c - \sigma)^2}{\Omega^3 \tilde{r}^2} \int_{r_{21}=r_{31}=\tilde{r}} \lambda(r_{23}) U(\Omega_1, \Omega_2) \times U(\Omega_2, \Omega_3) U(\Omega_1, \Omega_3) d\Omega_1 d\Omega_2 d\Omega_3 d\phi_2 d\phi_3. \quad (\text{A8})$$

Here, ϕ_2 is the azimuthal angle of particle 2 in a spherical coordinate system centered on particle 1 and ϕ_3 is the azimuthal angle of particle 3 in a spherical coordinate system centered on particle 1. Like the chain geometric integral the

ring integral $\tilde{\Psi}(\Delta z_{21}, \Delta z_{31})$ is evaluated using Monte Carlo integration.

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