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Quantitative description of the self-assembly of patchy particles into chains and rings

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We numerically study a simple fluid composed of particles having a hard-core repulsion complemented by two patchy attractive sites on the particle poles. An appropriate choice of the patch angular width allows for the formation of ring structures which, at low temperatures and low densities, compete with the growth of linear aggregates. The simplicity of the model makes it possible to compare simulation results and theoretical predictions based on the Wertheim perturbation theory, specialized to the case in which ring formation is allowed. Such a comparison offers a unique framework for establishing the quality of the analytic predictions. We find that the Wertheim theory describes remarkably well the simulation results. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4737930]

I. INTRODUCTION

The equilibrium self-assembly of particles into chains and rings has been the subject of thorough investigations in the past.[1–7] In the limit of non-interacting aggregates (i.e., low densities) and weakly T-dependent persistence length, a well defined temperature exists below which a ring of a characteristic size becomes equally probable as the chain of the same size. For lower T, rings start to populate the system and, under appropriate conditions, may become the most abundant aggregates. The basic elements controlling the competition between rings and chains are well understood.[8] Compared to linear polymers, rings are energetically stabilized by the presence of an additional bond but pay a significant cost proportional to the entropy loss associated to the necessity to constrain the end-to-end distance to distances of the order of the bonding length as well as a term proportional to the ring size arising from the number of ways a ring can open to form a chain. Despite the formal understanding, no quantitative parameter-free investigation of the ring-chain equilibrium for a well defined interaction potential has been reported so far. Two reasons suggest an effort in this direction: (i) the Wertheim perturbation theory[9,10] has been shown to be a predictive and quantitative theory for describing chaining of large persistence polymers, when rings do not compete.[11,12] While attempts to generalize to the case in which rings are relevant have been presented,[7,13–15] no quantitative comparison has been reported. (ii) The recent discovery that in the dipolar hard sphere (DHS) model a non-negligible fraction of rings appears at low T, in the region in which a gas-liquid critical point was expected to occur.[16,17] Analogous findings have been documented in both experiments and simulations of colloids in which the dipolar interaction is dominant.[18–22] Wertheim theory, when applied to patchy colloidal particles with asymmetric interactions,[23–26] provides a valuable model for interpreting the competition between chaining and branching, which is deemed to be essential in the physics of DHSs. It is thus important to extend it, under strict control, to the case in which rings are possible.

In the present article, we present a two-patch model with controlled persistence length and introduce an extension of Wertheim theory to cope with the presence of rings. For one specific value of the opening bond angle (a parameter of the interaction potential) we then solve the Wertheim theory augmented with rings and compare theoretical predictions with simulation results in a large density region, from $\rho\sigma^3 = 5 \times 10^{-6}$ up to $\rho\sigma^3 = 0.02$, illuminating the presence of an optimal density for ring formation. The quality of the resulting parameter-free description provides a stringent test of Wertheim theory as a model of the thermodynamics of the self-assembly of equilibrium chains and rings.

II. TWO PATCHY PARTICLE MODEL

We focus on a system of hard-sphere (HS) particles (of diameter σ, the unit of length) with two oppositely located patches. The patch-patch interaction is modeled via a Kern-Frenkel (KF) potential,[27] i.e., a square-well interaction of range Δ and depth u_0, multiplied by an angular function which accounts for the orientational contribution, such that particles bind only when distinct patches face each other. In the standard KF model the single-bond per patch condition depends on the patch angular width $\theta_{\max}$ and Δ. The maximum opening angle $\theta_{\max}$ must satisfy the condition $\sin(\theta_{\max}) \leq [2(1 + \Delta/\sigma)]^{-1}$. In the limit of a cohesive contact potential ($\Delta \to 0$), the maximum opening angle is 30°, a value for which the probability of ring formation is minute. To be able to extend the range of values of $\theta_{\max}$ beyond 30° and to decouple the choice of the angle from the choice of the range we take inspiration from the N_{max} model,[28,29] imposing numerically in the Monte Carlo (MC) code a constraint on the maximum number of bonds each patch can be involved in. In this way, only one particle can occupy the bonding volume, contributing u_0 to the potential energy. A double-stranded DNA with palindromic sticky overhangs at its extremities would be a possible experimental realization of such a particle. A careful choice of the strand sequences would make it possible to fulfill the single bond per patch condition and to control both the extension and the flexibility (i.e., the bonding volume) of the sticky ends.

Temperature is measured in units of the potential depth (i.e., $k_B/u_0 = 1$, where k_B is Boltzmann constant). The choice of a simple square-well interaction model to describe the association process between different particles is particularly convenient from a theoretical point of view. It allows for a clear definition of bonding and a clear separation of the bonding free energy in its energetic and entropic contributions, being unambiguously related to the depth of the well and to the bonding volume, respectively. In addition, the persistence length of the polymer is T-independent, due to the flatness of the attractive potential.

MC simulations in the NVT ensemble, with $N = 5000$ have been performed for five different densities $\rho = 0.000005$, 0.00007, 0.0005, 0.007, 0.02, and five different temperatures $T = 0.05$, 0.06, 0.07, 0.08, 0.09. The KF model parameters were set to $\Delta = 0.3$ and $\cos\theta_{\max} = 0.7077$, corresponding to a bonding volume $v_b = \frac{4}{3}\pi[(\sigma+\Delta)^3 - \sigma^3](1-\cos\theta_{\max})^2$. During equilibration, especially at very low ρ and T, we have implemented the Aggregation Volume Bias move proposed in Ref. 30, specialized to patchy particles. These moves are very effective at low densities, since they allow for a fast equilibration of the bonded–non-bonded chemical equilibrium. Such a move is described in depth in Ref. 25.

III. WERTHEIM THEORY

The first-order Wertheim thermodynamic perturbation theory (W-TPT) (Refs. 9, 10, and 31) provides an expression for the free energy of associating liquids. The Helmholtz free energy is written as a sum of the HS reference free energy F_{HS} plus a bond contribution F_{bond}, which derives by a summation over certain classes of relevant graphs in the Mayer expansion.[31] In the sum, closed loops graphs are neglected. The fundamental assumption of W-TPT is that the conditions of steric incompatibilities are satisfied: (i) no site can be engaged in more than one bond and (ii) no pair of particles can be double bonded. These steric incompatibilities are satisfied in the present model thanks to the location of the two sites and the chosen numerical algorithm which prevents multiple bonding.

The inclusion of the contribution of rings to the free energy is done like in Refs. 7, 13, and 14: the bonding free energy per particle of an homogeneous system is expressed as

$$\beta F_{bond}/N = \ln X_0 + 1 - 2X_A + \frac{X_A^2}{X_0} - f_c - f_r, \tag{1}$$

where X_0 is the fraction of particles that have no patches bonded ("free" monomers), X_A is the fraction of unbonded patches, and f_c and f_r are, respectively, the contribution of chains and of rings to the free energy. Under the assumptions of W-TPT, f_c is

$$f_c = 2\rho\Delta_{AA}X_A^2, \tag{2}$$

where ρ is the number density, and

$$\Delta_{AA} = \int g_{HS}(\vec{r})[\exp(\beta u_0) - 1]d\vec{r} = v_b[\exp(\beta u_0) - 1]. \tag{3}$$

In the previous expression, the pair correlation function of the reference fluid has been approximated by $g_{HS} = 1$, since only very low densities will be studied. The ring contribution is generalized to include the possibility of formation of rings of every size, and thus,

$$f_r = \frac{G_0}{\rho} \tag{4}$$

with

$$G_i = \sum_n n^i\,(2\rho\Delta_{AA}X_0)^n\,W_n. \tag{5}$$

This expression corresponds to the summation of closed loop graphs, and is calculated assuming that, consistently with the usual W-TPT, the bonds of a ring are independent. W_n is proportional to the number of configurations of a single ring with n bonds. In previous works,[7,13,14] W_n has been approximated using the exact expression for freely jointed chains.[32] Here we will use an expression based on simulation results (see Secs. IV and V A). It is also worth noticing that G_i is the ith moment of the ring size distribution. The formation of a ring of size n requires n particles with the two bonding sites available to form bonds: the density of such particles is ρX_0. Each of these particles can bond in two different orientations (thus the factor 2 in (5)) and the probability to form a bond, once the available sites of the two particles are chosen, is Δ_{AA}.

The bonding free energy (1) is then a function of X_0 and X_A and, at equilibrium, must be stationary with respect to variations of these densities. Minimizing (1) with respect to X_A and X_0, gives, respectively,

$$-1 + \frac{X_A}{X_0} - 2\rho\Delta_{AA}X_A = 0 \tag{6}$$

and

$$1 - \frac{X_A^2}{X_0} - \frac{G_1}{\rho} = 0. \tag{7}$$

These are the laws of mass action that establish the number of bonds and the number of rings in equilibrium, for a given set of thermodynamic variables (ρ, T). By replacing (6) in (1), one obtains for the equilibrium bonding free energy per unit volume,

$$\beta F_{bond}/V = \rho\ln X_0 + \rho - \rho X_A - G_0. \tag{8}$$

Notice that when there are no rings (i.e., $G_i = 0$ in the previous equations), one recovers the usual expressions obtained when only chain aggregates are considered (see, e.g., Refs. 23 and 25).

Thermodynamic calculations are straightforward, once an approximation for W_n is adopted. For fixed (ρ, T) the fractions X_0, X_A are calculated using (6) and (7) and the bonding free energy follows from (8).

IV. EQUIVALENCE WITH AN IDEAL GAS OF CHAINS AND RINGS DESCRIPTION

The free energy per unit volume of an ideal mixture of chains and rings can be written as

$$\beta F_{id.cl.}/V = \sum_n \rho_n^c \left(\ln \rho_n^c - 1 - \ln \tilde{q}_n^c \right) + \sum_n \rho_n^r \left(\ln \rho_n^r - 1 - \ln \tilde{q}_n^r \right), \tag{9}$$

where ρ_n^c is the density of chains of size n, ρ_n^r is the density of rings of size n, and $\tilde{q}_n^c$ and $\tilde{q}_n^r$ are the partition functions of a ring and of a chain of size n, divided by the volume V. The chemical equilibrium between chains and rings gives

$$\frac{\partial \beta F/V}{\partial \rho_n^c} = \frac{\partial \beta F/V}{\partial \rho_n^r} = n\beta\mu, \tag{10}$$

where μ is the chemical potential. Consistent with the ideal-gas hypothesis, the number density of monomers (i.e., particles with no bonds) ρ_1^c is related to μ by $e^{\beta\mu} = \rho_1^c$. Equations (9) and (10) give origin to the following expressions:

$$\frac{\rho_n^c}{\tilde{q}_n^c} = \frac{\rho_n^r}{\tilde{q}_n^r} = \exp(n\beta\mu) = (\rho_1^c)^n, \tag{11}$$

from which the relation between the chain and rings size distribution and partition functions follows

$$\rho_n^r = \rho_n^c \frac{\tilde{q}_n^r}{\tilde{q}_n^c}. \tag{12}$$

This shows that in the ideal-gas (of cluster) limit the ring size distribution is not an independent variable, but it is proportional to the chain size distribution times the ratio between the ring and chain partition functions.

The chain partition function can be written as

$$\tilde{q}_n^c = \lambda^{-3} \exp\left[-(n-1)\beta\mathcal{F}_b\right] \tag{13}$$

in terms of the thermal de Broglie wave length, λ, and of the free energy of a bond, $\mathcal{F}_b$. This expression corresponds to assuming that each of the $n - 1$ bonds lowers the free energy by $\mathcal{F}_b$. The ring partition function depends on the geometry of the model for short rings, while it reaches a well established asymptotic value for large n values, dictated by the self-similar nature of the growth process. More specifically, in the dilute limit,

$$\tilde{q}_n^r \propto \frac{v_b}{n R_{ee}^3(n)} \exp\left(-n\beta\mathcal{F}_b\right), \tag{14}$$

where v_b is the bonding volume and $R_{ee}(n)$ is the mean end-to-end distance of a chain of size n. Compared to linear polymers, rings are thus stabilized by the presence of n bonds (one more than a chain). On the other hand, the number of configurations allowing for ring formation are proportional to the ratio $v_b/R_{ee}^3(n)$. The additional n dependence arises from the number of ways a ring can open to form a chain.[4,5,33] Assuming that chains can be modeled with a self-avoiding walk process for large n (i.e., $R_{ee}(n) \sim n^{\nu_{SAW}}$, where $\nu_{SAW} = 0.588$ is the self-avoiding walk exponent), one can thus write

$$\tilde{q}_n^r = \alpha(n) n^{-(3\nu_{SAW}+1)} \exp\left(-n\beta\mathcal{F}_b\right), \tag{15}$$

where $\alpha(n)$ describes the model dependent short-n behavior and approaches a constant value for large n, when the self-similar nature of the ring is reached. The evaluation of $\alpha(n)$ for the chosen model is discussed in the following (Sec. V A).

Expression (9) can be simplified by using (11) to obtain,

$$\beta F_{id,cl.}/V = \rho \ln \rho_1^c - \sum_n \left(\rho_n^c + \rho_n^r\right). \tag{16}$$

Once approximations for $\mathcal{F}_b$ and $\alpha(n)$ are adopted, ρ_n^c and ρ_n^r can be expressed as a function of ρ_1^c via Eq. (12) and the latter can be calculated at a given (ρ, T) imposing the normalization condition,

$$\sum_n n\left(\rho_n^c + \rho_n^r\right) = \rho. \tag{17}$$

In order to demonstrate the equivalence between the ideal cluster of chains and rings description and that obtained using Wertheim theory (with the ideal gas as the reference system), we note that the quantities X_0 and X_A can be expressed in term of rings and chains distributions as

$$\rho X_A = \sum_n \rho_n^c \tag{18}$$

and

$$\rho X_0 = \rho_1^c. \tag{19}$$

The bond free energy $\beta\mathcal{F}_b$ can be related with the Mayer function of the bond via $\exp(-\beta\mathcal{F}_b) = 2\Delta_{AA}\lambda^{-3}$. Finally, the number of ring configurations W_n can be identified with

$$W_n = \alpha(n) n^{-(3\nu_{SAW}+1)}. \tag{20}$$

Via this set of equivalences, $\rho_n^r = (\rho_1^c)^n \tilde{q}_n^r$ (Eq. (11)) can be written as $(2\Delta_{AA}\rho X_0)^n W_n$ and Eq. (16) transforms to

$$\beta F_{id,cl.}/V = \rho \ln(\rho X_0) - \rho X_A - \sum_n (2\Delta_{AA}\rho X_0)^n W_n. \tag{21}$$

By defining the ideal gas free energy $F_{id} \equiv \rho \ln(\rho) - \rho$ and exploiting the definition of G_0 in Eq. (5) and of $\beta F_{bond}/V$ in Eq. (8), Eq. (21) becomes

$$\beta F_{id,cl.}/V = \beta(F_{bond} + F_{id})/V \tag{22}$$

proving that the free energy of an ideal gas of chains and rings can be written as the sum of the Wertheim bonding free energy and of the reference ideal gas free energy.

V. SIMULATION RESULTS

A. Estimate of the ring partition function

The evaluation of the free energy of a system of chains and rings requires the knowledge of the function $\alpha(n)$ introduced in Eq. (15). As discussed in Sec. IV, such function encodes all non-universal model properties and needs to be

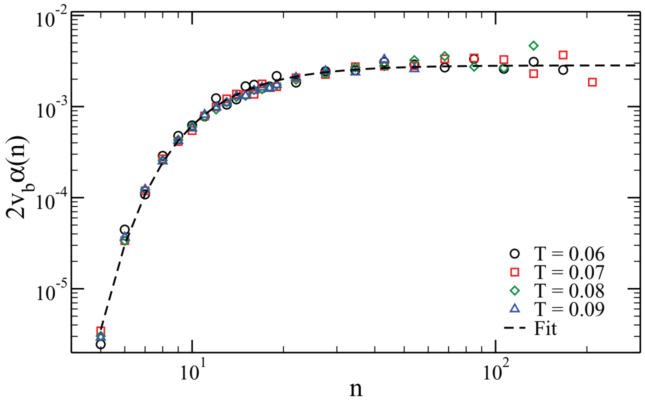

FIG. 1. Numerical evaluation of $\alpha(n)$ (Eq. (23)) at four different temperatures and $\rho = 0.007$. The line is the fit function (Eq. (24)).

evaluated independently.[34] For models (like the present one) in which the persistent length does not depend on T, the function $\alpha(n)$ does not depend on T and can thus be estimated at any (low density) state point, by evaluating the ratio between ρ_n^r and ρ_n^c. Indeed, from Eqs. (12) and (15),

$$\alpha(n) \equiv \frac{\rho_n^r}{\rho_n^c} n^{3\nu_{SAW}+1}\lambda^{-3}\exp(\beta\mathcal{F}_b). \tag{23}$$

Here we made use of the scaling relation between the ring exponent, ν exponent and the dimension $d = 3$,[35] and, consistently with the ideal gas of clusters approximation, use the value of ν for dilute systems , $\nu = \nu_{SAW}$.

Figure 1 shows $\alpha(n)$ evaluated at four different state points. The asymptotic value is reached only for chains longer than 30–50 particles. The minimum ring size is five. The numerical $\alpha(n)$ can be represented by the arbitrary fit function

$$\ln(2v_b\alpha(n)) = -5.86595\left[1+35.4697\cdot\exp\left(-\frac{\ln n}{0.468144}\right)\right], \tag{24}$$

and such expression has been used to evaluate theoretically all system properties.

B. Chain and ring distribution functions

Figure 2 shows the chain and the ring distribution functions for different T values at $\rho = 0.02$. The chain distributions are exponential, with a characteristic decay length that increases on cooling. The ring distributions are non-monotonic and increase their width and amplitude on cooling, signaling the progressive increasing concentration of rings. The position of the peak in the ring distribution functions, whose presence is due to the existence of a preferred cluster size determined by the interplay between energy and entropy, is model dependent and can be tuned by changing the angular width of the patches.

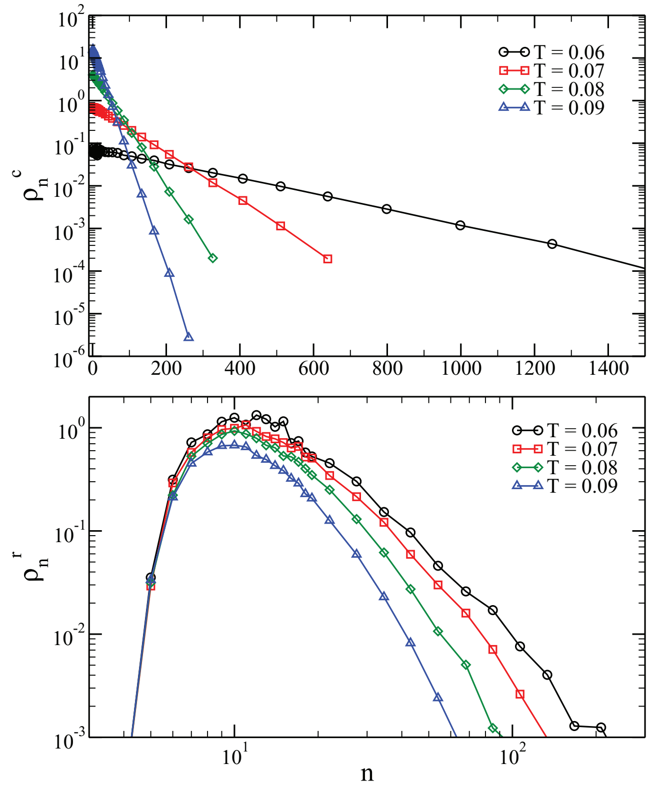

FIG. 2. Chain and ring size distribution functions at $\rho = 0.02$ and different temperatures T.

Figures 3 and 4 show the average size of chains M^c and rings M^r, defined respectively as $M^c = \sum n\rho_n^c/\sum \rho_n^c$ and $M^r = \sum n\rho_n^r/\sum \rho_n^r$, as a function of inverse T and ρ. Both M^c and M^r increase monotonically upon cooling the system and increasing density, but the effect of changing ρ and T is much more dramatic on M^c. Indeed, M^c spans three order of magnitude in the studied range of parameters, whereas M^r changes of a mere factor of 5 going from $T = 0.09$, $\rho = 0.000005$ to $T = 0.06$, $\rho = 0.02$.

The theoretical predictions shown in these figures are calculated using,

$$M^c = \frac{1 - G_1/\rho}{X_A} \tag{25}$$

and

$$M^r = \frac{G_1}{G_0}. \tag{26}$$

Given the low densities studied (that make Wertheim theory almost exact) and the numerical approximation adopted for the partition function of rings, the very good agreement with the simulation results is expected. In Figs. 3(a) and 4(a) the result obtained when rings are neglected is also shown. One can conclude that the effect of rings in the chain size distribution becomes important at low ρ and T. For fixed low ρ, the decrease in T increases this influence. On the other hand, for fixed low T, this effect is important in a range of intermediate ρ; this range increases for lower T.

C. The onset temperature

We have seen in Sec. IV that in the limit of non-interacting clusters, the ratio between ring and chain distributions is controlled by the ratio of the ring and chain partition

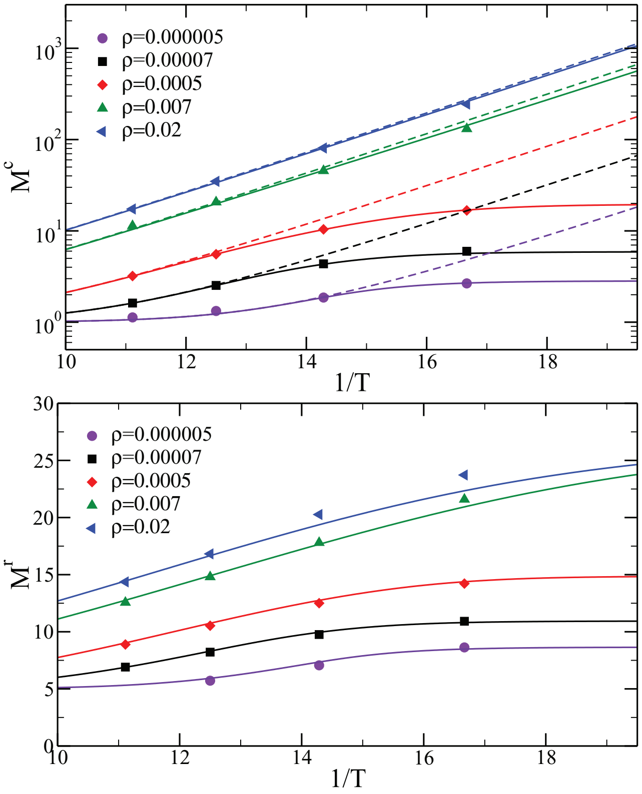

FIG. 3. Average cluster size of chains (top) and rings (bottom) as a function of the inverse temperature for different ρ. Symbols are numerical results; solid lines are the theoretical predictions of (25) and (26); dashed lines are the theoretical predictions when rings are excluded from Wertheim theory.

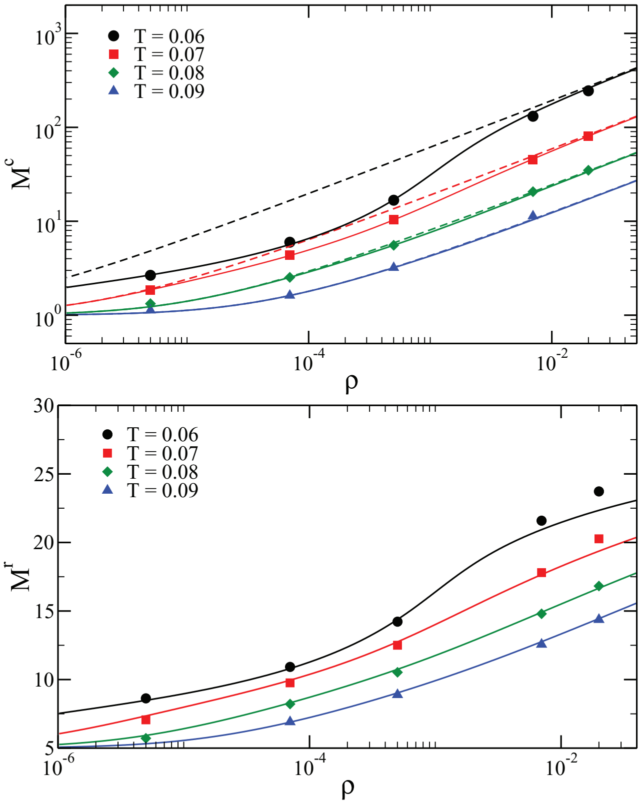

FIG. 4. Average cluster size of chains (top) and rings (bottom) as a function of ρ for different T. Symbols and lines as in Fig. 3.

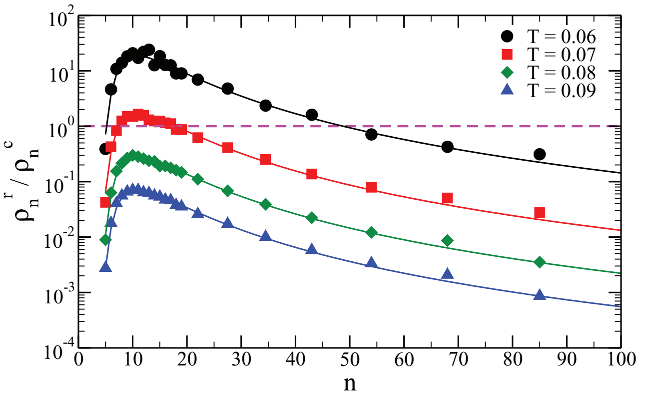

FIG. 5. Ratio between ρ_n^r and ρ_n^c at four different T and $\rho = 0.02$. The dashed line indicates $\rho_n^r/\rho_n^c = 1$, to visualize the range in n for which, at a given $T > T_{onset}$, rings become more probable than chains. The full lines are the theoretical predictions for this ratio calculated using (3), (23), and (24).

functions. Such ratio has a maximum at a specific ring size and approaches zero both at smaller sizes, due to the difficulty to form rings of sizes comparable to the persistence length and at large sizes, where the entropy cost of localizing the chain-ends controls aggregation. Figure 5 shows the ratio $\frac{\rho_n^r}{\rho_n^c}$ for the present model, at five different T and $\rho = 0.02$. All the curves retain the same shape, peaking at $n^c_{max} \approx 10 - 11$, but their amplitude strongly depends on T, via the factor $\exp \beta\mathcal{F}_b$. The T dependence provides a way of defining an onset temperature for rings (T_{onset}), for example as the T at which $\frac{\rho^r_{n_{max}}}{\rho^c_{n_{max}}} = 1$, as

$$\exp\left(\frac{\mathcal{F}_b}{k_B T_{onset}}\right) = \alpha(n_{max}) n_{max}^{-(3\nu_{SAW}+1)}. \qquad (27)$$

For the present model, $T_{onset} \approx 0.075$.

D. Potential energy

Fig. 6 shows the potential energy per particle U/N (proportional to the number of bonds) for different T and ρ. The energy decreases in a small interval of T, approaching a value $-u_0$, which describes the condition in which all possible bonds are formed, at the smallest investigated T. The figure also shows the Wertheim theoretical predictions, both including and excluding the possibility of ring formation. At large T, rings are negligible and both theories provide the same predictions, but around and below the onset temperature, the presence of rings significantly modify the T-dependence of U, giving rise to a faster approach to the ground state energy. The extended Wertheim theory captures extremely well the T and ρ dependence of the energy.

E. Fraction of particles in rings

To globally assess the behavior of the system, we evaluate the T and ρ dependence of the fraction of particles in rings, defined as

$$f_{pr} = \frac{\sum_n n\rho_n^r}{\rho} = \frac{G_1}{\rho}. \qquad (28)$$

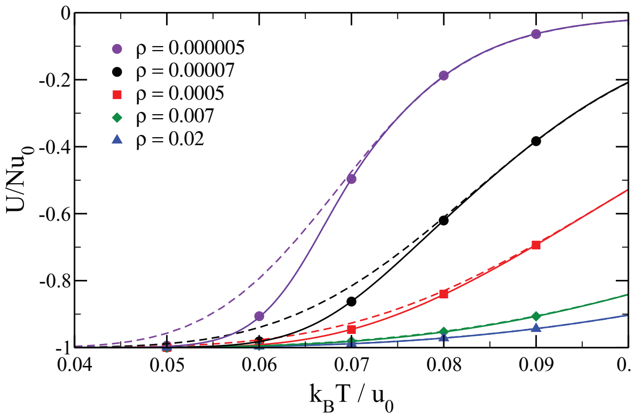

FIG. 6. Potential energy (proportional to the number of bonds) per particle as a function of T for several ρ values. Symbols are MC results. Lines are theoretical predictions for the case in which rings are either excluded or included in Wertheim theory.

The results are shown in Fig. 7. The quantity f_{pr} shows a non-monotonic behavior as a function of ρ, decreasing both for small and large densities. The non-monotonic behavior of f_{pr} is a consequence of the non-monotonic n dependence of the ratio $\frac{\rho_n^r}{\rho_n^c}$, which is strongly peaked around n_{max}. Along a constant T path, the concentration of rings is expected to have a maximum when the average size of the aggregates is of the order of n_{max} (see Fig. 4(b)). Hence, f_{pr} decreases when ρ is so small that only very small clusters are present as well as when ρ is so large that the average chain length is much longer than n_{max}. Indeed, on increasing ρ, the number of bonds in the system increases (see Fig. 6), favoring the formation of chains longer than n_{max}.

Figure 7 shows also the theoretical evaluation of f_{pr} based on the Wertheim theory, with no fitting parameters. As for the potential energy, the theory very accurately captures the ρ and T dependence of f_{pr}.

VI. CONCLUSIONS

Recent studies[12] have shown that an accurate modeling of chaining in patchy particle systems in dilute conditions can be achieved via the Wertheim thermodynamic perturbation theory, without resorting to any fitting parameter. In this article, we have extended this approach to the case in which chaining competes with the formation of ring structures, once more comparing "exact" numerical results with predictions based on the Wertheim thermodynamic perturbation theory, augmented to include the description of close loops of bonded particles.[7,13,14] While the Wertheim theory provides an expression for the chain partition function, valid in the limit of persistent chains, the ring partition functions is one additional input to the theory. We have resorted to a numerical evaluation of such a quantity, consistent with the expected limits—based on the statistic of self-avoiding walks—for large ring sized. The resulting model-dependent expression describes properly all ring sizes at low ρ, incorporating the non-universal properties of the KF-model.

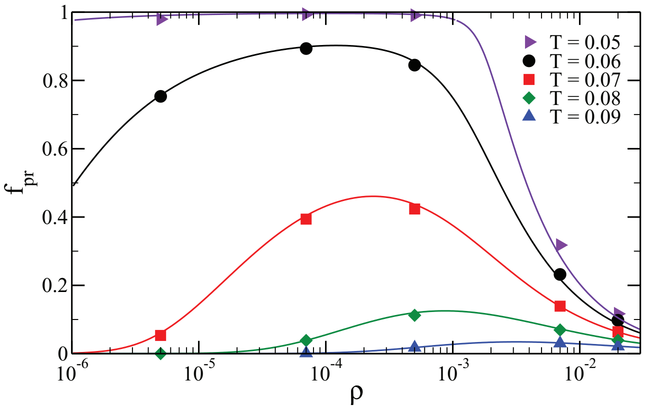

FIG. 7. Fraction of particles in rings f_{pr} evaluated from MC simulations (symbols), and with Wertheim theory (lines).

We find that the augmented Wertheim theory properly captures the ρ and T dependence of the aggregation phenomenon. It is able to predict with extreme accuracy the non-monotonic behavior of the fraction of particles in rings on increasing ρ at low T. Indeed, the system evolves from a collection of very short chains at extremely small densities, to a state in which almost of particles are in rings, and back to a state in which long polymers dominate again for large densities. The region where rings dominate is confined at low T (where the presence of an additional bond energetically stabilizes rings as compared to a chain of corresponding size) and at low densities (where the average cluster size is limited). The ρ and T dependence of the number of bonds (i.e., the energy) or of the average cluster size of chains and rings is also predicted with very high accuracy.

The ability of Wertheim theory to also model the delicate equilibrium between chains and rings, together with the previously explored ability of the Wertheim theory to model the thermodynamics of chaining and branching, suggests that it will be possible to combine the two approaches and derive an accurate theory for systems in which rings, chains and branched structures coexist. It is particularly important to find out under which conditions the branching-induced gas-liquid critical point, survive in the presence of ring formation. It has indeed been shown[36] that low-valence patchy particles are characterized by a branching driven critical point at rather low densities, i.e., in the same region where rings can be dominant. The scenario in which rings, chains and branched structures coexist and compete has been recently observed in low T simulations of dipolar hard sphere (DHS) fluids, in both two[37] and three[17] dimensions, one of the canonical models for self-assembly. It has been suggested that the observed increase in ring structures could possibly provide an example of phase separation suppressed by self-assembly.[16] Theories developed to describe the gas-liquid phase separation in these systems mainly focus on the delicate balance between chaining and branching.[24,25,38] Since the presence of rings alters this balance, a new theoretical framework which also takes into account rings is needed. The remarkably good agreement between numerical results and theoretical predictions based on the augmented Werheim reported in this article strongly suggests to tackle the low-T DHS behavior by further extending the theory to incorporate branching. Such a study is underway.

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APPENDIX A: SINGLE CHAIN PROPERTIES

In this section, we discuss the properties of the polymer chains resulting from the KF model, for different values of the patch angle $\theta_{\max}$. Simulation and theoretical results are compared.

The end-to-end distance $R_{ee}^2(n)$ is shown in Fig. 8 for several values of $\cos(\theta_{\max})$, from 0.5 up to one. The simulation results show that on increasing $\cos(\theta_{\max})$, chains becomes stiffer and the transition from the initial n^2 to the large n limit $n^{2\nu_{SAW}}$ progressively moves to larger and larger n values. The theoretical calculations are done assuming an analogy between the chains formed with KF interactions, and the freely rotating jointed chain model,[8] for which the end-to-end distance is

$$\left\langle R_{ee}^2(n)\right\rangle = \sum_{i=1}^{n}\sum_{j=1}^{n}\bar{\ell}^2(\cos\theta)^{|j-i|}, \tag{A1}$$

where $\bar{\ell}$ is the bond length, $\langle\dots\rangle$ represents an ensemble average and θ is the angle of two consecutive bonds (bond angle). The analogy proceeds by assuming that, in the *KF* model, the bond length and the bond angle are not fixed but are restricted to some values, that depend on the two parameters of the model (the range Δ and the angular width $\theta_{\max}$). The mean value of the square of the bond length for the *KF* model is

$$\bar{\ell}^2 = \frac{\int_\sigma^{\sigma+\Delta} r^4 dr}{\int_\sigma^{\sigma+\Delta} r^4 dr} = \frac{3}{5}\sigma^2\frac{(1+\frac{\Delta}{\sigma})^5-1}{(1+\frac{\Delta}{\sigma})^3-1}. \tag{A2}$$

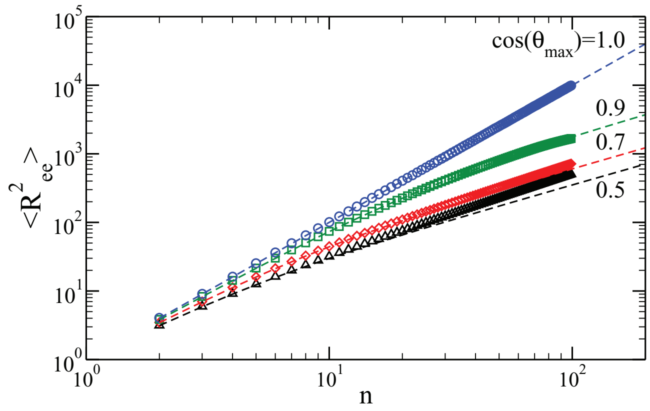

FIG. 8. Mean of the square of the end to end distance for the KF chains, for the indicated values of the parameter $\cos(\theta_{\max})$. The symbols are results from numerical simulations. The dashed lines are $\langle R_{ee}^2(n)\rangle/\bar{\ell}^2$, calculated using (A4).

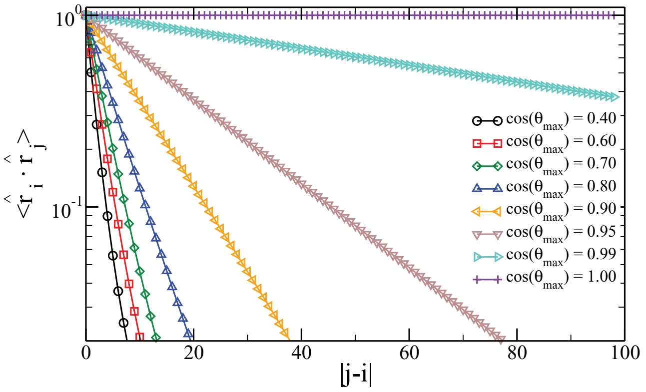

FIG. 9. Correlation function $\hat{r}_i \cdot \hat{r}_j$ as a function of $|j-i|$ for different $\cos\theta_{\max}$.

The mean bond angle can be calculated by considering 3 consecutive monomers in a chain $(i-1, i, i+1)$. Defining $\hat{r}_j$ as the unit vector of the direction of the bond between monomers $j-1$ and j, and $\hat{\mu}_j$ as the unit vector defining the position of the patch in monomer j, the mean bond angle is

$$\cos\theta = \frac{\int \hat{r}_i \cdot \hat{r}_{i+1} d\hat{r}_i d\hat{r}_{i+1} d\hat{\mu}_i}{\int d\hat{r}_i d\hat{r}_{i+1} d\hat{\mu}_i} = \left(\frac{1+\cos\theta_{\max}}{2}\right)^2. \tag{A3}$$

The integrals in this expression are calculated over the domain defined by the restrictions of the KF potential: $\hat{r}_i \cdot \hat{\mu}_i > \cos\theta_{\max}$ and $\hat{r}_{i+1} \cdot \hat{\mu}_i > \cos\theta_{\max}$. Therefore, the expression adopted for the mean square end-to-end distance is obtained using (A1),

$$\left\langle R_{ee}^2(n)\right\rangle = n\bar{\ell}^2\frac{1+\cos\theta}{1-\cos\theta}\left(1-\frac{2\cos\theta}{\sin^2\theta}\frac{1-\cos^n\theta}{n}\right), \tag{A4}$$

with $\bar{\ell}^2$ and $\cos\theta$ given by (A2) and (A3), respectively.

Figure 8 compares the predictions of the freely rotating jointed chains with the numerical results. The initial part is properly described by the model. As expected, the agreement deteriorates on increasing the polymer length due to the two different asymptotic behaviors characterizing the

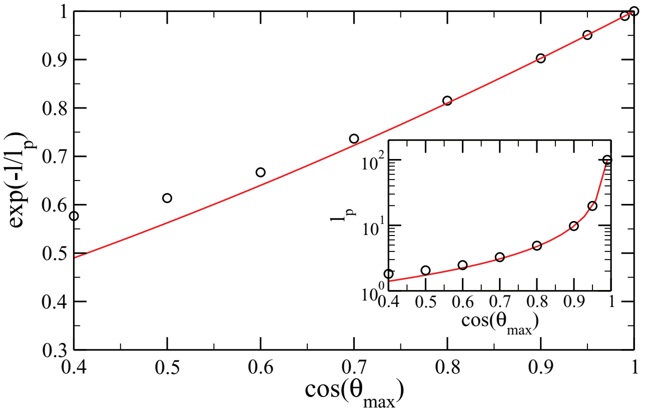

FIG. 10. Persistence length of the KF chains as a function of the parameter of the model $\cos(\theta_{\max})$. Symbols are the results of numerical simulations; the line is the calculation resulting from (A5).

MC data (SAW) and the theoretical predictions (mean field, $\nu_{MF} = 0.5$).

The correlation function $\hat{r}_i \cdot \hat{r}_j$ vs $|j - i|$ (the distance along the chain) for different values of $\cos(\theta_{\max})$ is reported in Fig. 9. The initial decay of this correlation function can be well described via an exponential decay, $\sim e^{-|i-j|/\ell_p}$ providing a mean to estimate the persistence length ℓ_p. This estimate is compared, in Fig. 10, with the theoretical prediction obtained from the analogy with freely rotating jointed chain,

$$\exp(-\ell/\ell_p) = \frac{(1+\cos(\theta_{\max}))^2}{4}. \tag{A5}$$

Agreement is obtained for large values of $\cos\theta_{\max}$, i.e., when ℓ_p is large.

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