P H Y S I C A L   R E V I E W   L E T T E R S

Self-Assembly in Chains, Rings, and Branches: A Single Component System with Two Critical Points

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We study the interplay between phase separation and self-assembly in chains, rings, and branched structures in a model of particles with dissimilar patches. We extend Wertheim's first order perturbation theory to include the effects of ring formation and to theoretically investigate the thermodynamics of the model. We find a peculiar shape for the vapor-liquid coexistence, featuring reentrant behavior in both phases and two critical points, despite the single-component nature of the system. The emergence of the lower critical point is caused by the self-assembly of rings taking place in the vapor, generating a phase with lower energy and lower entropy than the liquid. Monte Carlo simulations of the same model fully support these unconventional theoretical predictions.

Self-assembly of finite-size aggregates requires strong interaction energies compared to the thermal energy to guarantee that the generated structure is persistent. As a result, self-assembly competes with the ubiquitous macroscopic phase separation, the low-temperature tendency common to atoms, molecules, and larger particles to maximize the number of bonded neighbors and minimize the potential energy, giving rise to a condensed (liquid) state [1]. Soft matter and biology offer several examples of particles arranging themselves into low energy and weakly interacting finite-size aggregates (e.g., micelles, vesicles, capsids [2,3]), completely suppressing phase separation [4–6].

The possibility of forming ordered structures is facilitated by the presence of strong, directional, and saturable interactions (limited valence) [7–9]. Stimulated by the synthesis of new-generation patchy colloids [10–13], several studies have deepened our understanding of the competition between self-assembly and phase separation. More specifically, we refer to a numerical study of Janus colloids [14,15], where the formation of energetically stable vesicles stabilizes at low-temperature T the gas phase, and to a study of particles forming chains and branched structures [16–18], introduced to model the phase behavior of dipolar fluids [19]. In both models, at low T self-assembly opens up a low-density region of thermodynamic stability in which no macroscopic phase separation takes place.

In this Letter we investigate the competition between phase separation and self-assembly in a model specifically designed to favor the formation of energetically stable ring structures. Extending Wertheim's theory to the case in which chains, branched structures, and rings coexist, we are able to solve the model, providing a parameter-free analytic formulation of a thermodynamic system in which

phase separation is suppressed at low T by self-assembly. We find theoretically, and confirm numerically, that macroscopic phase separation can be limited to intermediate T via the intervention of a closed coexistence loop in the $T - \rho$ plane, providing a neat mechanism for understanding the smooth disappearance of the phase separation. Our results are consistent with and provide a theoretical base to a recent numerical investigation of a ring-forming model on a lattice in two dimensions [20].

Model.—We study a modification of the model of patchy particles which was specifically designed to present a competition between chains and branched structures. In Ref. [17] particles were modeled as hard spheres of diameter σ, with patches of two types on their surface: 2 patches of type A on the poles. and n patches of type B equally spaced over the equator. When two patches of type α and β ($\alpha, \beta \in A, B$) are close enough and properly oriented (see Supplemental Material [21] for details), a bond $\alpha\beta$ is formed. Each bond $\alpha\beta$ is characterized by a bonding energy $\epsilon_{\alpha\beta}$ (the decrease in energy upon bond formation) and a bonding volume $v_{\alpha\beta}$. By setting $\epsilon_{BB} = 0$, only AA and AB bonds are retained: AA bonds correspond to linear self-assembly (in chains or rings) and AB bonds to branching points or junctions. As in the previous study [17], we set $\epsilon_{AB} < 0.5\epsilon_{AA}$ to make the formation of chains energetically favorable at low T and $n = 9$ and $v_{AB} \gg v_{AA}$ to make branching entropically favorable [18]. The positions and sizes of the patches are chosen to satisfy the single-bond-per-patch condition.

Locating the two A patches on the poles (as in [17]) generates very long and persistent chains, effectively suppressing the formation of rings. In this case the competition between chains and branching originates a liquid vapor phase separation in which the gas-liquid binodal is

reentrant: the density of the coexisting liquid approaches the density of the coexisting gas [17,18,22]. In the present work we add the possibility of ring formation by selecting an off-pole position of the A patches [20]. This very simple modification alters the persistence length of the chains and favors the formation of rings, structures entropically unfavored but energetically stabilized by the additional bond compared to chains of the same size. Moreover, self-assembly in rings decreases the possibility of forming junctions. In fact, when two chains assemble to form a longer chain, two unbounded A patches (capable of forming a junction) still remain, but when a chain folds into a ring, A patches saturate and become unavailable to form junctions.

Theory.—Wertheim's theory has successfully described the effect of association in the phase diagram of molecular fluids [23] and has, more recently, provided free-parameter descriptions of the properties of patchy particle models [8,18,22,24]. Extensions of the theory to include the effects of ring formation have been limited to the cases of particles with two patches [25–29], with one patch, but allowing the formation of rings with three particles by double bonding [30] or, very recently, with three patches but with some limitations [31]. In any case, a single energy scale (the same for all patches) was considered and no study of phase diagrams was carried out. In this work, we extend Wertheim's first order perturbation theory for patchy particle models with dissimilar patches to the case where rings are formed. Rings can be of any size i and are considered to be sequences of particles bonded through i consecutive AA bonds, regardless of the presence of branching via the B patches. The free energy per particle βf is the sum of the reference hard-sphere free energy and a perturbative term βf_b that includes both the Wertheim's first order perturbation theory approximation βf_W and a ring contribution $-c_r$, such that $\beta f_b = \beta f_W - c_r$.

Following Wertheim's nomenclature [32,33], we define the following quantities: (i) Γ is the set of patches of each particle. In the present work, $\Gamma \equiv \{A_1, A_2, B_1 \ldots B_n\}$; the patches of each type are assumed to be equivalent (an approximation, given the location of the patches over the hard sphere in the model); (ii) γ is a subset of Γ, i.e., a group of patches, chosen from Γ, with no repetition (γ can be the empty set $\varnothing$); (iii) $P(\Gamma)$ is a partition of Γ; the elements of $P(\Gamma)$ are therefore groups of patches chosen from Γ (i.e., sets γ, except $\varnothing$), without repetition and using all the patches; $M(P)$ will denote the number of elements of the partition; (iv) ρ_γ is the density of particles whose patches contained in γ ($\gamma \subset \Gamma$) are bonded, and σ_γ is the density of particles whose patches that do not belong to γ are unbonded. These densities are linearly related: $\sigma_\gamma = \sum_{\gamma' \subset \gamma} \rho_{\gamma'}$; notice that the total density is $\rho \equiv \sigma_\Gamma$. (v) Using the densities σ_γ and the fact that all patches of each type are equal, one defines the probabilities $Y_{n_A(\gamma), n_B(\gamma)} \equiv \sigma_\gamma / \rho$, where $n_A(\gamma)$ and $n_B(\gamma)$ are the

number of A and the number of B patches of γ, respectively. $Y_{i,j}$ is therefore the probability of finding a particle with a specific set of $2 - i$ A and $n - j$ B patches unbonded. f_W is a function of the probabilities $Y_{i,j}$:

$$\beta f_W = \ln Y_{0,0} - 2Y_{1,n} - nY_{2,n-1} + 1 + K - c_b, \quad (1)$$

with [32–34]

$$c_b = 2Y_{1,n}^2 \rho \Delta_{AA} + 2n Y_{1,n} Y_{2,n-1} \rho \Delta_{AB} \quad (2)$$

and [32,33]

$$K = \sum_{P(\Gamma)} (-1)^M (M-2)! Y_{0,0}^{1-M} \prod_{\gamma \in P(\Gamma)} Y_{n_A(\gamma), n_B(\gamma)}. \quad (3)$$

In Eq. (2), $\Delta_{\alpha\beta}$ are integrals of the Mayer function of the interaction between patches α and β, weighted by the pair correlation function of the reference system [18]. In Eq. (3), the sum is over all possible partitions $P(\Gamma)$ with $M(P) \geq 2$.

The contribution of rings to the free energy is

$$c_r = \frac{G_0}{\rho}, \quad (4)$$

$$G_k = \sum_i i^k W_i (2\rho \Delta_{AA} Y_{0,n})^i. \quad (5)$$

Here, G_k is the kth moment of the ring density size distribution [28]: G_0 is then the total density of rings and G_1/ρ the fraction of particles in rings. Each term of the sum in Eq. (5) represents the density of rings of size i. W_i is the number of configurations of a ring of size i; the formation of such a ring requires i particles with the two A patches unbonded (the B's can be bonded or unbonded), whose density is $\rho Y_{0,n}$; each of these particles has two possible orientations and Δ_{AA} is the probability of forming an AA bond, once the two A unbonded sites are chosen. The quantities W_i are calculated numerically, similarly to what has been done in [28].

The calculation of the approximation for the free energy proceeds by minimizing $\beta f_b = \beta f_W - c_r$ [Eqs. (1) and (4)] with respect to all $Y_{i,j}$ with $(i, j) \neq (2, n)$. This minimization is done in two steps: (i) minimization with respect to the probabilities $Y_{i,j}$ on which the terms c_b and c_r do not depend, and (ii) minimization with respect to $Y_{2,n-1}$, $Y_{1,n}$ and $Y_{0,n}$. From minimization (i), the probabilities $Y_{i,j}$ are obtained as a function of $Y_{2,n-1}$, $Y_{1,n}$, $Y_{0,n}$,

$$Y_{i,j} = Y_{i,n} Y_{2,n-1}^{n-j}, \quad (6)$$

for $i = 0, 1, 2$. These equations express the independence of bonding probabilities, which is at the core of Wertheim's theory: the probability $Y_{i,j}$ is the product of the probability of finding a particle with a specific set of $2 - i$ sites A unbonded, $Y_{i,n}$, times the probability of finding a particle with a specific B patch unbonded raised to the power $n - j$, $Y_{2,n-1}^{n-j}$. After replacing Eq. (6) in Eq. (1), the second

minimization step is performed and the so-called laws of mass action are obtained:

$$X_A^2 = Y\left(1 - \frac{G_1}{\rho}\right), \tag{7}$$

$$1 - X_A = \frac{G_1}{\rho} + n\rho\Delta_{AB}X_B X_A + 2\rho\Delta_{AA}X_A^2, \tag{8}$$

$$1 - X_B = 2\rho\Delta_{AB}X_A X_B, \tag{9}$$

where we have changed to the simpler notation used in other works [18,28,34]: $X_A \equiv Y_{1,n}$, $X_B \equiv Y_{2,n-1}$, and $Y \equiv Y_{0,n}$. Note that X_A and X_B are the fraction of unbonded patches of type A and B, respectively, and Y is the fraction of particles with both patches A unbonded. Equation (7) shows that, because of ring formation, the state (bonded or unbonded) of the patch A_1 of a given particle is not independent of the state of the patch A_2, i.e., $Y \neq X_A^2$. The other laws of mass action have the usual meaning [35]: Eq. (8) states that the probability that an A patch is bonded $(1 - X_A)$ is equal to the sum of the probabilities that the particle belongs to a ring (G_1/ρ) and that an unbonded A patch bonds to a B or to a A patch; similarly, Eq. (9) states that the probability that a B patch is bonded $(1 - X_B)$ equals the probability that an unbonded B patch bonds to an A patch. After replacing Eqs. (6)–(9) in Eq. (1), a final expression for the (minimized) free energy is obtained:

$$\beta f_b = \ln(Y X_B^n) - X_A - \frac{n}{2}X_B + \frac{n}{2} + 1 - \frac{G_0}{\rho}. \tag{10}$$

This set of equations defines the thermodynamics of the model, within Wertheim's first order perturbation theory extended to include rings; the values of X_A, X_B, and $f_r \equiv G_1/\rho$ (the fraction of particles that belong to rings) provide information about the self-assembled structures.

Results.—Figure 1 shows the theoretical results for the gas-liquid coexistence, with and without rings. When rings are present the theory predicts, in a one-component system, a closed loop and the existence of two critical points at T_c^u, the critical temperature of the upper critical point, and at T_c^l, that of the lower critical point. The coexistence curve is characterized by a reentrant behavior in both the liquid and the vapor sides. Indeed, when T is decreased below a certain value, the density of the liquid decreases and the density of the vapor increases. Coexistence is present only for intermediate T. Below $T < T_c^l$ the system remains homogeneous for all T, completely suppressing any phase separation. Varying the parameters of the model, the closed loop can be progressively shrunk up to the point it disappears, leaving a system for which self-assembly is the unique mechanism for aggregation.

The structure of the coexisting phases may be investigated through the calculation at coexistence of the fraction of particles in rings f_r, the fraction of ends f_e, defined as
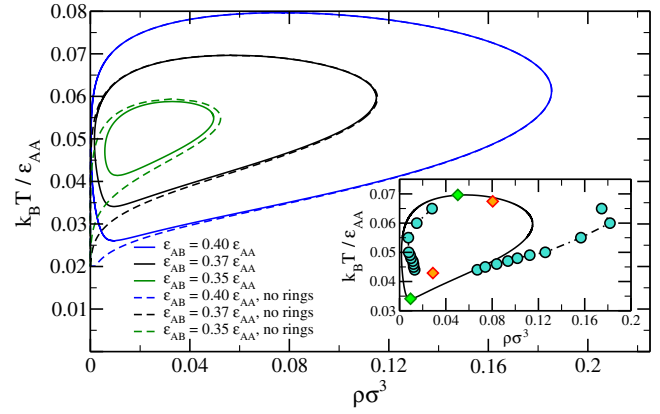

FIG. 1 (color online).   Theoretical phase diagram in the (ρ, T) plane, with (full lines) and without (dashed lines) ring clusters for three different values of the branching energy ϵ_{AB}. Inset: Theoretical (solid line) and simulation (circles) results for the $\epsilon_{AB} = 0.37\epsilon_{AA}$ model. Green and red diamonds mark theoretical and numerical critical points, respectively.

the number of unbonded A patches per particle $f_e \equiv 2X_A$ [18], and the fraction of junctions f_j, defined as the number of bonded B patches per particle $f_j \equiv n(1 - X_B)$ [18]. Figure 2 shows the T dependence of f_r, f_e, and f_j along the coexistence curve, for both gas and liquid phases. Close to T_c^u both phases exhibit almost no rings: the vapor is characterized by smaller f_j and larger f_e, meaning that it is formed by relatively short and isolated chains, while the liquid contains larger branched chains connected by junctions (a network fluid). Coexistence is then obtained
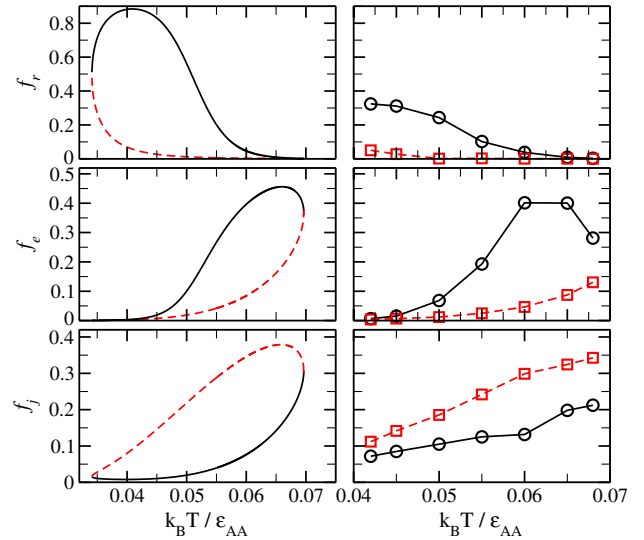

FIG. 2 (color online).   Structural properties calculated at coexistence using Wertheim's theory (left-hand panels) and simulation results (right-hand panels). From top to bottom: Fraction of particles in rings f_r, fraction of chain ends f_e, and fraction of junctions f_j. Solid black (dashed red) lines and symbols refer to the vapor (liquid) phase.

between a low-density gas of short chains with a few junctions and a network of long chains connected through junctions [17–19,36]. Upon cooling, in the vapor phase f_r increases to significant values, f_e decreases significantly, and f_j decreases slightly; this means that isolated chains start self-assembling into rings. On the other hand, in the liquid f_r remains small and f_e and f_j decrease slightly, thus meaning that the network of chains is formed by longer chains and fewer junctions. Therefore, coexistence at these intermediate T is between a vapor where rings dominate and a network fluid formed by chains and junctions. Finally, close to T_c^l, as T decreases, f_r decreases for the vapor phase and increases for the liquid phase, f_j slightly increases for the vapor phase and decreases for the liquid phase, while $f_e \approx 0$ for both phases. Thus, these phases are evolving toward a network of fully connected chains and rings (i.e., with practically all patches A bonded, since $f_e \approx 0$), with more particles in rings (chains) in the vapor (liquid) phase.

The theoretical evaluation of the differences in entropy (ΔS) and in internal energy (ΔU) between the liquid and the vapor phases, Fig. 3, is illuminating. It clarifies the different nature of the two critical points. Just below the upper critical point the liquid has, as usual, lower entropy and lower energy than the vapor. On the other hand, close to the lower critical point, it is the vapor that possesses lower energy and lower entropy. The self-assembled ring clusters are very stable energetically and more conformationally ordered. The loss of entropy associated with closing a chain into a ring is compensated by the energetic stabilization introduced by the additional bond. This facilitates the replacement of chains by rings in the vapor phase at low T. Rings have much lower energy and entropy than chains, causing the inversion of the usual order relation between the values of these quantities in coexisting phases.
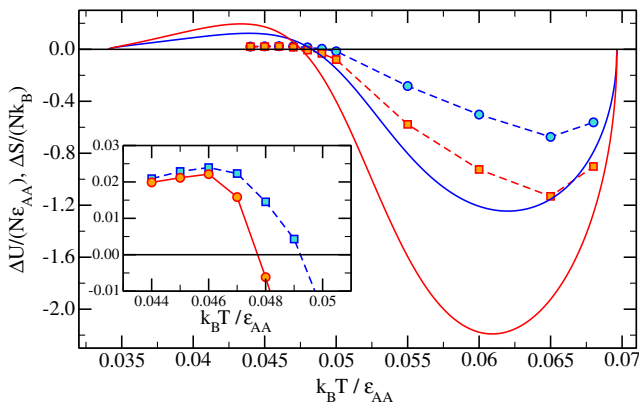

FIG. 3 (color online). Difference in internal energy per particle $\Delta U/(N\epsilon_{AA})$ (blue) and entropy per particle $\Delta S/(NK_B)$ (red) between the liquid and vapor phases, as computed by Wertheim's theory (solid lines) and in simulations (symbols and dashed lines). Inset: Enlargement of simulation results in the region near the lower critical point.

Simulations.—The phase equilibria is investigated with successive umbrella sampling simulations [37] in the grand canonical ensemble with specific moves significantly speeding up equilibration, allowing for the evaluation of the density of states $P(\rho, U)$, at fixed activity z, T, and volume V. Specifically, we have implemented the aggregation-volume bias [38] algorithm, its specialization to the case of chain-forming patchy colloids (end-hopping move [18]), and a novel cluster-swap move which attempts to swap chains and rings of the same size. All these methods are discussed in detail in the Supplemental Material [21]. With all these techniques and a significant amount of computation (of the order of 1000 months on a single core), we have been able to study the behavior of the system down to $T = 0.039$. The box side is $L = 14$ for $T > 0.055$ and $L = 22.2$ otherwise. We use the standard Bruce-Wilding method to pinpoint the location of the critical points [39]. In order to properly estimate the lower critical parameters, we join several $P(\rho, U)$ computed at different T by implementing the multiple-histogram reweighting method [40].

Figures 1–3 show the simulation results for the phase diagram, f_r, f_e, and f_j, ΔS and ΔU along the gas-liquid coexistence curve. In all cases, the Wertheim theory qualitatively, if not quantitatively, properly predicts the behavior of the system, confirming the unconventional theoretical predictions. Even the reversal of the entropic and energetic contribution to the transition is observed numerically. In addition to the well-known underestimate of the coexisting liquid density characteristic of Wertheim's theory, the proposed extension to ring formation appears to overestimate the amount of rings in the sample (Fig. 2).

Conclusions.—A comparison with simulation results shows that the parameter-free Wertheim's theory, extended to include rings, provides reliable predictions for the interplay between phase separation and self-assembly in complex linear structures. The theory offers a powerful instrument to control the competition between the formation of rings, chains, and junctions and to evaluate the resulting phase behavior. The thermodynamic stability at low T is shown to arise from the building up of noninteracting clusters of particles with low energy and low entropy. The theory also provides a theoretical foundation to the recent numerical observation of a gas reentrance arising from self-assembly into weakly or noninteracting aggregates [14,20]. Therefore, it allows us to deeply understand self-assembling in the absence of phase separation, a phenomenon that can be exploited in a variety of applications [41,42].

Finally, our results provide a reference system for understanding the low-T behavior of dipolar hard spheres (DHS), the paradigmatic model of anisotropic interactions [43]. Recent numerical studies of DHS have reported self-assembly into ring structures, possibly suppressing phase separation [44–46]. The similarity between the interactions

and the self-assembled structures formed in the DHS and those of the patchy model under study [47–51] can hopefully be used to establish a quantitative mapping between both models. The present study suggests that the absence of gas-liquid phase separation in DHS, despite the branching, could be a consequence of extensive ring formation.

[1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 2006), 3rd ed.

[2] R. Jones, *Soft Condensed Matter* (Oxford University Press, New York, 2002).

[3] J. Lidmar, L. Mirny, and D. R. Nelson, Phys. Rev. E **68**, 051910 (2003).

[4] M. A. Floriano, E. Caponetti, and A. Z. Panagiotopoulos, Langmuir **15**, 3143 (1999).

[5] F. Lo Verso, A. Z. Panagiotopoulos, and C. N. Likos, Phys. Rev. E **79**, 010401 (2009).

[6] A. Reinhardt, A. J. Williamson, J. P. K. Doye, J. Carrete, L. M. Varela, and A. A. Louis, J. Chem. Phys. **134**, 104905 (2011).

[7] S. C. Glotzer and M. J. Solomon, Nat. Mater. **6**, 557 (2007).

[8] E. Bianchi, J. Largo, P. Tartaglia, E. Zaccarelli, and F. Sciortino, Phys. Rev. Lett. **97**, 168301 (2006).

[9] C. N. Likos, Phys. Rep. **348**, 267 (2001).

[10] V. N. Manoharan, M. T. Elsesser, and D. J. Pine, Science **301**, 483 (2003).

[11] A. B. Pawar and I. Kretzschmar, Macromol. Rapid Commun. **31**, 150 (2010).

[12] L. Hong, A. Cacciuto, E. Luijten, and S. Granick, Langmuir **24**, 621 (2008).

[13] Q. Chen, S. C. Bae, and S. Granick, Nature (London) **469**, 381 (2011).

[14] F. Sciortino, A. Giacometti, and G. Pastore, Phys. Rev. Lett. **103**, 237801 (2009).

[15] F. Sciortino, A. Giacometti, and G. Pastore, Phys. Chem. Chem. Phys. **12**, 11 869 (2010).

[16] J. M. Tavares, P. I. C. Teixeira, and M. M. Telo da Gama, Mol. Phys. **107**, 453 (2009).

[17] J. Russo, J. M. Tavares, P. I. C. Teixeira, M. M. Telo da Gama, and F. Sciortino, Phys. Rev. Lett. **106**, 085703 (2011).

[18] J. Russo, J. M. Tavares, P. I. C. Teixeira, M. M. Telo da Gama, and F. Sciortino, J. Chem. Phys. **135**, 034501 (2011).

[19] T. Tlusty and S. A. Safran, Science **290**, 1328 (2000).

[20] N. G. Almarza, Phys. Rev. E **86**, 030101 (2012).

[21] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.111.168302 for additional details on theoretical and numerical methods.

[22] N. G. Almarza, J. M. Tavares, E. G. Noya, and M. M. T. da Gama, J. Chem. Phys. **137**, 244902 (2012).

[23] W. Chapman, K. Gubbins, G. Jackson, and M. Radosz, Fluid Phase Equilib. **52**, 31 (1989).

[24] F. Sciortino, E. Bianchi, J. F. Douglas, and P. Tartaglia, J. Chem. Phys. **126**, 194903 (2007).

[25] R. P. Sear and G. Jackson, Phys. Rev. E **50**, 386 (1994).

[26] A. Galindo, S. J. Burton, G. Jackson, D. P. Visco, and D. A. Kofke, Mol. Phys. **100**, 2241 (2002).

[27] A. S. Avlund, G. M. Kontogeorgis, and W. G. Chapman, Mol. Phys. **109**, 1759 (2011).

[28] J. M. Tavares, L. Rovigatti, and F. Sciortino, J. Chem. Phys. **137**, 044901 (2012).

[29] B. D. Marshall and W. G. Chapman, Phys. Rev. E **87**, 052307 (2013).

[30] B. D. Marshall, D. Ballal, and W. G. Chapman, J. Chem. Phys. **137**, 104909 (2012).

[31] B. D. Marshall and W. G. Chapman, J. Chem. Phys. **139**, 054902 (2013).

[32] M. S. Wertheim, J. Stat. Phys. **42**, 459 (1986).

[33] M. S. Wertheim, J. Stat. Phys. **42**, 477 (1986).

[34] W. G. Chapman, G. Jackson, and K. E. Gubbins, Mol. Phys. **65**, 1057 (1988).

[35] J. M. Tavares, P. I. C. Teixeira, and M. M. Telo da Gama, Phys. Rev. E **81**, 010501(R) (2010).

[36] A. Zilman, T. Tlusty, and S. A. Safran, J. Phys. Condens. Matter **15**, S57 (2003).

[37] P. Virnau and M. Müller, J. Chem. Phys. **120**, 10 925 (2004).

[38] B. Chen and J. I. Siepmann, J. Phys. Chem. B **105**, 11 275 (2001).

[39] N. B. Wilding and A. D. Bruce, J. Phys. Condens. Matter **4**, 3087 (1992).

[40] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. **63**, 1195 (1989).

[41] K. Kataoka, A. Harada, and Y. Nagasaki, Adv. Drug Delivery Rev. **64**, 37 (2012).

[42] D. F. Evans and H. Wennerström, *The Colloidal Domain: Where Physics, Chemistry, and Biology Meet* (Wiley-VCH, New York, 1999).

[43] P. G. de Gennes and P. A. Pincus, Phys. Kondens. Mater. **11**, 189 (1970).

[44] L. Rovigatti, J. Russo, and F. Sciortino, Phys. Rev. Lett. **107**, 237801 (2011).

[45] L. Rovigatti, J. Russo, and F. Sciortino, Soft Matter **8**, 6310 (2012).

[46] S. Kantorovich, A. O. Ivanov, L. Rovigatti, J. M. Tavares, and F. Sciortino, Phys. Rev. Lett. **110**, 148306 (2013).

[47] J. J. Weis and D. Levesque, Phys. Rev. Lett. **71**, 2729 (1993).

[48] J. M. Tavares, J. J. Weis, and M. M. Telo da Gama, Phys. Rev. E **65**, 061201 (2002).

[49] P. I. C. Teixeira, J. M. Tavares, and M. M. Telo da Gama, J. Phys. Condens. Matter **12**, R411 (2000).

[50] P. J. Camp, J. C. Shelley, and G. N. Patey, Phys. Rev. Lett. **84**, 115 (2000).

[51] G. Ganzenmüller, G. N. Patey, and P. J. Camp, Mol. Phys. **107**, 403 (2009).