

Criticality of colloids with distinct interaction patches: The limits of linear chains, hyperbranched polymers, and dimers

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(Received 8 June 2009; published 26 August 2009)

We use a simple model of associating fluids which consists of spherical particles having a hard-core repulsion, complemented by three short-ranged attractive sites on the surface (sticky spots). Two of the spots are of type *A* and one is of type *B*; the bonding interactions between each pair of spots have strengths ϵ_{AA} , ϵ_{BB} , and ϵ_{AB} . The theory is applied over the whole range of bonding strengths and the results are interpreted in terms of the equilibrium cluster structures of the phases. In addition to our numerical results, we derive asymptotic expansions for the free energy in the limits for which there is no liquid-vapor critical point: linear chains ($\epsilon_{AA} \neq 0$, $\epsilon_{AB} = \epsilon_{BB} = 0$), hyperbranched polymers ($\epsilon_{AB} \neq 0$, $\epsilon_{AA} = \epsilon_{BB} = 0$), and dimers ($\epsilon_{BB} \neq 0$, $\epsilon_{AA} = \epsilon_{AB} = 0$). These expansions also allow us to calculate the structure of the critical fluid by perturbing around the above limits, yielding three different types of condensation: of linear chains (*AA* clusters connected by a few *AB* or *BB* bonds); of hyperbranched polymers (*AB* clusters connected by *AA* bonds); or of dimers (*BB* clusters connected by *AA* bonds). Interestingly, there is no critical point when ϵ_{AA} vanishes despite the fact that *AA* bonds alone cannot drive condensation.

DOI: [10.1103/PhysRevE.80.021506](https://doi.org/10.1103/PhysRevE.80.021506)

PACS number(s): 64.70.F-, 64.75.Yz, 61.20.Qg

I. INTRODUCTION

The condensation of simple fluids is driven by the free-energy balance between the high-entropy gas and the low-energy liquid phases. This transition is generic in simple fluids interacting via isotropic intermolecular potentials that comprise a short-ranged repulsion and a longer-ranged attraction. Somewhat surprisingly, numerical simulations of dipolar hard sphere (DHS) [1] and also of Stockmayer fluids [2] have shown that the anisotropy of the dipolar potential promotes the formation of self-assembled aggregates (chains, rings and more complex clusters) if the dipolar interaction strength is of the order of the thermal energy. This is in sharp contrast with the isotropic compact clusters observed in simple fluids. Simulation results also suggest that when this dipolar clustering is significant the system fails to condense. It is unclear whether strong association precludes any kind of fluid-fluid phase separation as failure to observe it may be an artifact of the simulation techniques. The situation remains controversial [3–6], requiring the development of new simulation methods [7] to review the dipolar and related condensation problems in the light of recent theoretical results. There is also an urgent need to develop analytical treatments of strongly anisotropic correlated systems. Association theories for dipolar fluids [8–12] that include the effect of linear cluster formation in the thermodynamics, reproduce well the slow variation in the internal energy with the density and cluster size (or mass) distribution. The simplest of these approaches assumes that the only effect of the bonding interaction is to drive cluster formation and hence describes the fluid as an ideal mixture of self-assembling clusters, failing to predict the existence of phase transitions unless direct or indirect interactions between the clusters are added.

More recently a very active line of work that also addresses the interplay between self-assembly and condensation concerns the novel type of soft matter known as associ-

ating colloids. Unlike in atomic systems, we are now able to control the interactions between colloidal particles, thus opening up the possibility of new structural and thermodynamic behavior [13]. Of particular interest are the so-called patchy colloids, the surfaces of which are patterned so that they attract each other via discrete “sticky spots” of tunable number, size, and strength. Besides their relevance to applications or in biological systems (e.g., protein solutions), patchy colloids have important connections with notoriously difficult classical liquids such as water and the strongly dipolar fluids described above [14]. An understanding of these novel systems will therefore shed light on more traditional forms of liquid matter. In fact, the interplay between cluster formation and condensation is a general problem, relevant in a variety of other theoretical contexts.

Arguably the most successful thermodynamic perturbation theory for associating fluids was developed by Wertheim [15,16] more than two decades ago. Originally the theory considered fluids of associating hard spheres [15–18] but later it was realized that in the limit of infinite associating strength, a polydisperse mixture of polymers was recovered [19]. Chapman and co-workers extended the theory to monodisperse polymers [20] and realized that it was applicable to polymers with attractive monomers [21,22]. Since then, the theory has achieved enormous success and has been used to describe the equation of state of idealized polymers as it is computationally convenient and does not require any empirical parameters. Furthermore, it yields results that are of similar or superior quality to the available alternatives. In contrast, little attention has been devoted to the criticality of polymers as the number n of monomers increases. By invoking the polymer-solvent and polymer-vacuum analogies, one would expect, on the basis of Flory-Huggins (FH) theory, that the polymer fluid should approach an asymptotic, finite critical temperature as $n^{-1/2}$, whereas the critical mass density should become vanishingly small as $n^{-1/2}$, when $n \rightarrow \infty$.

In a recent contribution MacDowell *et al.* [23] analyzed the scaling behavior of the critical point of chain fluids using computer simulations and Wertheim's theory and found that the theory indeed reproduces FH results. The asymptotic critical temperature was found to be in good agreement with the Θ point of the polymer model as obtained from the temperature dependence of the single chain conformations, again in agreement with the FH predictions for the critical behavior of polymer-solvent mixtures.

In this paper we address the interplay between self-assembly and condensation, building on the pioneering work of Sciortino and co-workers [24–26], who investigated the phase diagram of patchy colloids by applying Wertheim's theory to patchy particles with identical interaction sites. We generalize the model by considering particles with three distinct interaction sites: two of type *A* and strength ϵ_{AA} , and one of type *B* and strength ϵ_{BB} . Unlike sites also interact, with strength ϵ_{AB} . This system is interesting as its phase behavior sheds light on the criticality of self-assembling fluids of particles with more than one type of bonding site, such as the class of systems known as hyperbranched polymers [27]. The model is also relevant in the context of dipolar and other associating fluids, as shown previously [28], and generalizes the requirements for the condensation of self-assembled fluids derived by Sciortino's group [24–26] for colloids with identical patches. Finally, our results indicate that fluid condensation is intimately related to the structure of the equilibrium clusters at the critical point. They are therefore directly relevant to the criticality of polymer systems and contribute to the general effort toward elucidating the phase behavior of self-assembled and structured fluids.

In the following we give an overview of the criticality of patchy colloids with three distinct sites, including the limits of identical sites [24–26] and of *X*- and *Y*-junction-driven criticalities [28] that were published previously. The case $\epsilon_{ij} = \epsilon$ (i.e., where each sphere has three identical bonding sites) was extensively studied in [24,26] by comparing simulations to Wertheim's theory: agreement for the phase diagrams was excellent. Furthermore, it was established that the number of bonding sites per particle, M , is the key parameter controlling the location of the liquid-vapor critical point: upon decreasing M , this moves toward ever lower densities and temperatures such that liquid-vapor coexistence ceases to exist if $M \leq 2$ [24–26]. Simulation and theory also provide evidence that, for mixtures of particles with two and three identical sticky spots, the average number $\langle M \rangle$ of bonding sites per particle can be varied continuously by changing the concentration of the two species, and the critical point may be made to approach zero density and temperature continuously as $\langle M \rangle \rightarrow 2$ [24]. This makes it possible to realize equilibrium liquid states with arbitrarily low density (empty liquids), which would be unfeasible with spherically symmetric interaction potentials.

If two of the three interaction strengths vanish simultaneously, there can be no liquid-vapor critical point. Because Wertheim's theory treats all bonds independently (see below), it does not provide any direct information on the structure of the resulting aggregates, but we can infer that these are the well-known limits of noninteracting linear chains [$\epsilon_{AA} \neq 0$ and $\epsilon_{AB} = \epsilon_{BB} = 0$; see Fig. 1(a)] [24,26,29], dimers

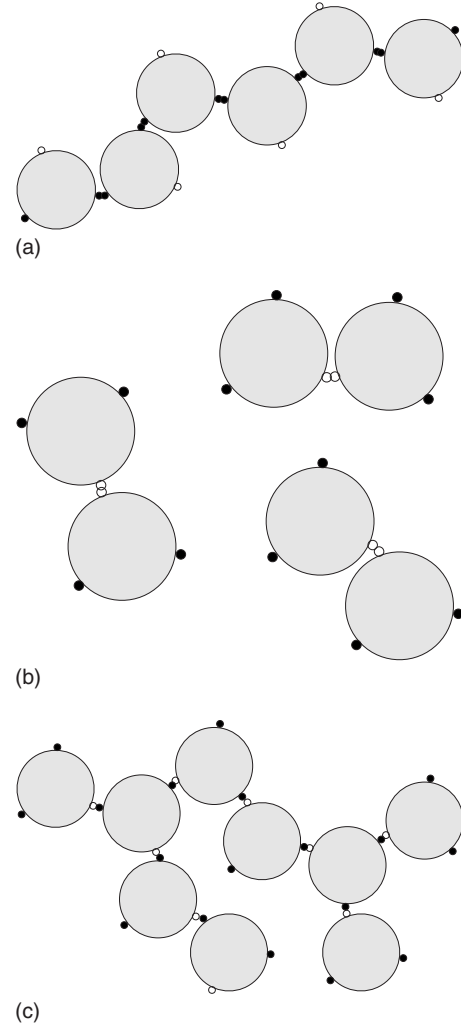
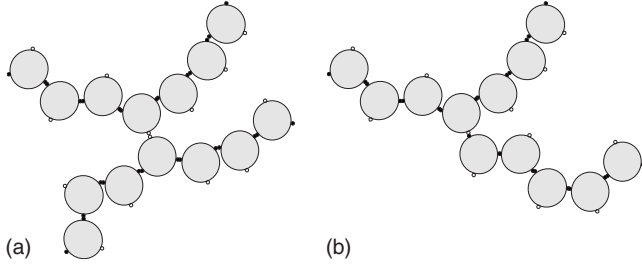


FIG. 1. Lowest-energy structures (without loops): (a) linear chains ($\epsilon_{AB} = \epsilon_{BB} = 0$, $\epsilon_{AA} \neq 0$) for which $X_A = 0$ and $X_B = 1$; (b) dimers ($\epsilon_{AA} = \epsilon_{AB} = 0$, $\epsilon_{BB} \neq 0$) for which $X_A = 1$ and $X_B = 0$; and (c) hyperbranched polymers ($\epsilon_{AA} = \epsilon_{BB} = 0$, $\epsilon_{AB} \neq 0$) for which $X_A = 0.5$ and $X_B = 0$. The small circles are the interaction sites: *A* (filled) and *B* (open).

[$\epsilon_{BB} \neq 0$ and $\epsilon_{AA} = \epsilon_{AB} = 0$; see Fig. 1(b)] [32], and hyperbranched polymers [$\epsilon_{AB} \neq 0$ and $\epsilon_{AA} = \epsilon_{BB} = 0$; see Fig. 1(c)]. In the first of these one expects a polymerization transition to occur when $T \rightarrow 0$ [30]. The detailed fashion in which the critical temperature vanishes as the bonding energies, ϵ_{AB} and ϵ_{BB} , decrease toward zero depends on the order in which the limits $\epsilon_{AB} \rightarrow 0$ and $\epsilon_{BB} \rightarrow 0$ are taken, which in turn determines the type of network that is formed. Indeed, in systems where unlike sites do not interact (i.e., where $\epsilon_{AB} = 0$), the critical point exists all the way to $\epsilon_{BB} = 0$. In contrast, when $\epsilon_{BB} = 0$, there is no critical point below a certain finite value of $\epsilon_{AB}/\epsilon_{AA}$. These results are rationalized in terms of the different network structures of the two systems: two long *AA* chains are linked by one *BB* bond [*X* junction, see Fig. 2(a)] in the former case and by one *AB* bond (*Y* junction, see Fig. 2(b)) in the latter. The vapor-liquid transition is then viewed as the condensation of these junctions, and it was found that *X* junctions condense for any strength of the *BB*

FIG. 2. (a) An X junction; (b) a Y junction.

attraction (i.e., for any fraction of BB bonds) whereas condensation of the Y junctions requires that the AB interaction strength be above a finite threshold (i.e., there must be a finite fraction of AB bonds) [28] in line with previous work [31].

We further note that, as the monomer density is increased or the temperature decreased, these systems will pass through a percolation threshold, where a network is formed that spans the entire volume. Unlike condensation, this transition is purely topological and has no thermodynamic signature. The percolation transition and the correlation between the structural and thermodynamic properties of this class of associating fluids will be addressed in future work.

This paper is organized as follows: in Sec. II we provide a derivation of the theory and apply it to the model with three different interaction patches. In Sec. III we present our results for the critical points, with special emphasis on the limits of linear chains, hyperbranched polymers, and dimers, which can be studied analytically. These are further discussed in Sec. IV, where we summarize our conclusions.

II. THEORY AND MODEL

We consider a system of N hard spheres (HSs) of diameter σ and volume $v_s = (\pi/6)\sigma^3$, each decorated with three bonding sites (or sticky spots) on their surface. Two of these spots are identical and labeled A , while the third is different and labeled B . In general, two spheres may form bonds of types AA , BB , or AB . Each bond corresponds to a short-ranged attractive interaction between two bonding sites, which is treated as a perturbation of the HS potential. We assume that these potentials are square wells, with depths ϵ_{ij} (where $i, j = A, B$), and their ranges are chosen so that each bonding site can only take part in one bond. The theory does not actually require us to specify the positions of the bonding sites over the surface of the sphere, only that they should be arranged in such a way that it is not possible to have more than one bond between any two spheres. Of course, in a simulation one would need to specify the site positions; one possible choice is to take them as uniformly distributed as possible, as in [26].

The above requirements are introduced to satisfy the assumptions made in Wertheim's theory, which then provides a general expression for the contribution of bonds to the free energy, F_b . Wertheim's derivation is based on a resummed cluster expansion, where the significance of each of the approximations is mathematically well understood [15,16]. The

results are, however, rather formal and have been reformulated by Jackson *et al.* [32] in a more convenient form that will be used here. An analysis of Wertheim's theory in the fully bonded limit reveals that it approximates (i) F_b by its low-density limit; and (ii) the n -body correlation function by a superposition of pair (two-body) correlation functions of the reference system [23]. This in fact amounts to a mean-field (MF) treatment plus pair correlations, so we expect it to predict the location of the critical point more accurately than plain MF but not to yield the correct critical exponents. On the basis of Sciortino *et al.*'s results for the model with three identical interaction sites [24,26,29], there will likely be good agreement between theory and simulation. This is probably aided by the fact that the critical point occurs at substantially lower densities than in simple fluids.

For the present model, a fluid of identical spheres with two A and one B bonding sites, the bonding free energy, F_b , is given by [32]

$$\beta f_b \equiv \frac{\beta F_b}{N} = 2 \ln X_A + \ln X_B - X_A - \frac{X_B}{2} + \frac{3}{2}, \quad (1)$$

where $\beta \equiv 1/(k_B T)$, T is the temperature, k_B is the Boltzmann constant, and X_i is the probability of having a sticky spot of type i not bonded. $1 - X_i$ is thus the fraction of bonding sites of type i that do take part in bonds. The variables X_i are related to the density and temperature through the law of mass action that is obtained by treating bond formation as a chemical reaction. We recall that this is equivalent to disregarding loops in the branched clusters, preserving only pair correlations [33]. Clusters consist of uncorrelated bonds; longer-range correlations, including intracluster self-avoidance, are neglected. The intercluster excluded volume is taken into account through the reference fluid entropic term.

The law of mass action then yields the following two equations [15,16,32]:

$$X_A + 2\eta\Delta_{AA}X_A^2 + \eta\Delta_{AB}X_AX_B = 1, \quad (2)$$

$$X_B + \eta\Delta_{BB}X_B^2 + 2\eta\Delta_{AB}X_AX_B = 1, \quad (3)$$

where $\eta \equiv (N/V)v_s$ is the packing fraction, and,

$$\Delta_{ij} = \frac{1}{v_s} \int_{v_{ij}} g_{ref}(\mathbf{r}) [\exp(\beta\epsilon_{ij}) - 1] d\mathbf{r}. \quad (4)$$

This integral is calculated over v_{ij} , the volume of bond ij , and g_{ref} is the pair-correlation function (PCF) of the reference system. $M_i M_j \Delta_{ij} / (1 + \delta_{ij})$ (with $M_A = 2$ and $M_B = 1$ the numbers of A and B sites per particle and δ_{ij} the Kronecker delta) plays the role of the equilibrium constant for the reaction between sites i and j [29].

Here we shall take all bonds to have the same volume, $v_{ij} = v_b$. The reference system is chosen to be the HS fluid, and the low-density (ideal-gas) approximation for the PCF, $g_{ref}(\mathbf{r}) = 1$, will be used. Within these two approximations, Eq. (4) becomes

$$\Delta_{ij} = \frac{v_b}{v_s} [\exp(\beta \epsilon_{ij}) - 1]. \quad (5)$$

The free energy per particle is, therefore,

$$\beta f = \beta f_{HS} + \beta f_b, \quad (6)$$

which is a function of (η, T) only. In what follows we shall use the Carnahan-Starling approximation for f_{HS} [34].

The critical point is found by equating to zero the first and second derivatives of the pressure with respect to the density or packing fraction,

$$\frac{\partial}{\partial \eta} (\beta p v_s) = 0, \quad (7)$$

$$\frac{\partial^2}{\partial \eta^2} (\beta p v_s) = 0. \quad (8)$$

These are solved, together with Eqs. (2) and (3), to get η_c , T_c , X_{Ac} , and X_{Bc} ; for details of the numerical procedure see the Appendix of [28]. For consistency with Sciortino *et al.*'s work, we set $v_b = 0.000\,332\,285\sigma^3$. Likewise we introduce the reduced density $\rho^* = (N/V)\sigma^3 = \eta/v_s$; a reduced temperature has to be defined in such a way that it will be a function of the relevant *ratio* of ϵ_{ij} (see below).

III. RESULTS

All interaction strengths, ϵ_{AA} , ϵ_{AB} , and ϵ_{BB} , can be varied independently, thereby affording the model great flexibility. Consequently, we choose to concentrate on the approach to the three known limits of chains, hyperbranched polymers, and dimers (see above) for which no liquid-vapor critical point exists. Guided by our analytical results we investigate what happens when each of these limits is perturbed by letting each of the interaction strengths be nonzero in turn, but smaller than the dominant one, i.e., chains when $\epsilon_{AA} \gg \epsilon_{AB} > 0$, $\epsilon_{BB} = 0$ or $\epsilon_{AA} \gg \epsilon_{BB} > 0$, $\epsilon_{AB} = 0$; dimers when $\epsilon_{BB} \gg \epsilon_{AA} > 0$, $\epsilon_{AB} = 0$, or $\epsilon_{BB} \gg \epsilon_{AB} > 0$, $\epsilon_{AA} = 0$; and hyperbranched polymers when $\epsilon_{AB} \gg \epsilon_{AA} > 0$, $\epsilon_{BB} = 0$ or $\epsilon_{AB} \gg \epsilon_{BB} > 0$, $\epsilon_{AA} = 0$ —a total of six different cases. Those for which $\epsilon_{AA} \neq 0$ have already been addressed in an earlier paper [28]; we include them here in the context of a systematic study of the criticality of patchy colloids with different interaction sites. We ask ourselves: how exactly does the critical point vanish? For clarity we shall consider separately the cases where the interaction between unlike sites has zero ($\epsilon_{AB} = 0$) or finite ($\epsilon_{AB} \neq 0$) strength, highlighting the role of the unlike bonding interactions.

A. Unlike sites do not interact: $\epsilon_{AB} = 0$

In this case $\Delta_{AB} = 0$, and the laws of mass action [Eqs. (2) and (3)], can be solved to obtain explicit expressions for the probabilities X_A and X_B ,

$$X_B = \frac{-1 + \sqrt{1 + 4\eta\Delta_{BB}}}{2\eta\Delta_{BB}}, \quad (9)$$

$$X_A = \frac{-1 + \sqrt{1 + 8\eta\Delta_{AA}}}{4\eta\Delta_{AA}}. \quad (10)$$

The bonding contribution to the pressure can be derived by combining Eq. (1) with Eqs. (9) and (10),

$$\beta p_b v_s = -\frac{\eta}{2}(1 - X_B) - \eta(1 - X_A). \quad (11)$$

The full pressure is then obtained by adding the HS contribution [cf. Eq. (6)].

Figure 3 shows the critical density ρ_c^* , critical temperature $T_c^* = k_B T / (\epsilon_{AA} \epsilon_{BB})^{1/2}$, fraction of unbonded *A* sites at the critical point X_{Ac} , fraction of unbonded *B* sites at the critical point X_{Bc} , and the inverse mean size of aggregates $1/\langle L \rangle$, as $\epsilon_{AA}/\epsilon_{BB}$ is varied. As already reported in [28], the critical point exists for all values of this ratio of interaction strengths; the limits where it goes to zero or to infinity will be addressed analytically in the next two subsections.

1. *BB* dimers connected by *AA* bonds

In the limit $\epsilon_{BB} \gg \epsilon_{AA}$, the system consists of *BB* dimers, some of which are connected through *AA* bonds. This corresponds to the rightmost portion of Fig. 3. To study the phase behavior we assume full *BB* association, i.e., we set $X_B = 0$ in Eq. (11) [consistently with the numerical result, see Fig. 3(c)], and obtain, for the pressure at low density,

$$\beta p v_s = -\frac{\eta}{2} + \eta X_A + \frac{B_2}{2} \eta^2 \quad (12)$$

where, here and in what follows, B_i is the dimensionless *i*-th virial coefficient of the HS fluid. Equations (7) and (8), combined with Eqs. (10) and (12), can be solved analytically for the critical point. This requires finding the roots of a third-degree polynomial, whereupon we obtain, for the critical packing fraction, $\eta_c \approx 0.0168$, and for the critical temperature, $\eta_c \Delta_{AA,c} \approx 0.808$ [or $k_B T_c \approx \epsilon_{AA} / \ln(48.25 v_s / v_b)$], which are close to the numerical solutions of the full equations for the critical point: from Figs. 3(a) and 3(b), $\eta_c \approx 0.0170$ and $\eta_c \Delta_{AA,c} \approx 0.867$. Notice that this discrepancy can only have originated in the approximations for the HS pressure, $\beta p_{HS} \approx \eta + \frac{B_2}{2} \eta^2$, and for the fraction of unbonded *B* sites, $X_B = 0$.

We conclude that when $\epsilon_{AA}/\epsilon_{BB} \rightarrow 0$ a liquid-vapor critical point exists, with nonvanishing density [see Fig. 3(a)] and vanishing temperature [see Fig. 3(b)]. The numerical calculation shows that this limit for the critical density is reached for $\epsilon_{BB}/\epsilon_{AA} \gtrsim 3$ [see Fig. 3(a)]. Remarkably, it is also possible to verify that the bonding contribution to the pressure in the present case [Eq. (11) with $X_A = 0$] is the same as that for a model with four equal bonding sites [29] and half the density.

2. *AA* chains connected by *X* junctions (*BB* bonds)

In the limit $\epsilon_{AA} \gg \epsilon_{BB}$, the system consists of long *AA* chains connected by some *BB* bonds (*X* junctions). This corresponds to the leftmost portion of Fig. 3. We expect $X_A \approx 0$ (i.e., very long chains) and $X_B \approx 1$ (i.e., only a few *X* junctions), which is indeed borne out by the numerical cal-

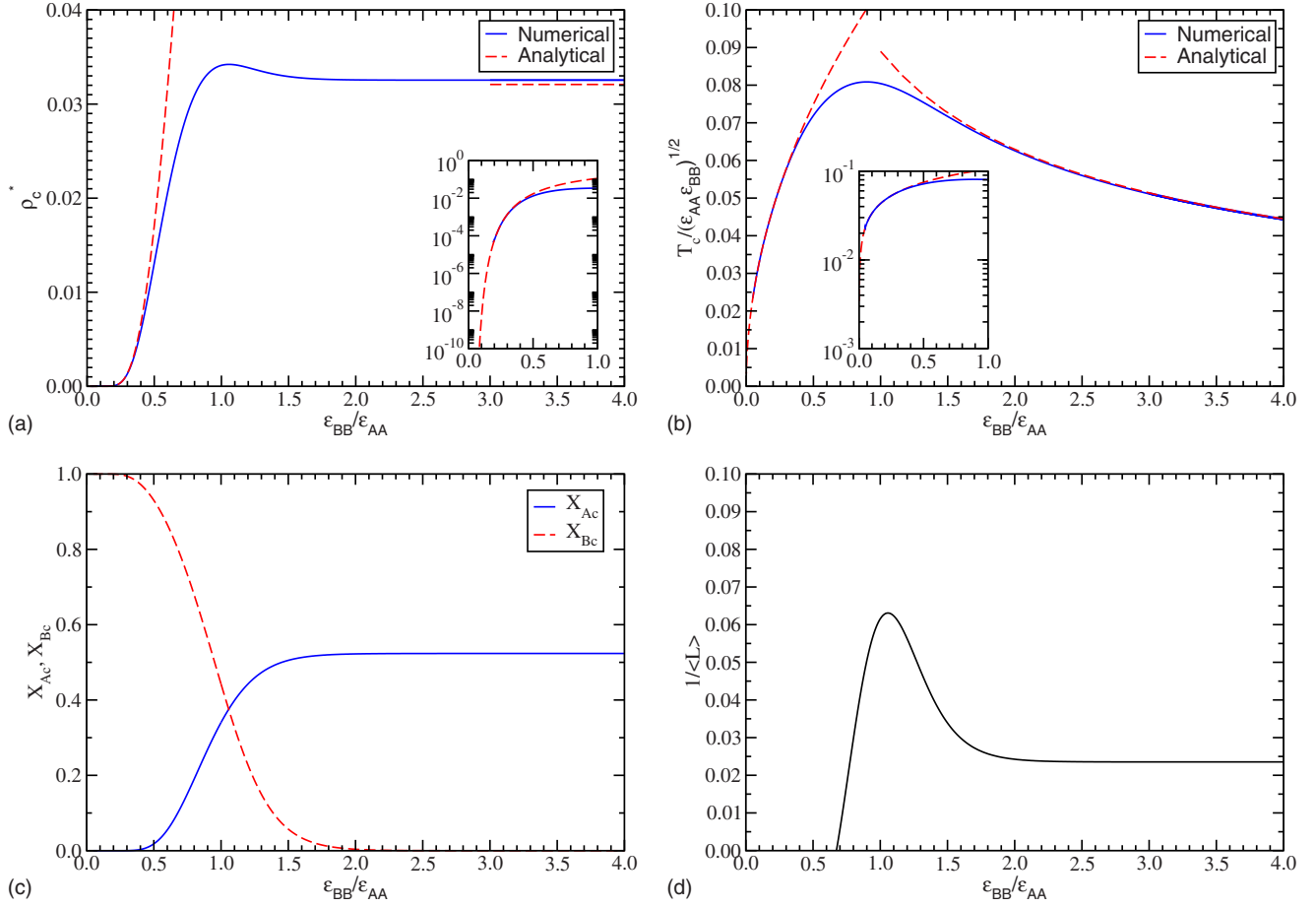


FIG. 3. (Color online) Critical point vs $\epsilon_{BB}/\epsilon_{AA}$ for $\epsilon_{AB}=0$: (a) critical density ρ_c^* ; (b) reduced critical temperature $T_c/(\epsilon_{AA}\epsilon_{BB})^{1/2}$; (c) X_{Ac} and X_{Bc} , the fractions of unbonded A and B sites, respectively; and (d) inverse mean size of aggregates, $1/\langle L \rangle$. The reduced critical temperature vanishes in the limits of linear chains ($\epsilon_{BB}/\epsilon_{AA} \rightarrow 0$) and dimers ($\epsilon_{BB}/\epsilon_{AA} \rightarrow \infty$), albeit much more slowly in the latter case. In parts (a) and (b), the solid lines are the numerical solution of Eqs. (7) and (8), the dashed lines are the asymptotic solutions, and the insets show the behavior for small $\epsilon_{BB}/\epsilon_{AA}$; see the text for details.

culations [see Fig. 3(c)]. Expanding Eqs. (9) and (10) to the lowest nontrivial order in $\eta\Delta_{BB}$ and $\eta\Delta_{AA}$, respectively, around these limits, one obtains

$$X_B \approx 1 - \eta\Delta_{BB} + 2\eta^2\Delta_{BB}^2, \quad (13)$$

$$X_A \approx \frac{1}{\sqrt{2\eta\Delta_{AA}}} - \frac{1}{4\eta\Delta_{AA}}, \quad (14)$$

which, when substituted into Eq. (11), give the following low-density approximation for the total pressure:

$$\beta p v_s = \frac{1}{4\Delta_{AA}} \left(4\sqrt{\frac{\eta\Delta_{AA}}{2}} - 1 \right) + (B_2 - \Delta_{BB}) \frac{\eta^2}{2} + \left(\frac{B_3}{6} + \Delta_{BB}^2 \right) \eta^3. \quad (15)$$

The first term in this expression corresponds to the entropy of a gas of chains; the term $-\Delta_{BB}\eta^2/2$ shows that the formation of X junctions can be seen as an effective pairwise attraction between the particles, as pointed out in [31]; finally,

the remaining terms account for excluded volume interactions, through the pressure of a HS fluid.

From Eq. (15) we derive the following relation between the critical density and the critical temperature:

$$\eta_c = \left[\frac{9}{8(B_3 + 6\Delta_{BB,c}^2)\Delta_{AA,c}} \right]^{1/5}. \quad (16)$$

In order to obtain analytical expressions for the critical quantities, we make the approximations $\Delta_{AA,c} \approx (v_b/v_s)\exp(\epsilon_{AA}/k_B T_c)$ and $\Delta_{BB,c} = B_2$ [which is what we would get for the critical temperature if the expansions in Eqs. (13) and (14) were truncated at lower order]. The critical temperature and the critical density then become

$$k_B T_c = \frac{\epsilon_{BB}}{\ln b}, \quad (17)$$

$$\eta_c = \left[\frac{9v_b}{8v_s(B_3 + 6B_2^2)} \right]^{1/5} \exp\left(-\frac{\epsilon_{AA} \ln b}{5\epsilon_{BB}}\right), \quad (18)$$

where $b = 1 + B_2(v_s/v_b)$. Therefore, in the limit $\epsilon_{BB}/\epsilon_{AA} \rightarrow 0$, there is always a critical point with (exponentially) vanishing

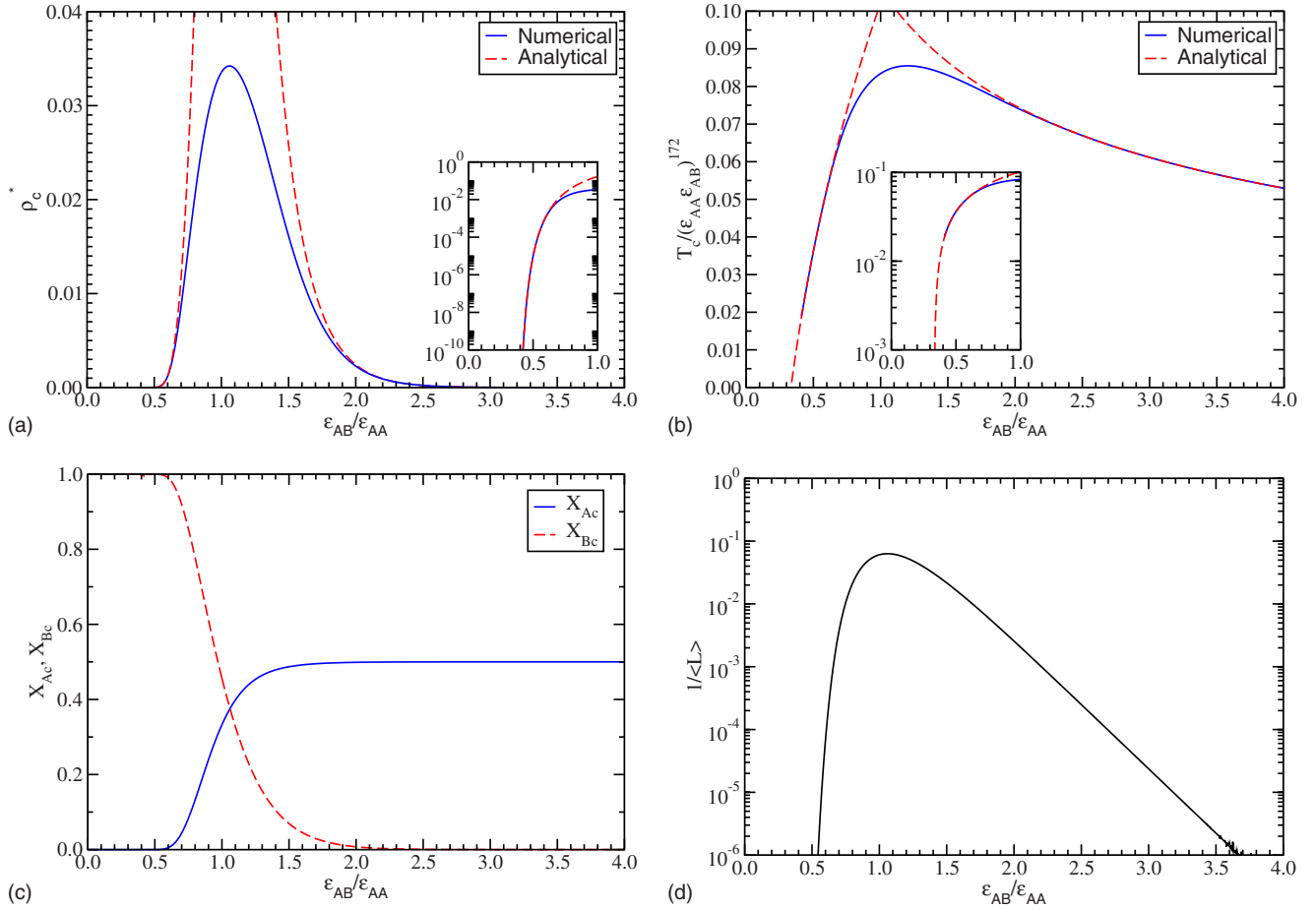


FIG. 4. (Color online) Critical point vs $\epsilon_{AB}/\epsilon_{AA}$ for $\epsilon_{BB}=0$: (a) critical density ρ_c^* ; (b) reduced critical temperature $T_c/(\epsilon_{AA}\epsilon_{AB})^{1/2}$; (c) X_{Ac} and X_{Bc} , the fractions of unbonded A and B sites, respectively; and (d) inverse mean size of aggregates, $1/\langle L \rangle$. The reduced critical temperature vanishes in the limits of linear chains ($\epsilon_{AB}/\epsilon_{AA} \rightarrow 0$) and hyperbranched polymers ($\epsilon_{AB}/\epsilon_{AA} \rightarrow \infty$), albeit much more slowly in the latter case, as in Fig. 3. In parts (a) and (b), the solid lines are the numerical solution of Eqs. (7) and (8), the dashed lines are the asymptotic solutions, and the insets show the behavior for small $\epsilon_{AB}/\epsilon_{AA}$; see the text for details

packing fraction [see Fig. 3(a)] and (linearly) vanishing temperature [see Fig. 3(b)], as we had found earlier [28] [note, however, that the numerical prefactor in Eq. (18) differs from that in Eq. (14) of [28] because in the earlier paper X_A and X_B had been expanded to lower order]. This critical point driven by X junctions is similar to the Θ point of polymer solutions in that it has (asymptotically) zero density but a finite temperature [23].

B. Unlike sites interact: $\epsilon_{AB} \neq 0$

If $\epsilon_{AB} \neq 0$, it is not possible to obtain from Eqs. (2) and (3) the probabilities X_A and X_B as explicit functions of η , T , and the energy parameters. Figure 4 shows the critical density ρ_c^* , critical temperature $T_c^* = k_B T / (\epsilon_{AA}\epsilon_{AB})^{1/2}$, fraction of unbonded A sites at the critical point X_{Ac} , fraction of unbonded B sites at the critical point X_{Bc} , and the inverse mean size of aggregates $1/\langle L \rangle$ as $\epsilon_{AB}/\epsilon_{AA}$ is varied. As we shall see below, this is the only relevant ratio of interaction strengths since there is no critical point if $\epsilon_{AA}=0$.

Asymptotic expressions for the bonding free energy can now be derived as follows: consider the limit where $\epsilon_{ij}=0$ and $\epsilon_{kl} \ll \epsilon_{nm}$ ($i, j, k, l=A, B$). Then:

(1) start by calculating the bonding free energy when both nondominant interaction strengths vanish, $\beta f_{0,b} \equiv \beta f_b(\epsilon_{ij}=0, \epsilon_{kl}=0)$;

(2) define a small parameter $\alpha = \Delta_{kl}/\Delta_{nm}$ and use it to rewrite the laws of mass action so that Eqs. (1)–(3) define the free energy as an implicit function of α . Notice that, in the limit under study, $\alpha \ll 1$;

(3) expand the bonding free energy to first order in α ,

$$\beta f_b \approx \beta f_{0,b} + \left(\frac{d\beta f_b}{d\alpha} \right)_{\alpha=0} \alpha, \quad (19)$$

which yields an approximation for the bonding free energy as an explicit function of η , T , α , and ϵ_{nm} . This allows the critical behavior to be studied analytically in the limits of interest: weakly connected chains, dimers, or hyperbranched polymers.

1. Mostly BB dimers, a few AB bonds

In the limit $\epsilon_{AA}=0$ and $\epsilon_{BB} \gg \epsilon_{AB}$, the system consists mostly of dimers (two particles connected by a BB bond), plus a small number of other aggregates in which particles connect via AB bonds. From Eqs. (1)–(3), we obtain the

bonding free energy when $\epsilon_{AB}=\epsilon_{AA}=0$ (i.e., when only dimers can form) as an explicit function of $y=1/\sqrt{\eta\Delta_{BB}}$,

$$\beta f_{0,b}(\epsilon_{AB}=0, \epsilon_{AA}=0) = \ln X_{B,0} - \frac{X_{B,0}}{2}, \quad (20)$$

where

$$X_{B,0} = \frac{y^2}{2} \left(-1 + \sqrt{1 + \frac{4}{y^2}} \right). \quad (21)$$

For strong BB association, i.e., in the dimer limit, $y \rightarrow 0$, Eq. (20) becomes, to second order in y ,

$$\beta f_{0,b} \approx \ln y - y + \frac{y^2}{4}. \quad (22)$$

Defining the small parameter $\alpha = \Delta_{AB}/\Delta_{BB}$ and setting $\epsilon_{AA}=0$ (or, equivalently, $\Delta_{AA}=0$), the laws of mass action [Eqs. (2) and (3)] become

$$X_A + \frac{\alpha X_B X_A}{y^2} = 1, \quad (23)$$

$$X_B + 2 \frac{\alpha X_B X_A}{y^2} + \frac{X_B^2}{y^2} = 1, \quad (24)$$

These equations define $X_A(y, \alpha)$ and $X_B(y, \alpha)$ implicitly; and, through Eq. (1), also the bonding free energy as a function of y and α , $\beta f_b(y, \alpha)$. The latter is now expanded to first order in powers of α for fixed y ; whence,

$$\left(\frac{\partial \beta f_b}{\partial \alpha} \right)_{\alpha=0} = 1 - \sqrt{1 + \frac{4}{y^2}}. \quad (25)$$

We now consider the limit $y \rightarrow 0$. From Eqs. (21) and (24) we conclude that we must have $\alpha/y \ll 1$ in order to recover the dimer limit when both y and $\alpha \rightarrow 0$. On the other hand, $(\partial \beta f_b / \partial \alpha)_{\alpha=0} \rightarrow -2/y$ and $(\partial^2 \beta f_b / \partial \alpha^2)_{\alpha=0}$ is dominated by a term of order y^{-2} . Consequently, we assume that $\alpha y^{-1} \sim y$, and make the following approximation for the bonding free energy to first order in α :

$$\beta f_b = \ln y - y - \frac{2\alpha}{y}. \quad (26)$$

The pressure is then

$$\beta p v_s = \frac{\eta}{2} + 2 \sqrt{\frac{\eta}{\Delta_{BB}}} - \frac{\Delta_{AB}}{\sqrt{\Delta_{BB}}} \eta^{3/2} + \frac{B_2}{2} \eta^2. \quad (27)$$

The first two terms represent the entropy associated with dimer formation, the third term the effective attraction promoted by dimer dissociation and AB bond formation, and the last term the excluded volume entropy. It can be shown that Eqs. (7) and (8) are never satisfied and condensation never occurs in this limit. This result is corroborated by the full numerical calculation, where it was found that a finite AA attraction is always needed to effect condensation when $\epsilon_{AB} \ll \epsilon_{BB}$ [28].

2. AA chains connected by Y junctions (AB bonds)

In the limit $\epsilon_{BB}=0$, $\epsilon_{AA} \gg \epsilon_{AB}$, leftmost portion of Fig. 4, the system consists of chains connected by a few AB bonds (Y junctions). Although this was already treated in our earlier paper [28], we redo it here in a more systematic fashion. Results are qualitatively the same, but some of the numerical prefactors differ as they appear to depend sensitively on the order of various approximations employed.

From Eqs. (1) and (3), we obtain the bonding free energy when $\epsilon_{BB}=\epsilon_{AB}=0$ (i.e., when only linear chains can form) as an explicit function of $y=1/\sqrt{\eta\Delta_{AA}}$,

$$\beta f_{0,b}(\epsilon_{AB}=0, \epsilon_{BB}=0) = 2 \ln X_{A,0} - X_{A,0}, \quad (28)$$

where

$$X_{A,0} = \frac{y^2}{4} \left(-1 + \sqrt{1 + \frac{8}{y^2}} \right). \quad (29)$$

For strong AA association, i.e., in the chain limit, $y \rightarrow 0$, Eq. (28) becomes, to second order in y ,

$$\beta f_{0,b} \approx 2 \ln y - \sqrt{2}y + \frac{y^2}{4}. \quad (30)$$

Defining the small parameter $\alpha = \Delta_{AB}/\Delta_{AA}$ and setting $\epsilon_{BB}=0$ (or, equivalently, $\Delta_{BB}=0$), the laws of mass action [Eqs. (2) and (3)] become

$$X_A + \frac{\alpha X_B X_A}{y^2} + \frac{2X_A^2}{y^2} = 1, \quad (31)$$

$$X_B + \frac{2\alpha X_B X_A}{y^2} = 1. \quad (32)$$

These equations define $X_A(y, \alpha)$ and $X_B(y, \alpha)$ implicitly; and, through Eq. (1), also the bonding free energy as a function of y and α , $\beta f_b(y, \alpha)$. The latter is expanded to first order in powers of α , for fixed y ; whence,

$$\left(\frac{\partial \beta f_b}{\partial \alpha} \right)_{\alpha=0} = \frac{1}{2} \left(1 - \sqrt{1 + \frac{8}{y^2}} \right). \quad (33)$$

We now consider the limit $y \rightarrow 0$. From Eqs. (29) and (31), we conclude that one must have $\alpha/y \ll 1$ in order to recover the chain limit when both y and $\alpha \rightarrow 0$. On the other hand, $(\partial \beta f_b / \partial \alpha)_{\alpha=0} \rightarrow -\sqrt{2}/y$ and $(\partial^2 \beta f_b / \partial \alpha^2)_{\alpha=0}$ is dominated by a term of order y^{-2} . Consequently, we assume that $\alpha y^{-1} \sim y$, and, using Eqs. (19) and (30), make the following approximation for the bonding free energy to first order in α :

$$\beta f_b = 2 \ln y - \sqrt{2}y - \frac{\sqrt{2}\alpha}{y}. \quad (34)$$

From this approximation, the pressure is found to be

$$\beta p v_s = \sqrt{\frac{\eta}{2\Delta_{AA}}} - \frac{\Delta_{AB}}{\sqrt{2\Delta_{AA}}} \eta^{3/2} + \frac{B_2}{2} \eta^2, \quad (35)$$

where the different terms have fairly obvious meanings: the first represents the entropy of chains, the second the effective attraction promoted by Y junctions, and the third the ex-

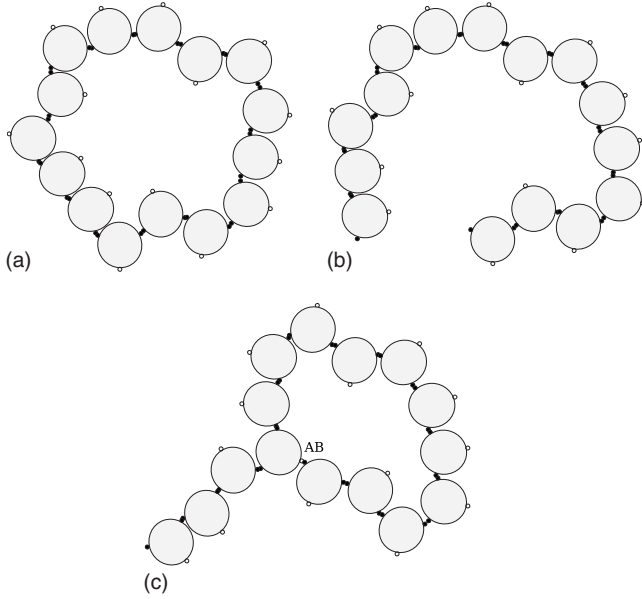


FIG. 5. (a) A (large) ring of particles connected by AA bonds; its energy is $E=0$. (b) When the ring opens, two ends are created (or an AA bond is broken), so the energy becomes $E=2\epsilon_e=\epsilon_{AA}$. (c) When a Y junction forms, an end is lost and an AB bond is created; the energy becomes $E=\epsilon_j=-\epsilon_{AB}+\epsilon_{AA}/2$.

cluded volume interactions. The critical packing fraction and the critical temperature can then be calculated from Eq. (35),

$$k_B T_c = \frac{3\epsilon_{AB} - \epsilon_{AA}}{b}, \quad (36)$$

$$\eta_c = \frac{v_b}{v_s} \exp\left(-\frac{b\epsilon_{AB}}{3\epsilon_{AB} - \epsilon_{AA}}\right), \quad (37)$$

where $b=2 \ln[2B_2 v_s / (3\sqrt{3} v_b)]$. Note that Eqs. (36) and (37) differ slightly from Eqs. (19) and (20) in [28] because the former have been derived via a more consistent route, providing more accurate results [see Figs. 4(a) and 4(b)].

We conclude that a critical point exists only when $\epsilon_{AB} > \epsilon_{AA}/3$, i.e., a minimum amount of AB attraction is needed to drive chain condensation promoted by Y-junction formation, as found in [28]. This result is almost the same as that obtained by Zilman and Safran [31] for Y-junction-driven criticality. In that paper, formation of a Y-junction was assumed to raise the energy of a ring of bonded particles without branching points by $\epsilon_j(>0)$; and formation of a chain (creation of two ends) from such a ring was assumed to raise the energy by $2\epsilon_e(>0)$. It was also shown that Y junctions, apart from increasing the energy, also increase the entropy of the system in such a way that, if $\epsilon_j < \epsilon_e/3$, there is coexistence between an end-rich gas and a junction-rich liquid. The energy parameters of [31] are related to those of the present model by (see Fig. 5) $2\epsilon_e = \epsilon_{AA}$ (since on creating two ends a AA bond is broken) and $\epsilon_j = -\epsilon_{AB} + \epsilon_{AA}/2$ (since on forming a Y junction, one end and one AB bond are created). Given these relations, Zilman and Safran's condition for the existence of a critical point translates to $\epsilon_{AB}/\epsilon_{AA} > \frac{1}{3}$, and the condition for "repulsive" junctions becomes $\epsilon_{AB}/\epsilon_{AA} < \frac{1}{2}$.

Our result may therefore be interpreted in terms of Y-junction formation. If $\epsilon_{AB}/\epsilon_{AA} > \frac{1}{2}$, the formation of Y junctions lowers the energy (relative to a chain-rich liquid phase), so we obtain the usual liquid phase (this range of parameters was not considered in [31]). If, on the other hand, $\frac{1}{3} < \epsilon_{AB}/\epsilon_{AA} < \frac{1}{2}$, the increase in energy is compensated by the increase in the entropy of junction formation, and a junction-rich liquid phase is still possible. Finally, if $\epsilon_{AB}/\epsilon_{AA} < \frac{1}{3}$ the energy cost of creating a junction is too large and condensation becomes impossible.

3. AB hyperbranched polymers connected by BB bonds

In the limit $\epsilon_{AA}=0$ and $\epsilon_{AB} \gg \epsilon_{BB}$, the system consists of hyperbranched polymers connected by a few BB bonds. From Eqs. (1)–(3), we obtain the bonding free energy when $\epsilon_{AA}=\epsilon_{BB}=0$ (i.e., when only hyperbranched polymers can form) as an explicit function of $y=1/\eta\Delta_{AB}$,

$$\beta f_{0,b}(\epsilon_{BB}=0, \epsilon_{AA}=0) = 2 \ln X_{A,0} - X_{A,0} + \ln X_{B,0} - \frac{X_{B,0}}{2}, \quad (38)$$

where

$$X_{B,0} = \frac{1}{2}[-(1+y) + \sqrt{(1+y)^2 + 4y}], \quad (39)$$

$$X_{A,0} = \frac{1}{2}(1 + X_{B,0}). \quad (40)$$

For strong AB association, i.e., in the hyperbranched polymer limit, $y \rightarrow 0$, Eq. (38) becomes

$$\beta f_{0,b} \approx \ln y - y + y^2. \quad (41)$$

Defining $\alpha = \Delta_{BB}/\Delta_{AB}$ and setting $\epsilon_{AA}=0$ (or, equivalently, $\Delta_{AA}=0$), the laws of mass action [Eqs. (2) and (3)] become

$$X_A + \frac{\alpha X_B X_A}{y} = 1, \quad (42)$$

$$X_B + \frac{2X_B X_A}{y} + \frac{\alpha}{y} X_B^2 = 1. \quad (43)$$

These equations define $X_A(y, \alpha)$ and $X_B(y, \alpha)$ implicitly; and, through Eq. (1), also the bonding free energy as a function of y and α , $\beta f_b(y, \alpha)$. The latter is expanded to first order in powers of α , for fixed y ; whence,

$$\left(\frac{\partial \beta f_b}{\partial \alpha}\right)_{\alpha=0} = -\frac{[1+y - \sqrt{(1+y)^2 + 4y}]^2}{8y}. \quad (44)$$

Now it follows from Eqs. (39), (40), (42), and (43) that one must have $\alpha y \ll 1$ in order to recover the hyperbranched polymer limit when both y and $\alpha \rightarrow 0$. Therefore, if we let $\alpha \rightarrow 0$ and $y \rightarrow 0$ we always get the hyperbranched polymer limit, whatever the "path" followed. So we may posit that α is going to zero independently of y and expand the bonding free energy, Eq. (19), to second order in y ,

$$\beta f_b \approx \ln y - y + y^2 + \alpha \left(-\frac{1}{2}y + 2y^2 \right). \quad (45)$$

The pressure is then

$$\beta p v_s = -\frac{2(1+2\alpha)}{\eta \Delta_{AB}^2} + \frac{B_2}{2} \eta^2 + \frac{B_3}{6} \eta^3, \quad (46)$$

whose first derivative with respect to η is always positive. Hence in the limit $\epsilon_{AA}=0$, $\epsilon_{BB} \ll \epsilon_{AB}$ no critical point exists.

4. AB hyperbranched polymers connected by AA bonds

In the limit $\epsilon_{BB}=0$ and $\epsilon_{AB} \gg \epsilon_{AA}$, rightmost portion of Fig. 4, the system consists of hyperbranched polymers connected by some AA bonds. The bonding free energy $\beta f_{b,0}$ is the same as in the previous case [Eq. (38)]. Defining the small parameter $\alpha = \Delta_{AA}/\Delta_{AB}$ and setting $\epsilon_{BB}=0$ (or, equivalently, $\Delta_{BB}=0$), the laws of mass action [Eqs. (2) and (3)] become

$$X_A + \frac{X_A X_B}{y} + \frac{2\alpha}{y} X_A^2 = 1, \quad (47)$$

$$X_B + \frac{2X_A X_B}{y} = 1, \quad (48)$$

where, as before, $y=1/\eta \Delta_{AB}$. These equations define $X_A(y, \alpha)$ and $X_B(y, \alpha)$ implicitly; and, through Eq. (1), also $\beta f_b(y, \alpha)$. The bonding free energy is now expanded to first order in powers of α , for fixed y , to yield Eq. (19), with

$$\left(\frac{\partial \beta f_b}{\partial \alpha} \right)_{\alpha=0} = -\frac{[1-y-\sqrt{(1+y)^2+4y}]^2}{8y}. \quad (49)$$

When $y \rightarrow 0$ and $\alpha \rightarrow 0$, we conclude from Eqs. (40) and (47) that one must have $\alpha/y \ll 1$ in order to recover the limit of hyperbranched polymers. On the other hand, $(\partial \beta f_b / \partial \alpha)_{\alpha=0} \rightarrow -1/2y$ and $(\partial^2 \beta f_b / \partial \alpha^2)_{\alpha=0}$ is dominated by a term of order y^{-2} . Therefore, if we assume that $\alpha y^{-1} \sim y$, the expansion of the bonding free energy to first order in α is

$$\beta f_b = \ln y - y - \frac{\alpha}{2y}. \quad (50)$$

Calculation of the critical point within this approximation yields $y_c=0$ and $\Delta_{AA}=B_2$ (i.e., the Θ point of a fluid of AA chains), which disagrees with the full numerical calculation: from Fig. 4(a), η_c only approaches zero asymptotically as $\epsilon_{AB}/\epsilon_{AA} \rightarrow \infty$. We therefore expand the bonding free energy to second order in α , with the result

$$\beta f_b = \ln y - y + y^2 - \frac{\alpha}{2y} + \frac{1}{2} \left(\frac{\alpha}{y} \right)^2. \quad (51)$$

The pressure now becomes, at low densities,

$$\beta p v_s = \frac{1}{\Delta_{AB}} \left(1 - \frac{2}{\eta \Delta_{AB}} \right) + (B_2 - \Delta_{AA}) \frac{\eta^2}{2} + (B_3 + 6\Delta_{AA}^2) \frac{\eta^3}{6}, \quad (52)$$

and the following relation holds between the critical density and the critical temperature:

$$\eta_c = \left(\frac{12}{B_3 + 6\Delta_{AA,c}^2} \right)^{1/4} \frac{1}{\Delta_{AB,c}^{1/2}}. \quad (53)$$

To obtain an analytical estimate for the critical point, we take $\Delta_{AB,c} \approx (v_b/v_s) \exp(\epsilon_{AA}/\epsilon_{AB})$ and $\Delta_{AA,c}=B_2$ to get the critical temperature. Combining these with Eq. (53) yields the critical density. The final results are

$$k_B T_c = \frac{\epsilon_{AA}}{\ln b}, \quad (54)$$

$$\eta_c = \left[\frac{12v_s^2}{v_b^2(B_3 + 6B_2^2)} \right]^{1/4} \exp\left(-\frac{\epsilon_{AB} \ln b}{2\epsilon_{AA}} \right), \quad (55)$$

where $b=1+B_2(v_s/v_b)$.

C. Mean cluster size and the percolation threshold

The shapes of the self-assembled clusters of patchy colloids with two A and one B sites may be identified easily when one of the interaction strengths vanishes and another dominates. This allowed us to carry out a detailed analysis of the criticality of fluids of BB dimers, interacting through AA or AB bonds; of AA chains, interacting through BB or AB bonds; and of AB hyperbranched polymers, interacting through AA or BB bonds. In particular, the way in which the critical point vanishes was investigated both analytically and numerically and the asymptotic expansions were shown to be very accurate over wide ranges of the interaction parameters. We proceed to show that, at the MF level, it is straightforward to calculate the mean equilibrium cluster size and to locate the percolation threshold, for which the size of these clusters diverges. Although we will return to a general discussion of the percolation threshold in future work, we give here an introductory discussion of the mean cluster size and the corresponding MF percolation threshold of patchy colloids with dissimilar sites. This is framed within Wertheim's theory of associating fluids. The calculation is exceedingly simple, and complements the analysis of the thermodynamics with a simple but complete description of the fluid structure.

Let us assume that the equilibrium clusters all have the same size and no loops, which is equivalent to neglecting any fluctuations (MF approximation). Under these conditions all clusters have a size equal to the mean cluster size, which is determined by the probabilities X_A and X_B that sites A and B are not bonded, which in turn are given by the laws of mass action [Eqs. (2) and (3)] for a given thermodynamic state. In the following we outline the calculation of the mean cluster size for a system of chains with Y junctions, i.e., a system where $\epsilon_{BB}=0$ and $\epsilon_{AB} \ll \epsilon_{AA}$.

Let us consider long AA chains connected by Y junctions (AB bonds). At the MF level, clusters comprise n_s linear strands, each of which contains ℓ particles. The mean cluster size is then given by the number of particles in one cluster, $\langle L \rangle = n_s \ell$. Clearly, the number of A sites in the cluster is $2\langle L \rangle$, the number of B sites is $\langle L \rangle$, the number of bonded B sites is $n_s - 1$ and the number of unbonded A sites is $n_s + 1$ (see Fig. 6). The equilibrium probabilities that A and B sites are unbonded become

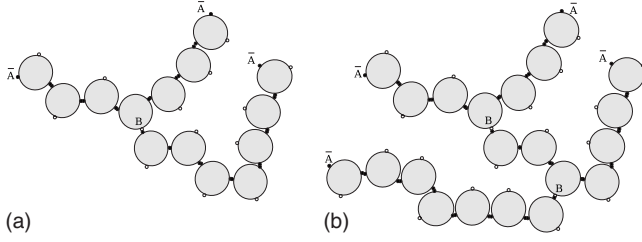


FIG. 6. (a) A cluster composed of two linear strands ($n_s=2$), each of size $\ell=7$; the number of unbonded A sites (labeled \bar{A}) is $n_s+1=3$, and the number of bonded B sites (labeled B) is $n_s-1=1$. (b) When a third linear strand is added, one new bonded B site and one new unbonded A site are created.

$$X_A = \frac{n_s + 1}{2\langle L \rangle}, \quad (56)$$

$$X_B = 1 - \frac{n_s - 1}{\langle L \rangle}. \quad (57)$$

Eliminating n_s , we obtain the mean cluster size in terms of X_A and X_B ,

$$\langle L \rangle = \frac{2}{2X_A + X_B - 1}. \quad (58)$$

This equation gives the mean cluster size, in the limit $\epsilon_{BB}=0$ and $\epsilon_{AB} \ll \epsilon_{AA}$. Analogous derivations follow for the mean cluster sizes in the other limits. The structure of the clusters depends on the limit considered and so do the relations between the probabilities X_A and X_B and the structural parameters. However, the dependence of the mean cluster size $\langle L \rangle$ on X_A and X_B is universal and given by Eq. (58). In fact, this equation may be derived simply by assuming that the equilibrium clusters have no loops and that the number of bonded sites per monomer is equal to its average (MF approximation): $\langle k \rangle = 2(1 - X_A) + (1 - X_B)$. The no-loop condition implies that when one bond is formed the number of clusters N_{cl} decreases by one; N_{cl} is then related to the number of monomers N and the number of bonds N_b through $N_{cl} = N - N_b$. The average number of bonds per monomer is $N_b/N = \langle k \rangle / 2$, and thus the mean cluster size becomes

$$\langle L \rangle \equiv \frac{N}{N_{cl}} = \frac{1}{1 - \frac{\langle k \rangle}{2}} = \frac{2}{2X_A + X_B - 1}. \quad (59)$$

Within MF the mean cluster size diverges at the percolation threshold [35] and the previous expressions for the mean cluster size apply only below this threshold, which occurs at $2X_A + X_B = 1$. Figures 3(d) and 4(d) show $1/\langle L \rangle$ at the critical point vs $\epsilon_{BB}/\epsilon_{AA}$ and $\epsilon_{AB}/\epsilon_{AA}$. In both cases $\langle L \rangle$ has a minimum for $\epsilon_{BB}/\epsilon_{AA} \sim 1$ or $\epsilon_{AB}/\epsilon_{AA} \sim 1$, which corresponds to nearly isotropic interactions and therefore the smallest clusters (as all sites are bonded with equal probabilities). The cluster size diverges in the limits of AA chains with X junctions [Fig. 3(d), left-hand side], AA chains with Y junctions [Fig. 4(d), left-hand side], and hyperbranched polymers [Fig. 4(d), right-hand side]. In contrast, in the dimers limit [Fig. 3(d), right-hand side], aggregates saturate at a finite mean size. This is consistent with the critical density going to zero

in the former three limits, but to a finite value in the latter.

A very similar result for the percolation threshold was obtained by Zilman and Safran [31] in a MF analysis of a model of self-assembled networks, based on the explicit calculation of the transverse spin correlations of a zero-component Heisenberg model with a particular three-spin term. The transverse correlation function measures the correlations between chain ends in the same cluster, and the MF correlation length (a measure of the average cluster size) for a system of chains with Y junctions was found to diverge at the percolation threshold, when the density of ends is three times that of the junctions, or

$$\eta \exp[-(\epsilon_j - \epsilon_e)/T] = \text{const}, \quad (60)$$

where ϵ_j and ϵ_e are the energies of junctions and ends, respectively [31].

In our model of chains with Y junctions, X_A and X_B are given by

$$X_A \approx \frac{1}{(2\Delta_{AA}\eta)^{1/2}}, \quad (61)$$

$$X_B \approx 1 - \frac{2\Delta_{AB}}{(2\Delta_{AA})^{1/2}} \eta^{1/2}, \quad (62)$$

leading to, for the MF percolation threshold,

$$\eta\Delta_{AB} = 1. \quad (63)$$

Recalling that $\Delta_{AB} \approx \exp(\epsilon_{AB}/T)$ and $\epsilon_{AB} = -(\epsilon_j - \epsilon_e)$, we find that, apart from the numerical prefactor, this is the same as the percolation threshold obtained by Zilman and Safran [Eq. (60)]. It is also easy to check that in our model the critical density [Eq. (37)] and the critical temperature [Eq. (36)] of the fluid of chains with Y junctions are related through $\Delta_{AB,c} \eta_c = 1$, implying that, in the limit of very low critical densities, the percolation line intersects the phase diagram at the critical point. We note that this differs from the result of Zilman and Safran [31], who found that the percolation transition always occurs at a density lower than ρ_c [the prefactor in Eq. (60) is smaller than that in Eq. (63)]. As noted by Zilman and Safran, the numerical prefactors depend rather sensitively on the details of the models and approximations, and we expect that the behavior reported above will become a zero-density limit within a higher-order approximation.

At the present level of approximation, we conclude that the difference between our result and that of Zilman and Safran is related to the consistency (or lack thereof) of the expansions for the thermodynamics and structural properties of the models. We note that our expansions for the thermodynamics are consistent and that the same model was used to calculate both thermodynamic and structural properties. Finally, we stress that our derivation is much simpler (lines rather than pages) and more transparent, yielding the correct zero-density behavior that appears to be lacking in Zilman and Safran's analysis.

IV. CONCLUSIONS

We have applied Wertheim's theory to patchy colloids with three sites: two of type A , with interaction strength ϵ_{AA} ,

and one of type B and strength ϵ_{BB} . Unlike sites also interact, with strength ϵ_{AB} . Our results are summarized below,

$$\epsilon_{AB} = 0 \begin{cases} \epsilon_{BB} \gg \epsilon_{AA}: \text{dimers connected by } AA \text{ bonds} \\ \epsilon_{AA} \gg \epsilon_{BB}: \text{chains connected by } BB \text{ bonds}(X \text{ junctions}) \end{cases}$$

$$\epsilon_{AB} \neq 0 \begin{cases} \epsilon_{AA} = 0 \begin{cases} \epsilon_{AB} \gg \epsilon_{BB}: \text{no critical point} \\ \epsilon_{BB} \gg \epsilon_{AB}: \text{no critical point} \end{cases} \\ \epsilon_{BB} = 0 \begin{cases} \epsilon_{AB} \gg \epsilon_{AA}: \text{hyperbranched polymers connected by } AA \text{ bonds} \\ \epsilon_{AA} \gg \epsilon_{AB}: \text{chains connected by } AB \text{ bonds}(Y \text{ junctions}) \end{cases} \end{cases}$$

When the unlike (AB) interactions vanish there are two types of criticality: dimer criticality driven by the AA attraction, with critical parameters related to those of a system of patchy colloids with four identical sites; and chain criticality, driven by BB attractions (X junctions). In the latter case the critical parameters are those of a Θ point, at which interchain attractions and repulsions balance, and tend to zero as the BB attraction vanishes. When the unlike interactions are finite, we find that condensation requires a finite strength of the AA attraction, leading to: (i) hyperbranched polymer criticality, driven by the AA attraction. The critical parameters are those of a Θ point, where attraction and repulsion between the hyperbranched chains balance, and which tend to zero as the AA attraction vanishes. (ii) chain criticality, driven by AB attractions (Y junctions). In the latter case a finite amount of AB attraction is required for condensation to occur.

In summary, we distinguish three types of condensation, based on the structure of the underlying networks: linear chains (AA clusters connected by BB or AB bonds); hyperbranched polymers (AB clusters connected by AA bonds); or dimers (BB clusters connected by AA bonds). In the first two cases the size of aggregates goes to infinity as the limit of infinite chains or hyperbranched polymers is approached, yielding a vanishing critical density, whereas in the third case the aggregates remain finite, with a finite critical density that

is related to that of a system with four identical patches. Furthermore, it is interesting to note that there can be no critical point in the absence of AA attraction, although such attraction by itself cannot drive condensation.

Finally, at the MF level, we find that the mean cluster size is a universal function of X_A and X_B , the fractions of unbonded A and B sites, and thus independent of cluster structure. From this we have derived the percolation line and concluded that, for AA chains with Y junctions, it always intersects the binodal line at the critical point in the limit of vanishing critical density. This is similar, but not identical, to Zilman and Safran's finding [31] for a lattice model of association. It should, however, be noted that the numerical prefactors in the asymptotic expressions depend sensitively on the model(s) and the level(s) of the approximations so that our result must be viewed as the zero-density limit, rather than a universal feature, of the model of patchy colloids investigated in this paper.

ACKNOWLEDGMENTS

Financial support from the Foundation of the University of Lisbon and the Portuguese Foundation for Science and Technology (FCT) under Contracts No. POCI/FIS/55592/2004 and No. POCTI/ISFL/2/618 is gratefully acknowledged.

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