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Percolation of colloids with distinct interaction sites

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We generalize the Flory-Stockmayer theory of percolation to a model of associating (patchy) colloids, which consists of hard spherical particles, having on their surfaces f short-ranged-attractive sites of m different types. These sites can form bonds between particles and thus promote self-assembly. It is shown that the percolation threshold is given in terms of the eigenvalues of a $m \times m$ matrix, which describes the recursive relations for the number of bonded particles on the ith level of a cluster with no loops; percolation occurs when the largest of these eigenvalues equals unity. Expressions for the probability that a particle is not bonded to the giant cluster, for the average cluster size and the average size of a cluster to which a randomly chosen particle belongs, are also derived. Explicit results for these quantities are computed for the case $f=3$ and $m=2$. We show how these structural properties are related to the thermodynamics of the associating system by regarding bond formation as a (equilibrium) chemical reaction. This solution of the percolation problem, combined with Wertheim's thermodynamic first-order perturbation theory, allows the investigation of the interplay between phase behavior and cluster formation for general models of patchy colloids.

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A system of bonding particles may form a gel if the probability of finding an infinite spanning cluster is nonzero. Indeed, a percolating aggregate is a gel if the bonds are long lived, as in chemical (irreversible) gelation, but need not be if the bonds are not necessarily long lived, as in physical (reversible) gelation. Percolation theory was applied to chemical gelation by Flory and Stockmayer (FS) [1–5]. The FS theory is a random-bond percolation model, and thus the fluid structure is determined by f, the particle valence (i.e., the maximum number of bonds that a particle can form), and p, the probability of bond formation. Despite its simplicity, FS theory adequately describes the gelation transition, as well as the cluster size distributions, both in the percolated or gel and in the nonpercolated or sol phases.

Recently there has been much interest in models of patchy colloids: micron-sized particles formed by controlled assembly of nanoconstituents, the surfaces of which are patterned so that they attract each other via discrete "sticky spots" of tunable number, size, and strength [6]. This opens up the possibility of tailoring their behavior, in particular to design and control physical gels [7]. The interplay between phase separation and percolation has been elucidated [7,8] for models with f identical bonding sites. Bond formation (overlap of two sites) lowers the energy, and as a result the particles self-assemble to form clusters whose sizes follow an equilibrium distribution. Computer simulations have revealed that when the valence $f \rightarrow 2^+$, the critical point is much depressed [8]. Consequently, equilibrium gels may form at very low densities and temperatures since bond lifetimes are then longer. The thermodynamic properties were found to be in good agreement with Wertheim's theory [9,10], which also provides an approximation for the bonding probability p. A combination of Wertheim's and FS theories yields an accurate description of the cluster distribution and percolation threshold of the simulated model patchy colloids [7].

An immediate generalization of the model (see Fig. 1) considers distinct patches or bonding sites [11,12]. Its thermodynamics is still described by Wertheim's theory. The FS random-bond percolation model, however, is no longer applicable as there are now (several) distinct bonding probabilities. In this Rapid Communication we derive a generalization of FS theory to models with several bonding probabilities applicable to (and inspired by) patchy colloids with distinct interaction sites (see Fig. 1).

We consider a system of N identical hard spheres (HSs), each with f bonding sites on its surface. These are of m different types and there are f_α sites of type $\alpha (\Sigma_{\alpha=1}^{m} f_\alpha = f)$. Equal bonding sites corresponds to $m=1$ and the thermodynamics of the model with $f=3$ and $m=2$ was investigated in [11,12]. Bond formation between a site α and a site β lowers the energy by $\epsilon_{\alpha\beta}$. At low enough temperatures, clusters with a number of particles connected by distinct bonds are formed. At percolation, an infinite spanning cluster appears. Here (as in [1,2]) we will assume that the clusters are treelike (i.e., there are no loops), and in order to characterize the cluster size distribution, we define the probabilities:

(i) p_α as the probability of finding a bonded site α; this equals $n_\alpha / (f_\alpha N)$, where n_α is the average number of bonded sites α;

(ii) $p_{\alpha \rightarrow \beta}$ as the probability of bonding a given site α to a

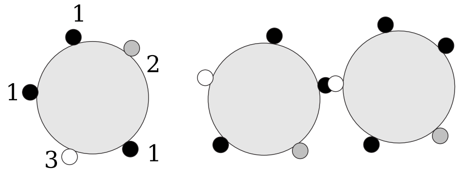

FIG. 1. Left: schematic representation of the particles—hard spheres (large disks) with bonding sites on their surfaces (small disks); there are f bonding sites of m types (f_α of type α); here $f=5$, $m=3$, $f_1=3$, and $f_2=f_3=1$. Right: when two bonding sites (α and β) overlap, a bond $\alpha\beta$ forms, decreasing the energy by $\epsilon_{\alpha\beta}$; here a bond 13 has formed.

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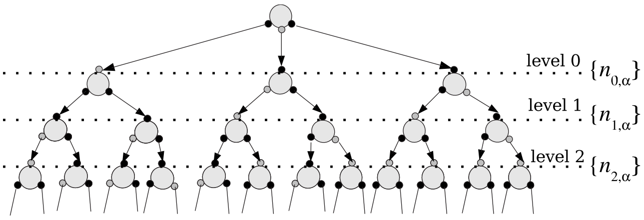

FIG. 2. Schematic representation of the treelike clusters. After choosing a random particle (at the top of the figure), the cluster can be represented by levels as shown; on each level there are n_α bonded sites of type α. The arrows represent the bonds that, in this description, allow one to go from one level to the next; each bond (arrow) connecting a site α to a site β occurs with probability $p_{\alpha\to\beta}$.

site β; this equals $p_{\alpha\to\beta}=(1+\delta_{\alpha\beta})n_{\alpha\beta}/(f_\alpha N)$, where $\delta_{\alpha\beta}$ is the Kronecker delta and $n_{\alpha\beta}$ is the total number of bonds between sites α and β; note that $p_\alpha=\Sigma_{\beta=1}^m p_{\alpha\to\beta}$ and $f_\alpha p_{\alpha\to\beta}=f_\beta p_{\beta\to\alpha}$.

(iii) Q_α as the probability that a particle is not bonded to the giant cluster through one of its sites α; $P_s=\Pi_{\alpha=1}^m Q_\alpha^{f_\alpha}$ is then the probability that a particle belongs to a finite cluster.

The $\{Q_\alpha\}$ are obtained from the $\{p_\alpha\}$ and $\{p_{\alpha\to\beta}\}$ by noting that given a random particle, one of its α sites is not bonded to the giant cluster if the site (1) is not bonded (with probability $1-p_\alpha$) or (2) is bonded to a site of another particle, but none of the other sites of that particle are bonded to the giant cluster. Then, under the no loop condition,

$$Q_\alpha = 1 - p_\alpha + \sum_{\beta=1}^{m} p_{\alpha\to\beta} \times \prod_{\gamma=1}^{m} \frac{Q_\gamma^{f_\gamma}}{Q_\beta}, \tag{1}$$

$Q_\alpha=1,\ \forall\,\alpha$ is always a trivial solution of Eq. (1). When this is the only solution the system is below the percolation threshold, which is reached when a nontrivial solution appears for some $\{p_\alpha\}$ and $\{p_{\alpha\to\beta}\}$. Here, however, we will calculate the percolation threshold following Flory's derivation for a system with f identical bonding sites. Briefly, the treelike clusters are described by a succession of levels; a particle on a given level is bonded to $(f-1)p$ particles on the level below; the number of particles on each level increases as a geometric progression of ratio $(f-1)p$. An infinite cluster exists when $(f-1)p>1$ and the percolation threshold occurs for $p_c=1/(f-1)$. We start by describing the treelike clusters of the general model by levels, as depicted in Fig. 2: to reach a site α on level $i+1$ one can start from an arbitrary site γ on level i and then follow a path through another site β of the same particle; the number of paths (once γ is chosen) is of course f_β if $\gamma\neq\beta$ and $f_\beta-1$ if $\gamma=\beta$; each path $\beta\to\alpha$ appears with probability $p_{\beta\to\alpha}P_s/(Q_\beta Q_\alpha)$, the probability of bonding β to α, given that β is not bonded to the infinite cluster. Therefore the number of bonded sites α on a given level is related to the number of bonded sites of all types on the previous level by

$$n_{i+1,\alpha} = \sum_{\gamma=1}^{m}\sum_{\beta=1}^{m} p_{\beta\to\alpha}\frac{P_s}{Q_\beta Q_\alpha}(f_\beta-\delta_{\beta\gamma})n_{i,\gamma}. \tag{2}$$

These recursion relations are linear so they can be written in matrix form

$$\tilde{n}_i = \tilde{T}^i\tilde{n}_0, \tag{3}$$

where $\tilde{n}_i$ is a column matrix with m rows whose entries are $n_{i,\alpha}$ and $\tilde{T}$ is a $m\times m$ matrix with entries $t_{\alpha\gamma}=\Sigma_{\beta=1}^m p_{\beta\to\alpha}P_s/(Q_\beta Q_\alpha)(f_\beta-\delta_{\beta\gamma})$. If the matrix $\tilde{T}$ is diagonalizable, then $n_{i,\alpha}=\Sigma_{\beta=1}^m c_{\alpha\beta}\lambda_\beta^i$, where λ_β are the eigenvalues of $\tilde{T}$. On the other hand, if the matrix is not diagonalizable, it can nevertheless be transformed into a Jordan form: the $n_{i,\alpha}$ are then finite sums of terms $c_{\alpha\beta}i^k\lambda_\beta^i$, k being an integer smaller than the (algebraic) multiplicity of eigenvalue λ_β. In either case, $c_{\alpha\beta}$ are constants that depend on $\tilde{n}_0$ and on the eigenvectors of $\tilde{T}$. Therefore, the m progressions represented by Eq. (3) will all converge to 0 if and only if $|\lambda_\alpha|<1,\ \forall\ \alpha$. Percolation occurs when there exists an α for which $|\lambda_\alpha|=1$. Thus the problem of finding the percolation threshold is transformed into the problem of calculating the eigenvalues of $\tilde{T}$. Notice that this calculation can be simplified if one considers the approach to the percolation threshold from a nonpercolated state (i.e., $Q_\alpha=1,\ \forall\ \alpha$).

The finite clusters formed in this system are fully characterized by their size distribution, usually defined as $r(n)$, the number of clusters of size n divided by the total number of particles in the system. Below percolation, $\Sigma nr(n)=1$; above percolation $\Sigma nr(n)$ equals the probability that a given particle does not belong to the giant cluster since this distribution does not contain the giant cluster. In order to proceed we define: (i) $N_n\equiv\Sigma_n nr(n)/\Sigma_n r(n)$ is the mean cluster size and (ii) $N_w\equiv\Sigma_n n^2 r(n)/\Sigma_n nr(n)$ is the mean size of a cluster to which a randomly chosen particle belongs. It is known that only N_w (and not N_n) diverges at percolation [or, in other words, only the second and higher moments of $r(n)$ diverge at percolation].

The calculation of N_n is straightforward because, under the no-loop condition, the number of clusters is decreased by one whenever a bond is formed. Consequently, the number of clusters is $N\Sigma_n nr(n)\times(1-n_b)$, where $n_b=\frac{1}{2}\Sigma_{\alpha=1}^m f_\alpha\Sigma_{\beta=1}^m p_{\alpha\to\beta}P_s/(Q_\alpha Q_\beta)$ is the mean number of bonded sites per particle that belongs to a finite cluster. Therefore,

$$N_n = \frac{2}{2-\sum_{\alpha=1}^{m} f_\alpha \frac{p_\alpha+Q_\alpha-1}{Q_\alpha}}. \tag{4}$$

Notice that this holds for both percolated and nonpercolated systems (in the latter case $Q_\alpha=1,\ \forall\ \alpha$).

The derivation of N_w follows simply with the aid of Fig. 2: from a randomly chosen particle a tree graph is built and the number of particles at each level is summed. The number of particles on level i equals $\Sigma_{\alpha=1}^m n_{i,\alpha}$, whence

$$N_w = 1 + \sum_{i=0}^{\infty}\sum_{\alpha=1}^{m} n_{i,\alpha}, \tag{5}$$

with $n_{i,\alpha}$ given by Eq. (3) and $n_{0,\alpha}=\Sigma_{\beta=1}^m f_\beta p_{\beta\to\alpha}P_s/(Q_\beta Q_\alpha)$. Once the eigenvalues and the eigenvectors of $\tilde{T}$ have been calculated, the sum in Eq. (5) can be performed. In the most general case where all eigenvalues are different, Eq. (5) becomes

$$N_w = 1 + \sum_{\alpha=1}^{m} \frac{a_\alpha}{1-\lambda_\alpha}, \tag{6}$$

where $\{a_\alpha\}$ are constants given in terms of $\{n_{0,\alpha}\}$ and of the eigenvectors of $\tilde{T}$.

The above expressions are consistent with previously known results when all bonding sites are identical ($m=1$). In what follows, we derive the percolation threshold, N_n and N_w, for the simplest nontrivial model with dissimilar bonding sites: three sites ($f=3$) of two types ($m=2$); two of the sites will be called $A(f_A=2)$ and the other $B(f_B=1)$ [11,12]. Probabilities Q_A and Q_B are obtained as implicit functions of p_α and $p_{\alpha\to\beta}(\alpha,\beta=A,B)$ using Eq. (1). The trace of $\tilde{T}$ is $T=p_{A\to A}Q_B+2p_{B\to B}Q_A$ and its determinant is $D=2Q_A^2(p_{B\to A}p_{A\to B}-p_{A\to A}p_{B\to B})$. The eigenvalues of $\tilde{T}$ are then $\lambda_\pm=\frac{1}{2}(T\pm\sqrt{T^2-4D})$, and it can be shown that they are real and $\lambda_+\geq|\lambda_-|$, for all sets of probabilities $\{p_\alpha\}$ and $\{p_{\alpha\to\beta}\}$. The percolation threshold is thus given by $\lambda_+=1$. The explicit expressions for N_w depend on the multiplicity of $\lambda_\pm$:

(i) Identical eigenvalues ($\lambda_+=\lambda_-$). This happens if and only if $p_{A\to A}=0$; since $p_{A\to A}=0$ implies $p_A<\frac{1}{2}$ and $Q_A=Q_B=1$ [from Eq. (1)], one has $\lambda_+=1-2p_A$. Therefore, no percolation occurs. N_w is obtained from Eq. (5) with the result

$$N_w = \frac{1-2p_A+p_B-2p_A^2}{(1-2p_A)^2}. \tag{7}$$

(ii) Different eigenvalues ($\lambda_+\neq\lambda_-$). This is the generic case. N_w is obtained from Eq. (6):

$$N_w = 1 + \frac{2\dfrac{Q_A-1+p_A}{Q_A}+\dfrac{Q_B-1+p_B}{Q_B}-\dfrac{3}{2}D}{1-T+D}. \tag{8}$$

Finally, N_n is obtained directly from Eq. (4): $N_n=2/\{2-2[(Q_A-1+p_A)/Q_A]-[(Q_B-1+p_B)/Q_B]\}$.

In summary, once $\{p_\alpha\}$ and $\{p_{\alpha\to\beta}\}$ are known, $\{Q_\alpha\}$ are calculated using Eq. (1), and all other quantities of interest can be computed. In general, the eigenvalues of $\tilde{T}$ (and thus N_w) will have to be found numerically.

Up to this point, percolation has been considered a geometric or connectivity problem. However, the N particles of the model are an interacting thermodynamic system: they are contained in a volume V at a temperature T. Bond formation between a site α and a site β lowers the energy by $\varepsilon_{\alpha\beta}$, and the HSs provide an excluded-volume repulsion. The relation between percolation and the thermodynamic properties of this system may be established as follows. Formation of a bond between an α and a β bonding sites and the breaking of this bond can be seen as a chemical reaction: $\alpha+\beta\leftrightarrow\alpha\beta$. Chemical equilibrium between these species (nonbonded sites and bonds) can thus be expressed by

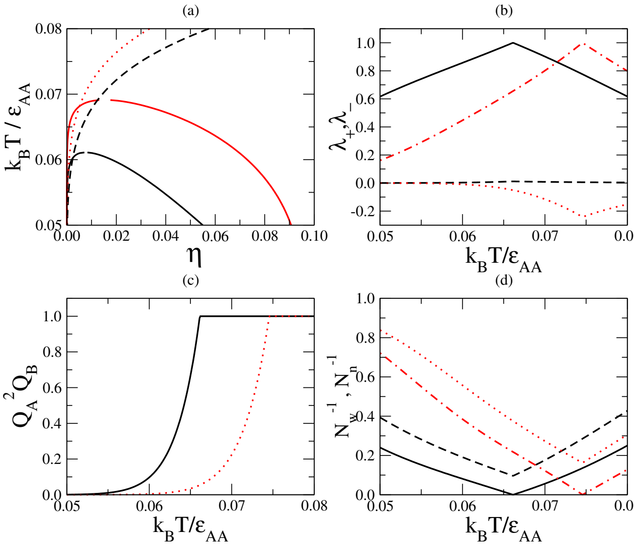

FIG. 3. (Color online) Two realizations of the model $2A+1B$: solid and dashed (black) lines are for $\epsilon_{BB}=0, \epsilon_{AB}=0.75\epsilon_{AA}$; dashed-dotted and dotted (red) lines are for $\epsilon_{AB}=0, \epsilon_{BB}=0.75\epsilon_{AA}$. (a) Phase diagrams and percolation lines; (b) eigenvalues of $\tilde{T}$ (λ_+: solid and dot-dashed lines; λ_-: dashed and dotted lines); (c) $Q_A^2Q_B$, fraction of particles in the sol phase; (d) N_w (solid and dot-dashed lines) and N_n (dashed and dotted lines). In (b)–(d) all quantities are calculated as functions of temperature at the critical density.

$$\frac{n_{\alpha\beta}}{(f_\alpha N-n_\alpha)(f_\beta N-n_\beta)} = \frac{\chi_{\alpha\beta}}{V}, \tag{9}$$

where $\chi_{\alpha\beta}$ is the equilibrium constant for the reaction. Combining chemical equilibrium and the relations between p_α, n_α and $p_{\alpha\to\beta}, n_{\alpha\beta}$ yields

$$p_{\alpha\to\beta} = \eta\Delta_{\alpha\beta}f_\beta(1-p_\alpha)(1-p_\beta), \tag{10}$$

where $\eta\equiv v_sN/V$ is the packing fraction, v_s is the HS volume, and $\Delta_{\alpha\beta}=(1+\delta_{\alpha\beta})\chi_{\alpha\beta}/v_s$. Using the (normalization) relation between p_α and $p_{\alpha\to\beta}$, $p_\alpha=\Sigma_{\beta=1}^{m}p_{\alpha\to\beta}$, the following m equations result:

$$p_\alpha = \eta(1-p_\alpha)\sum_{\beta=1}^{m}\Delta_{\alpha\beta}f_\beta(1-p_\beta). \tag{11}$$

Equations (10) and (11) express the bonding probabilities as functions of η and $\Delta_{\alpha\beta}$, and so to complete the relation between percolation and thermodynamics, an approximation for the equilibrium constant is needed. Wertheim's first-order perturbation theory [9,10] relates these probabilities to the density and temperature through m laws of mass action [with exactly the same dependence on f_α and p_α as Eq. (11)] and thus provides an approximation for the equilibrium constant that we shall adopt. This approximation depends on the interaction potential between the bonding sites, $V_{\alpha\beta}(\vec{r})$, and on the pair correlation function of the reference HS system $g_{ref}(\vec{r})$: $v_s\Delta_{\alpha\beta}=\int g_{ref}(\vec{r})\{\exp[-V_{\alpha\beta}(\vec{r})/(k_BT)]-1\}d\vec{r}$ (k_B is Boltzmann's constant). If the interaction between bonding sites α and β is taken to be a square well of depth $\epsilon_{\alpha\beta}$ and volume $v_{b,\alpha\beta}$ (the bond volume), and the ideal gas approximation is used for g_{ref},

$$\Delta_{\alpha\beta} = \frac{v_{b,\alpha\beta}}{v_s}\{\exp[\epsilon_{\alpha\beta}/(k_B T)] - 1\}. \tag{12}$$

Therefore, for a model with any f and m, at a given η and T, one proceeds as follows: first, Eq. (12) is used to compute $\Delta_{\alpha\beta}$; then Eqs. (1), (10), and (11) yield p_α, $p_{\alpha\rightarrow\beta}$, and Q_α. The percolation threshold N_w and N_n can then be found as a function of η and T.

As an example we consider again the model with $f=3, m=2$ and $v_{b,\alpha\beta}=6,357\times 10^{-4} v_s$ [7], and study numerically two cases: (i) $\epsilon_{AB}=0$ and $\epsilon_{BB}=0.75\epsilon_{AA}$; and (ii) $\epsilon_{BB}=0$ and $\epsilon_{AB}=0.75\epsilon_{AA}$. The liquid-vapor binodals are calculated as described in [11]. The phase diagram [Fig. 3(a)] contains a percolation line where $\lambda_+=1$: below this line there is nonzero probability of finding an infinite cluster in the system. Figure 3(a) shows that the liquid phase is in fact a network (since it is found below the percolation line) and therefore may form a gel. In Figs. 3(b)–3(d) we plot several relevant quantities as functions of temperature at the critical density for either system. Figure 3(b) shows the eigenvalues $\lambda_\pm$: we note that $\lambda_+ \leq 1$ and $\lambda_- < \lambda_+$; $\lambda_+=1$ defines a percolation temperature for the chosen density. In Fig. 3(c), $Q_A^2 Q_B$, i.e., the probability that a given particle does not belong to the gel phase, is plotted: above the percolation temperature $Q_A^2 Q_B = 1$. Finally, in Fig. 3(d) we plot results for N_n and N_w: as expected, N_w diverges at the percolation temperature.

We have derived the percolation threshold and the first moments of the cluster distribution function for a generalized patchy model under the no-loop assumption. We showed how Wertheim's theory may be used to calculate the bonding probabilities for models with any number and type of interacting sites, paving the way for a general investigation of the interplay between cluster formation and criticality. As discussed elsewhere, the model provides a much deeper understanding of the onset of criticality in systems of low-valence particles [12], enabling us to go from independent chains to hyperbranched polymers and thence to simple dimers. It provides the key to controlling the bond lifetimes of various types of equilibrium networks by depressing their critical point so as to pre-empt phase separation, thereby allowing the realization of ideal gels in single-component one-phase systems.

The results reported in this Rapid Communication can be generalized to mixtures of particles of general f, m, and f_α. This, combined with Wertheim's theory [8,10], allows a complete description of the thermodynamics and percolation of mixtures of any type of patchy particles. A much more challenging task, however, concerns the calculation of the cluster size distribution or the construction of a generating function for its moments. This remains an open problem even for the single-component model with distinct interaction sites [13].

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