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**Title:** Equilibrium self-assembly of colloids with distinct interaction sites: Thermodynamics, percolation, and cluster distribution functions

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**Abstract:** We calculate the equilibrium thermodynamic properties, percolation threshold, and cluster distribution functions for a model of associating colloids, which consists of hard spherical particles having on their surfaces three short-ranged attractive sites (sticky spots) of two different types, A and B. The thermodynamic properties are calculated using Wertheim's perturbation theory of associating fluids. This also allows us to find the onset of self-assembly, which can be quantified by the maxima of the specific heat at constant volume. The percolation threshold is derived, under the no-loop assumption, for the correlated bond model: In all cases it is two percolated phases that become identical at a critical point, when one exists. Finally, the cluster size distributions are calculated by mapping the model onto an effective model, characterized by a-state-dependent-functionality ( $\bar{f}$ ) over bar and unique bonding probability ( $\bar{p}$ ) over bar. The mapping is based on the asymptotic limit of the cluster distributions functions of the generic model and the effective parameters are defined through the requirement that the equilibrium cluster distributions of the true and effective models have the same number-averaged and weight-averaged sizes at all densities and temperatures. We also study the model numerically in the case where BB interactions are missing. In this limit, AB bonds either provide branching between A-chains (Y-junctions) if  $\epsilon_{AB}/\epsilon_{AA}$  is small, or drive the formation of a hyperbranched polymer if  $\epsilon_{AB}/\epsilon_{AA}$  is large. We find that the theoretical predictions describe quite accurately the numerical data, especially in the region where Y-junctions are present. There is fairly good agreement between theoretical and numerical results both for the thermodynamic (number of bonds and phase coexistence) and the connectivity properties of the model (cluster size distributions and percolation locus). (C) 2010 American Institute of Physics. [doi:10.1063/1.3435346]

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