Connectivity in a binary mixture of randomly centered spheres with selective particle clustering

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I. INTRODUCTION

Some attention has been recently paid to study the percolation properties of binary mixtures using different models.[1,2] The simplicity of the randomly centered spheres model (RCS) makes it a suitable system to continuum percolation studies both from theoretical[3,4] and simulation points of view.[5] The RCS model is made of penetrable spheres; the radius of the spheres R_{cl} serves only to define the connectivity between particles, i.e., two particles are part of the same cluster if their spheres overlap. The investigations have been mainly focused on the one-component RCS system. Nevertheless, a mixture of RCS particles may exhibit *specificities* derived from the fact that a label (or color) is assigned to each particle. The selective particle connectivity criterion—only direct links between particles of different species (colors) are allowed—is appropriate for the study of such specific mixing effects. Wu and Chiew[6] used this criterion to study the percolation threshold and pair-connectedness functions of mixtures by means of the Percus–Yevick (PY) integral equation. A simulation of mixtures of overlapping spheres has been reported, but it is centered on the polydispersity effect produced by the different radii of the components.[7] As far as we are aware, no simulation results using the selective particle connectivity have been published.

In a recent paper,[8] we have investigated the connectivity properties (pair connectedness functions and percolation thresholds) of highly charged electrolyte solutions. The RCS properties are obvious references to assess real structural features—by distinguishing the effects of the interionic potentials from mere consequences of the different labeling of the ions (the sign charge)—in electrolyte solutions. The motivation for this work is then twofold; namely, to provide pseudoexperimental data to (i) check theoretical predictions and (ii) provide a reference to assess association phenomena in ionic systems.[9]

II. RESULTS

The system is an equimolar binary mixture of randomly centered spheres of equal size. The configurations were generated by randomly placing 216 particles in a cubic box with periodic boundary conditions. To analyze the effect of the system size, we have done some computations using 512 spheres. Since the results were substantially the same, we will report only the data for the 216 particle system. A label was given to every particle in order to assign it to a given specie. In these conditions, there are two independent pair connectedness functions hereafter referred to as p_{+-} and p_{++}. Most of the results in this paper correspond to the *selective* clustering criterion (the overlapping spheres must carry different labels to consider the particles directly connected), but we have also studied the effect of removing such condition. The box length was chosen to give a total number density $\rho=1$; thus, the clustering radius R_{cl} defines the reduced density $\rho^*=\rho R_{cl}^3$. The averages were performed over samples of, typically, 5000 configurations.

In Fig. 1, $p_{++}(r)$ and $p_{+-}(r)$ at $\rho^*=0.8$ are shown. The condition $p_{+-}(r)=1$ must hold for $r<R_{cl}$ thus giving an idea of the statistical accuracy. The noise is in general acceptable unless r approximates zero. As previously noted,[6,8] this condition does not apply to $p_{++}(r)$ because of the selective particle condition. Other condition easily explained with heuristic arguments[8] is that $p_{++}(r) > p_{+-}(r)$ for r close to but greater than R_{cl}. Note that both functions converge at a distance roughly twice the clustering radius. Also included in Fig. 1 are the integral equation results for $p_{++}(r)$.[6] The PY approximation underestimates the pair connectedness function and, therefore, overestimates the percolation threshold. Though this effect was already observed in the one-component system, it is slightly amplified when the selective clustering criterion is considered.

Plotted in Fig. 2 are the unlike-label pair connectedness functions p_{+-} at two representative densities. Our interest is to study the influence of the selective particle clustering, so the results obtained by allowing direct links between particles of the same color are also displayed. The drop produced by the selective condition is drastic. (Incidentally, this makes more relevant the results for highly charged electrolytes for which both curves are almost identical.[8]) A consequence of the departures shown in Fig. 2 is the difference in the percolation thresholds computed with both criteria. For the equimolar equisized RCS mixture with selective clustering, we have obtained $\rho_c^*=0.982$ whereas the same system with the selective condition removed has $\rho_c^*=0.654$. The effect of the selective clustering criterion is to increase the percolation threshold. As the latter criterion makes the result indistinguishable from that of the single-component RCS, the value can serve to check the accuracy of our calculation. It agrees with the more confident values previously reported that locate the percolation threshold in a range between 0.64 and 0.67 (see Ref. 10, and references therein). As commented above the imposition of a selective clustering enhances the departures

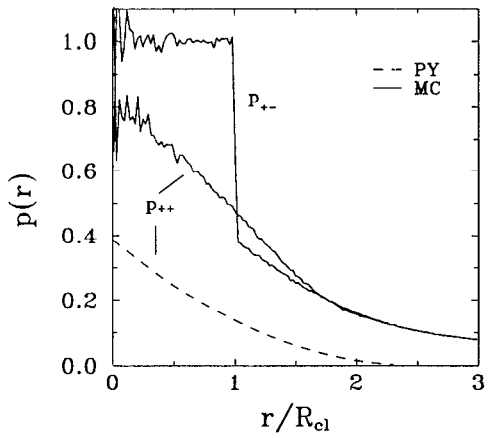

FIG. 1. The pair-connectedness functions $p_{+-}(r)$ and $p_{++}(r)$ plotted as a function of r/R_{cl} for $\rho^*=0.8$. PY results taken from Ref. 6 are included for comparison.

between simulation and integral equation results already known for pure RCS systems. From Fig. 1, it is not surprising that the PY percolation density reported by Wu and Chiew[6] ($\rho_c^* \approx 2.2$) is about twice the simulation result.

By integrating the pair connectedness functions, it is possible to calculate the connected coordination numbers which inform about the number of neighbors with color j connected to the average particle with label i. For an equimolar mixture

$$n_{ij}^{\dagger}(r)=\rho_j \int_0^r 4\pi r^2 p_{ij}(r')dr', \tag{1}$$

ρ_j being the bulk number density of species j. We define the *excess coloring* as

$$q_{exc}^{\dagger}(r)=n_{+-}^{\dagger}(r)-n_{++}^{\dagger}(r). \tag{2}$$

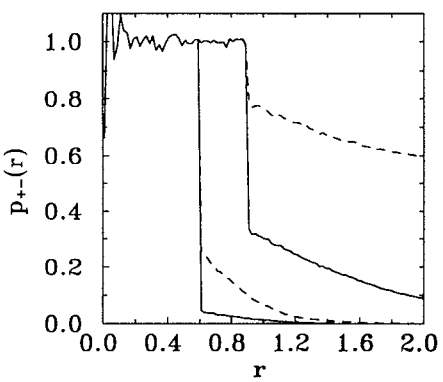

FIG. 2. The unlike-label pair connectedness function p_{+-} at two densities, $\rho^*=\rho R_{cl}^3=0.9^3$ (upper curves) and 0.6^3 (lower curves). Full lines represent results using the selective particle clustering and dotted lines are for the unrestricted labeling connectivity.

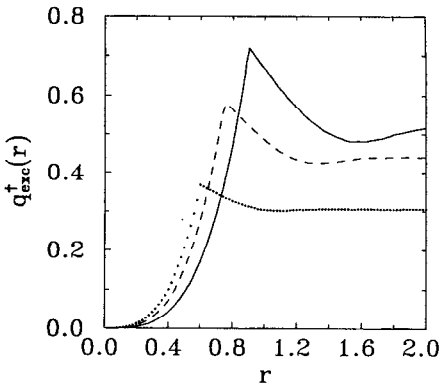

FIG. 3. The excess coloring function for the RCS mixture at different densities, $\rho^*=\rho R_{cl}^3=0.9^3$ (full lines), 0.75^3 (dashed), and 0.6^3 (dotted).

This function is of particular interest when a charged system is considered because it represents the cancellation of the charge of a particle due to other ions belonging to the same cluster[8] (hence, the name excess connected charged used in this specific case).

Figure 3 displays the excess coloring at several densities. The presence of a singularity (a cusp at $r=R_{cl}$) and the existence of oscillations beyond that point is a new result (note that $q_{exc}^{\dagger}(r)$ would be a continuous function reaching the unity at $r\to\infty$ if the selective clustering were removed). The height at the cusp as well as the amplitude of the oscillations increase with density. Since the infinite dilution limit of electrolyte solutions is the RCS mixture, the results for the latter system with the selective particle clustering are specially revealing because the apparent structural features are brought about exclusively by the labeling of particles (the particles do not interact). It is thus needed to take into account such features when studying the structure of interacting systems.

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