Electronic Supplementary Material (ESI) for Soft Matter.

Influence of protein charge patches on the structure of protein-polyelectrolyte complexes: Supplementary Information

Rituparna Samanta, Venkat Ganesan

A. Mixtures of Polyanions and Positively Charged Particles

In this section, we present results on the influence of charge heterogeneity on the particle structure for the case where the particle does not possess any negatively charged patches (non-zwitterionic particles).

1. Influence of Net Charge and Inhomogeneity of Charge Distribution

Figures 1(a-d) presents results for the influence of particle net charge on the structure of PI1 and PI2 particles at a fixed particle volume fraction. From the results displayed in Figure 1(a), for low particle charges of $Q_{net} = 5$, we observe a peak in the particle-particle RDF at contact. In such cases, the polymer depletion attraction dominates the interparticle electrostatic repulsion, resulting in clusters of direct particle aggregates. Not surprisingly, with increase in particle charge, the peak at contact reduces due to the increased electrostatic repulsion between the like charged patches. At a higher particle charge of $Q_{net} = 40, 50$, the RDFs for both PI1 and PI2 particles are seen to exhibit a peak at a distance of approximately $\sim 0.5R_g$, indicating the formation of polymer-bridged particle clusters. The RDF's for intermediate particle charges $Q_{net} = 20$, display a mixed behavior where it has a non-zero value of RDF both at the particle contact and at a finite interparticle distance.

The above results can be understood by noting that with increase in particle charge, two factors come to play: On the one hand, the interparticle electrostatic repulsion become stronger and reduces the tendency for direct particle aggregation. Secondly, polymer adsorption and bridging becomes more relevant and leads to the formation of polymer-bridged clusters.

Behavior consistent with such trends are also seen to manifest in the particle cluster statistics displayed in Figure 1(b) in which there is a reduction in the sizes of particle clusters with increase in Q_{net}. Correspondingly, the cluster size distributions relating to the polymer-bridged aggregates (Figure 1(c)) are seen to display a shift towards formation of larger clusters. Figure 1(d) supports the above observations with increasing value of B_r with increase in net charge.

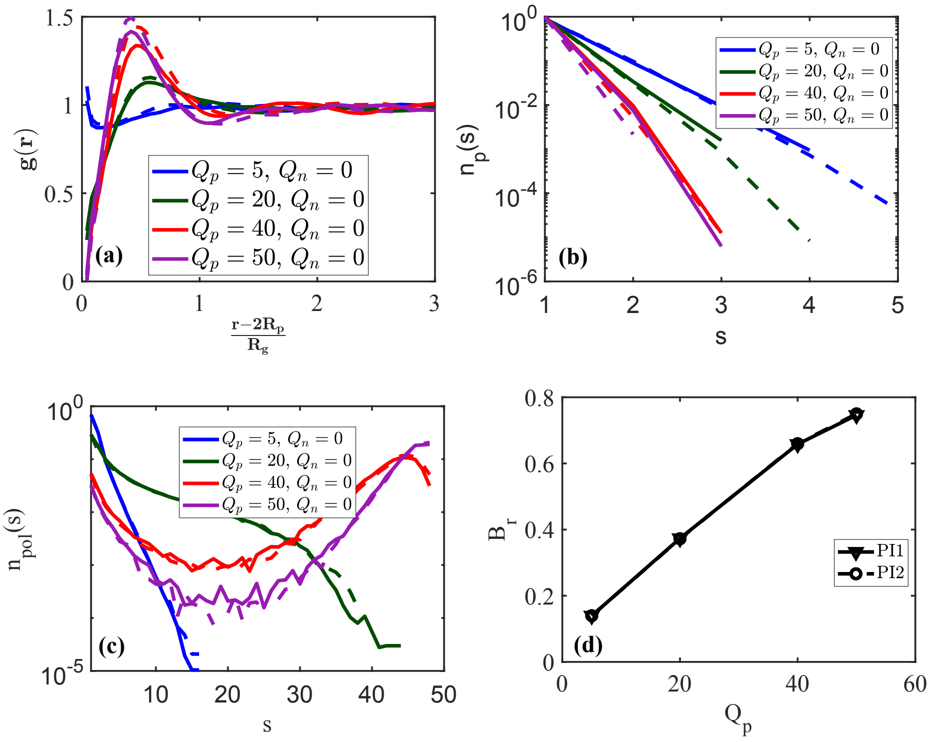

Figure 1. Influence of Particle Charge Q_{net}: (a) Particle-particle RDF; (b) Size distribution of the particle-particle clusters; (c) Particle-polymer cluster distribution; (d) Bridging fraction. For all the results, bulk polymer concentration $C/C^* = 0.092$ and $\phi_p = 0.025$. Solid lines represent PI1 and dashed lines represent PI2 particles:

Figures 2(a)-(d) presents the effect of inhomogeneous charge distribution corresponding to a system at a fixed volume fraction of the particles $\phi_p = 0.025$ and net charge, $Q_{net} = 40$. From the results of Figure 2(a), it can be seen that for all the patterns of charge heterogeneities, the particle-particle RDFs suggests formation of polymer-bridged particle clusters. The particle-particle and particle-polymer cluster size distributions shown in Figure 2(b-c) also support such a hypothesis. Explicitly the particle-particle cluster distribution show that most of the particles form clusters of 1-2 particles. On the other hand, the characteristics of the polymer-bridged clusters presented in Figure 2(c) displays a peak in the cluster distribution near $s = N_p$ which depicts that there are clusters bridged by polymers which encompasses almost all the particles.

In comparing the different patterns of charge heterogeneities, we observe that the intensity of the RDF peak is seen to follow the order PI0 < PI1 < PI2 < PI4 < PI3. Overall the

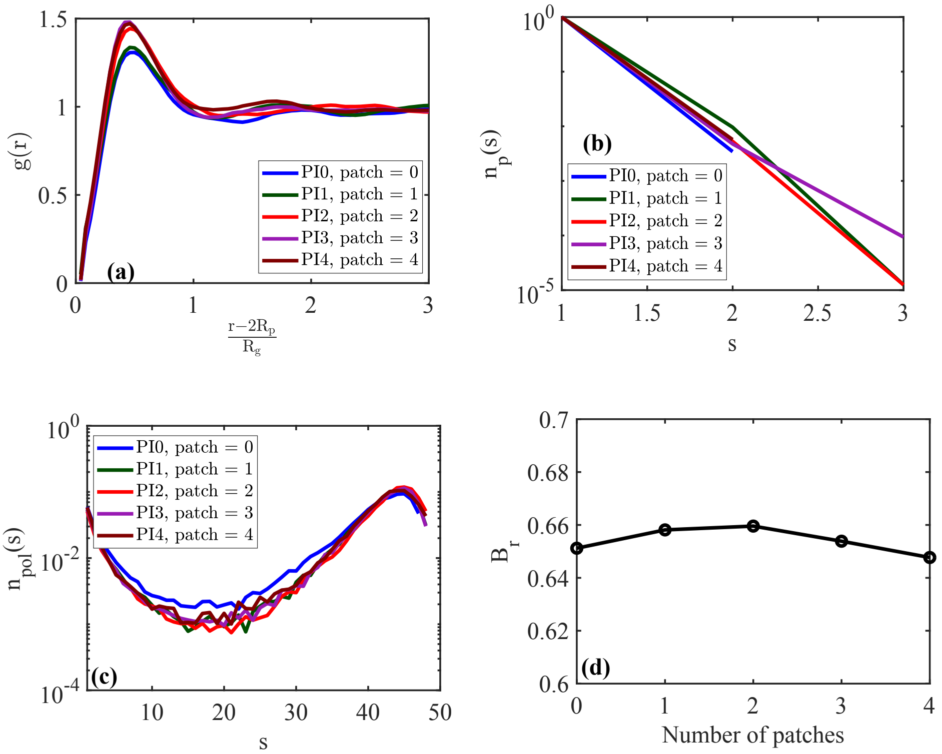

Figure 2. Effect of charge heterogeneity.: (a) Particle-particle RDF for different patterns of charge heterogeneities; (b) Size distribution of the particle-particle clusters; (c) Size distribution of the polymer-bridged particle clusters; (d) Bridging fractions. All the results are for $\phi_p = 0.025$, bulk polymer concentration $C/C^* = 0.092$ and $Q_p = 40, Q_n = 0$

particle-particle clusters for heterogeneous charged particles are seen to be slightly larger than the homogeneously charged particle. In the context of the cluster size distribution of polymer-bridged particle clusters, the effect of charge heterogeneity is seen to have a minor effect. Mainly, the value of second peak, which corresponds to the most probable size of the clusters, are seen to be higher for the patchy (PI1, PI2, PI3 and PI4) particles than the PI0 particles, suggesting the formation of clusters consisting of more particles when the particle possesses charge heterogeneities. Figure 2(d) shows the polymer bridging fraction, which is almost invariant with number of patches.

The results of Figure 2 can be rationalized by arguing that distributing the charge of the particle as multiple patches leads to decreased electrostatic repulsion between the particles. However, it also creates a region of higher charge density on the surface of the particles.

More explicitly, PI1 has Q_{net} distributed over half of the particle surface than PI0 where the charge is distributed over the whole surface. Therefore, compared to PI0 particles, for PI1 particles the electrostatic attraction between the particles and the polymers are expected to be increased, leading to increased propensity for forming polymer bridged clusters. Similar to the zwitterionic patchy particles, the increase in the number of patches, due to the presence of multiple patches, the charge per patch reduces. As a result, the particle-particle repulsion is weakened, and thus the RDF peak value increases. However when the number of patches are increased further, there is more likelihood of finding similarly patched charges of two different particles in the proximity. As a result, the electrostatic repulsion interactions is expected to again increase and lead to the reduction in the peak value of RDF. Such a reasoning explains the results seen for PI4 particles relative to PI2 and PI3 cases.

In summary, non-zwitterionic particles form direct particle aggregates at low net charges and transition to polymer-bridged aggregates at higher charges due to increased electrostatic repulsion and adsorption of oppositely charged polyelectrolytes. However, the charge heterogeneity is seen to exert only a small influence on the structural characteristics.

2. Influence of particle volume fraction

Figures 3 (a-d) presents results for the influence of particle volume fraction on the structure of PI1 and PI2 particles at a fixed particle net charge, $Q_{net} = 40$. At all particle volume fractions ϕ_p, the peaks of the RDF are seen to be shifted from the particle surface, indicating the occurrence of polymer-bridged clusters. With increase in particle volume fraction, electrostatic repulsion is expected to be screened. Consistent with such expectations, the RDF peak value and the particle-particle cluster sizes increase with increase in particle volume fraction. The particle-polymer cluster size distribution for higher particle distributions, shows a second peak for s $\simeq N_p$ corresponding to the formation of a percolation behavior. Consistent with such results, the bridging fractions $\simeq 1.0$ for larger particle volume fractions.

In comparing the influence of particle charge heterogeneities, consistent with the reduced electrostatic interactions, the peak of RDF of PI2 particles are seen to be higher than that of PI1 particles at all volume fractions. Interestingly at any specific particle volume fraction,

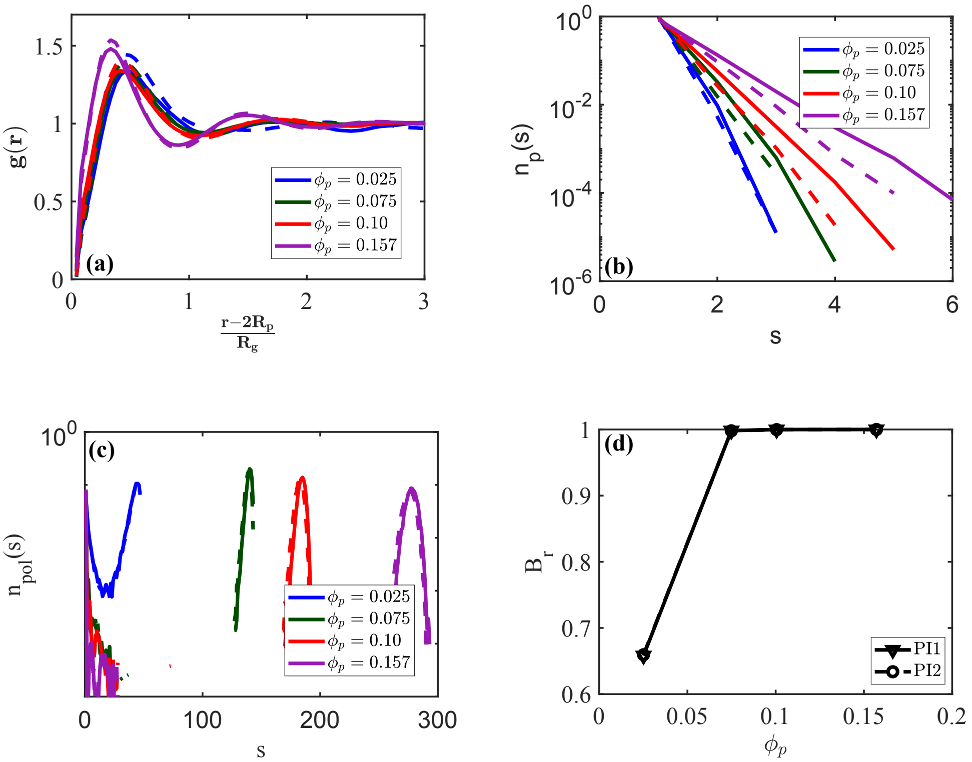

Figure 3. Influence of particle volume fraction. (a) Particle-particle RDF at different particle volume fraction; (b) Size distribution of the particle-particle cluster; (c) Size distribution of the particle polymer cluster. Cluster sizes are normalized by the total number of particles.(d) Bridging fraction at different ϕ_p. (e) Normalized pore size distribution The dashed lines represent the PI2 and the solid lines are for PI1 particles with $Q_{net} = 40$, bulk polymer concentration $C/C^* = 0.092$

for PI1, there is a greater fraction of particles involved in larger clusters. We speculate that this arises because the charged patches are separated by larger distance in PI1 than PI2. Despite such differences, the particle-polymer cluster size distribution and the bridging fractions exhibits no perceptible difference for the two heterogeneous geometries for all volume fractions.

3. Phase Diagrams

Based on the classification of phases described in the main article, in Figure 4 we collate the results in terms of “phase diagrams” for the PI0, PI1 and PI2 geometries. For all the cases, we observe that at lower particle charges, there is a propensity to form particle-particle aggregates. With increase in the particle charge, there is seen to be an increase in tendency to form polymer-bridged complexes. When compared to homogeneously charged particle (PI0), while the structural characteristics exhibited by PI1, PI2 particles were different, when categorized in terms of phase behavior, there was little to no influence of charge inhomogeneities. Hence, we do not present distinct phase diagrams for the different patterns of charge heterogeneities.

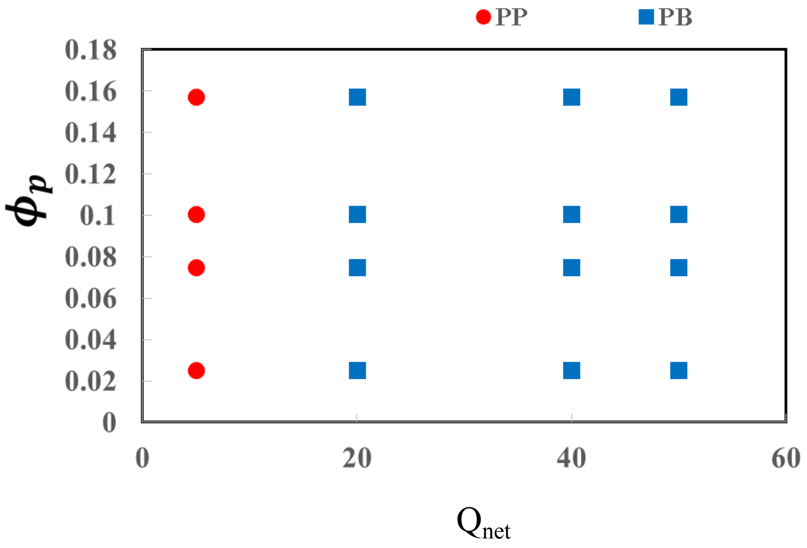

Figure 4. Phase diagram for PI0/PI1/PI2 particles. For all the results, bulk polymer concentration $C/C^* = 0.092$. PP - Direct particle aggregation; PB - Polymer bridged aggregation.