Supporting information for: Interactions and Aggregation of Charged Nanoparticles in Uncharged Polymer Solutions

Gunja Pandav, Victor Pryamitsyn, and Venkat Ganesan*

The University of Texas at Austin, McKetta Department of Chemical Engineering, Austin, TX 78712.

E-mail: venkat@che.utexas.edu

1 Details of semi grand canonical framework

In Section 3.4 of the main article, we carry out SCMF simulations at the conditions corresponding to the same chemical potential of the polymer at the infinite dilution conditions. In this section, we discuss the procedure employed to deduce such concentration of polymers.

For such an exercise, we fix the positions of the particles at random locations and polymer uptake at a fixed chemical potential is calculated using self-consistent field theory framework (See Section 2.3 of the main text). In Figure S1, we display the polymer concentration in presence of particles denoted as $C_{colloid}$ as a function of bulk polymer concentration for varying particle volume fraction. With increasing volume fraction of particles (ϕ_p), we observe that the polymer uptake from the reservoir decreases as a result of high entropic costs. With increasing bulk polymer concentration, the polymer uptake is seen to increase. Such an effect arises as a consequence of reduction in depletion shell around the particle as a result of high polymer concentration. In the

^{*}To whom correspondence should be addressed

limit of very high polymer concentration, the depletion shell around the particles is expected to vanish leading to the same polymer concentration in presence of particles as in the bulk.



Figure S1: Polymer uptake as a function of bulk polymer concentration for varying particle volume fractions. $C_{colloid}$ represents the polymer concentration with the particles and C^* indicates the overlap concentration.

In the results presented in Figure S1, the chemical potential of polymers is assumed to be proportional to $\ln(C/C_{bulk}^*)$. The polymer uptake data is averaged from different fixed particle configurations corresponding to each particle concentration.

2 Radius of gyration of clusters

The average radius of gyration of the cluster calculated from SCMF simulations is presented in Figure S2 as a function of particle volume fraction and polymer concentration (we note that the average size of the clusters also includes the contributions from monomer dominated aggregates, and thus the actual size of the most dominating clusters is likely to be higher than depicted). The size of the markers are correlated with the radius of gyration of clusters and the dotted lines indicate approximate boundaries between the cluster sizes. We also display the fractal dimension, d_f , for the percolated cluster states. Consistent with the phase diagrams presented in Figure 6 of the main text, overall clustering is seen to increase with decreasing particle charge and increasing polymer concentration. The region corresponding to intermediate sized clusters (20 – 40 nm) corresponding to clustered states is seen to shift to higher particle loadings with increasing particle charge. Also,



the fractal analysis indicates that the percolated states are seen to exhibit globular conformations.

Figure S2: The size of aggregates formed as a function of particle volume fraction and polymer concentration for $Q_p = 5$, $Q_p = 10$ and $Q_p = 20$. The size of the marker corresponds to the size of the cluster. The number on the marker denotes the fractal dimension, d_f .

3 Results for constant screening length

In this section we present results for simulations carried out at a constant Debye-Huckel screening length of 10.9 nm. With increasing number of particles, the counterions in the solution increase. Hence, the salt concentration is adjusted in order to maintain a constant screening length. In Figure S3 we display the effect of polymer concentration and particle volume fraction on the particle-particle radial distribution function. In Figure S4 we display the effect of particle charge on the radial distribution functions. See main text Figures 3 and 4 respectively for the comparison with a system having a variable screening length due to addition of counterions arising from particles at a fixed salt concentration. We observe similar qualitative behavior among these two systems. Moreover, the phase diagrams for aggregate states are seen to be identical to the ones reported in main text. However, the preferred cluster size is seen to exhibit minor differences (not shown).



Figure S3: Particle-particle radial distribution functions, g(r) (a) as a function of polymer concentration for $\phi_p = 0.05$ and as a function of particle volume fraction for polymer concentrations (legend indicated in (c) is common to (b) and (c)) (b) $C/C^* = 0.5$, (c) $C/C^* = 1.0$.

To examine the influence of multibody effects in systems in which the screening length is kept constant for different particle volume fractions, we carry out the same analysis discussed in the main text for a system with a fixed salt concentration. In Figure S5 and Figure S6 we display the results corresponding to Figure 7 and Figure 8 of the main text respectively. The multibody effects in this case also lead to a reduction in effective attraction between particles. Moreover, the multibody effects for the case of only electrostatic interactions exhibit reduction in electrostatic



Figure S4: Effect of particle charge on the particle-particle radial distribution function for polymer concentrations (a) $C/C^* = 0.5$, (b) 1.0.

repulsion with increasing particle volume fraction. Such a trend is similar to the one observed in case of fixed salt concentration. The results for the case of only depletion interactions are independent of the way we incorporate salt and are only displayed for the sake of comparison of multibody effects between purely electrostatic and purely depletion driven system.



Figure S5: (a) The particle-particle radial distribution functions obtained from particle only MC simulations using PMF as the polymer mediated interparticle potential (case (i)) and the same obtained from SCMF simulations (case (ii)) for two polymer concentrations at $\phi_p = 0.05$. (b) $U_2(r;\phi_p)$ obtained using Inverse Boltzmann method for different particle volume fractions at a fixed $C/C^* = 1.0$.



Figure S6: The effective two body potentials, $U_2(r; \phi_p)$, obtained using from SCMF simulations (a) for the case of only electrostatic interactions (just CNP system) at $Q_p = 10$ and (b) for only depletion interactions (uncharged particles) for $C/C^* = 1.0$