Interaction between like-charged polyelectrolyte-colloid complexes in electrolyte solutions: a Monte Carlo simulation study in the Debye-Hückel approximation

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We study the effective interaction between differently charged polyelectrolyte-colloid complexes in electrolyte solutions via Monte Carlo simulations [1]. These complexes are formed when short and flexible polyelectrolyte chains adsorb onto oppositely charged colloidal spheres (Fig. 1), dispersed in an electrolyte solution. In our simulations the bending energy between adjacent monomers is small compared to the electrostatic energy, and the chains, once adsorbed, do not exchange with the solution, although they rearrange on the particles surface to accomodate further adsorbing chains or due to the electrostatic interaction with neighbor complexes. Rather unexpectedly, when two interacting particles approach each others, the rearrangement of the surface charge distribution invariably produces anti-parallel dipolar doublets, that invert their orientation at the isoelectric point (Fig. 1). These findings clearly rule out a contribution of dipole-dipole interactions to the observed attractive interaction between the complexes, pointing out that such suspensions can not be considered dipolar fluids. On varying the ionic strength of the electrolyte, we find that a screening length, short compared with the size of the colloidal particles, is required in order to observe the attraction between like charged complexes (Fig.1) due to the non-uniform distribution of the electric charge on their surface (“patch attraction” [2,3,4]). On the other hand, by changing the polyelectrolyte/particle charge ratio, the interaction between like-charged polyelectrolyte-decorated (pd) particles, at short separations, evolves from purely repulsive to strongly attractive. Hence, the effective interaction between the complexes is characterized by a potential barrier, whose height depends on the net charge and on the non-uniformity of their surface charge distribution.

Fig 1: From left to right: a snapshot of complexes at the isoelectric point; dipolar doublets orientation above and below the isoelectric point ($\xi_s=1$) and effective interaction profiles between charged complexes ($\xi_s=0.57$ with $R_c$ = Radius of colloid = 3.41 nm.) at different values of screening length $\kappa^{-1}$.