

Interactions between Surfaces Mediated by Polyelectrolytes

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Introduction

Colloidal particles are often used to enhance rheological, optical, mechanical, or electrical properties of a fluid. The formation of colloid aggregates can degrade dispersion performance. There are two main ways of stabilizing colloidal dispersions - sterically or electrostatically (Fig. 1). Polyelectrolytes can exploit both methods of stabilization. With a vast parameter space, understanding the underlying physics of stabilization via polyelectrolytes can enable the rational design of polymer dispersant materials.

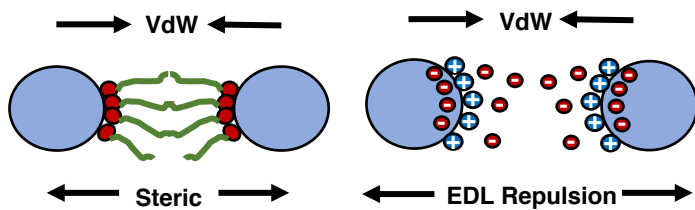


Figure 1. Stabilizing colloids using steric barriers (left) and electrostatic stabilization from double-layer repulsion (right)

Methods

In polyelectrolyte systems, correlation (both electrostatic and intra/interchain) significantly impacts polymer conformation and adsorption behavior near surfaces. Classical density functional theory (cDFT) is a convenient tool for capturing correlation¹.

$$f[\{\rho\}] = f_{ideal} + f_{hs} + f_c + f_{el} + f_{ch} + f_{vdw}$$

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Coul.
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TPT-1
LJ 9-3

Methods

Model the two colloids as a 1D slit pore. Salt ions and counterions are identical.

4 Component System

- Salt ions (+/-)
- Polyanion (e.g. PAA)
- Solvent (water)

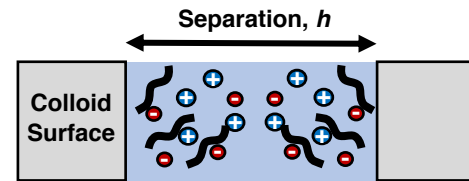
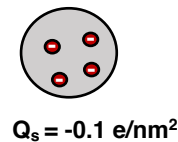


Figure 2. Graphic of 1D slit pore system



3 different architectures, N=30

Results

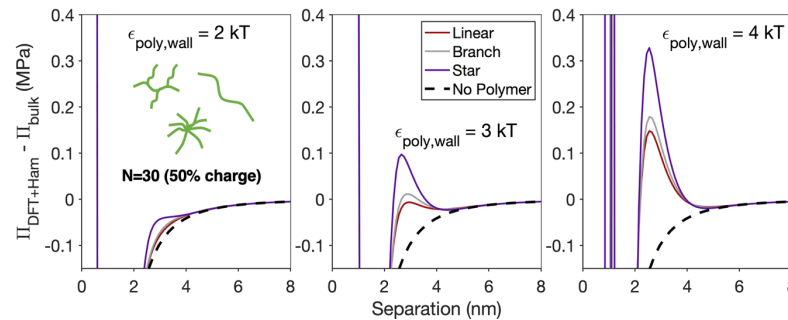


Figure 3. By varying the depth of attractive potential between the polyanion and colloid surface, one can obtain three phases of stability (left to right) – unstable/aggregation, flocculation (local minima), and full stability. Star polymers induce largest repulsive barrier due to thinner adsorption layer (less bridging between surfaces at close approach).

Results

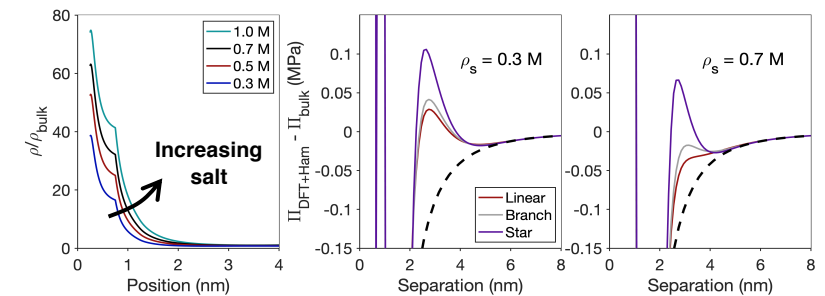


Figure 4. For a linear polyanion with non-electrostatic attraction to the surface, a ~2nm thick adsorption layer forms at the colloid surface. Increasing salt concentration screens the intrachain and surface-polymer repulsion leading to more adsorption (left). Increasing salt decreases the repulsive barrier due to enhanced bridging adsorption between the surfaces (middle/right).

Conclusions

- For a polyelectrolyte to induce repulsion between two colloids, there must be sufficient non-electrostatic attraction to the surface.
- Increasing the salt concentration increases the amount of adsorbed polymer but can degrade the repulsive interaction barrier by enabling deeply attractive bridging between the colloids
- Polymer architecture plays an important role in dictating the width of the adsorption layer and thus, the interplay between bridging and steric repulsion

Acknowledgements & Citations

The Dow Chemical Company is acknowledged for funding.
1. J. Jiang, V. Ginzburg, Z.-G. Wang. Density functional theory for charged fluids. *Soft Matter*, **14**, 2018