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Block polyelectrolytes and colloidal stability

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ABSTRACT

We simulate interactions between charged flat surfaces in the presence of block polymers, where the end blocks carry a charge opposite to the surfaces. Using a recently developed simulation technique, we allow full equilibrium, i.e. the chemical potential of the polyelectrolyte is retained as the separation is changed. In general, the block polyions will adsorb strongly enough to overcharge the surfaces. This results in a double layer repulsion at large separation, with a concomitant free energy barrier. At short separations, the surfaces are pulled together by bridging forces. We make some efforts to theoretically design the polymers to be efficient flocculants, i.e. minimize the free energy barrier and still allow for a long-ranged bridging attraction. Here, we also take into account the possibility of nonequilibrium circumstances, which may be relevant in practice. Our results suggest that short chains, with small charged end blocks and a (relatively speaking) long neutral mid block, are likely to promote rapid flocculation.

1. Introduction

Colloid dispersions are of substantial scientific and technological interest [1]. In many cases, the stability of such dispersions can be regulated by adding polymers or, particularly when the particles are charged, polyelectrolytes. The description of how the presence of polyelectrolytes influences the interaction between colloids has attracted a considerable experimental and theoretical interest. Theoretical progress has at least partially been thwarted by the lack of simulation methods that are able to establish surface forces in simple geometries (large surfaces) under full equilibrium conditions. We have recently developed a technique that permits such simulation studies, even in the presence of chains with a reasonably realistic degree of polymerization (≈60) [2]. Results from such simulations suggest that dispersions containing polyelectrolytes often will resist flocculation. The reason is that charged chain molecules have a very strong propensity to adsorb at oppositely charged surfaces—even to the extent that the "effective" charge of the colloid-polymer complex changes sign. This overcharging leads to a double layer repulsion, and a considerable free energy barrier. It should be noted that this conclusion relies upon the existence of a large bulk solution. In experimental situations, such as flocculation experiments, there are regimes where the total amount of polyion charge is smaller than the total charge on the colloids, simply because only a small amount of polyelectrolyte has been added to the sample. In such cases, overcharging (on average) by polyions is impossible. Typically, a maximal flocculation rate is observed close to perfect neutralization conditions, i.e. when the total polyion charge exactly matches the total colloid charge [3–6]. This is in qualitative agreement with collective findings from a considerable amount of simulation work [7–9].

These findings suggest that in situations where a rapid flocculation is desirable, one should make efforts to disperse the polyelectrolyte uniformly, and make sure that a "charge compensating" amount is added. Still, in many real situations, this may be difficult to achieve. For instance, during paper production, the fibres need to flocculate extremely rapidly (the band speed is typically 90 km/h!), and it is virtually impossible to disperse the added polyelectrolyte uniformly, in which case there will invariably exist regions with an excess of polyion charge. In this work, we will try to obtain theoretically based guidelines for the construction of polyelectrolytes that will present a minimal barrier against flocculation, even in the presence of a large bulk reservoir, in which case the polyions *in principle* can generate charge inversion.

2. Simulating block polymers

2.1. Model system

The objective is to investigate interactions between negatively charged colloids dispersed in a block polyelectrolyte solution by Monte Carlo simulations. The block polymers are modeled as freely jointed chains with a bond length $b = 7$ Å. The neutral mid block consists of a fixed number of hard spheres with a diameter $d = 4$ Å. At the ends of the mid block, positively charged blocks are attached, consisting of a number of hard spheres, each with a unit point charge placed in the center, see Fig. 1. Simple monovalent ions are also present, modeled as negative point charges

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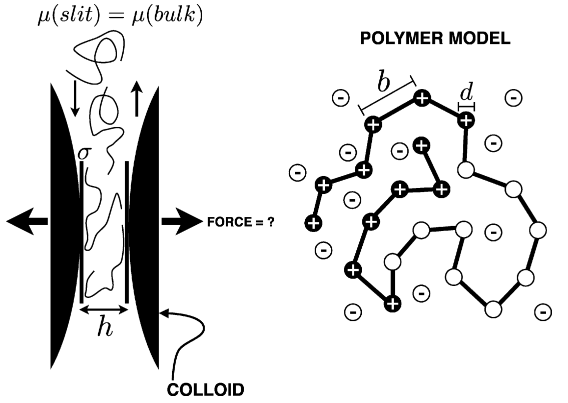

Fig. 1. Model System. The surfaces of two colloids are modeled as planar surfaces carrying a negative charge density (σ). The block polymers (curly lines) are modeled as freely jointed chains, each consisting of a neutral mid block and two charged end blocks. Explicit negatively charged monovalent ions are also present in the system. Surface interactions as a function of the inter surface separation (h) of two colloids, are calculated under the condition that the polymer chemical potential in the slit ($\mu(slit)$) and the in bulk ($\mu(bulk)$) is equal.

inside hard spheres of diameter d. To sample the configuration space, we make use of three different types of Monte Carlo moves, namely reptations, crank shaft moves and translations of whole polymers. In the reptation steps, one of the end monomers (of a randomly chosen chain) is detached and placed, at random angle, at the other end of the polymer. Our system mimics a situation where the dimensions of the colloidal objects are assumed to be much larger than their mutual surface separation. This justifies our choice of surface model which replaces the "real" colloidal surfaces with two parallel flat surfaces separated with a distance h (see Fig. 1). All kinds of surface inhomogeneities are neglected and the surface charges are uniformly distributed, described by surface charge density σ (defined to be negative). The z direction is defined to be perpendicular to the impenetrable surfaces, located in $z = 0$ and $z = h$. Periodic boundary conditions are applied in the $x - y$ directions (parallel to the surfaces).

The volume of the simulation box, $V = Sh$, is determined by the separation and the surface area, S $(= L^2)$, where L is the side length of the simulated quadratic surface area. The minimum image convention is adopted and all pair interaction energies $U(R)$ (between species i and j) are calculated within the restricted primitive model, treating solvent (water) effects implicitly, via a uniform dielectric response of $\epsilon_r = 78.3$:

$$U(R) = \begin{cases} z_i z_j e^2/4\pi\epsilon_0\epsilon_r R, & R > d, \\ \infty, & R \leqslant d. \end{cases} \tag{1}$$

R, z_i, e and ϵ_0 are the separation between two species, the valency of species i, the elementary charge and the permittivity of vacuum, respectively.

All species interact with the charged surfaces [10] and a correction for the long ranged nature of electrostatic interactions, is included [11]. In addition, all monomers and free ions sense a repulsive potential V_{ex}, from the walls:

$$V_{\text{ex}} = w(z) + w(h - z), \tag{2}$$

where ($\tau = 1$ Å);

$$\beta w(z) = 405\left(\frac{e^{-z/\tau}}{(z/\tau)^3}\right). \tag{3}$$

The repulsive soft wall potential renders the total particle density $\rho_t(z)$, zero at the positions of the walls, i.e., $\rho_t(0) = 0$ and $\rho_t(h) = 0$.

This facilitates the osmotic pressure calculations considerable, as we can formulate the pressure in terms of two separate contributions (calculated over a plane located at $z = h$):

$$P_{\text{osm}} = P_{\text{soft}} + P_{\text{Maxwell}}. \tag{4}$$

The first term originates from the nonelectrostatic soft wall repulsion:

$$P_{\text{soft}} = -\int_0^h \rho_t(z)\left(\frac{dw(h-z)}{dh}\right)dz, \tag{5}$$

whereas the second one stems from the interactions between the charged particles and the charged wall. For uniformly charged surfaces, this so called Maxwell term can be written as:

$$P_{\text{Maxwell}} = -\frac{\sigma^2}{2\epsilon_r\epsilon_0}. \tag{6}$$

In this work we will merely use Eq. (4) as a check to verify that we have obtained the correct equilibrium osmotic pressure, since (as will be shown) we can obtain the same quantity in a much more efficient way.

2.2. Chemical equilibrium

Our model imposes chemical equilibrium between the block polyelectrolyte (chains and counterions) residing between the two surfaces and in the surrounding bulk solution. This model is quite delicate to simulate since it requires control over the polyelectrolyte chemical potential as the surface–surface separation changes.

The infinite dilution limit we can quite easily attain by canonical simulations of systems containing no simple ions, but merely a number of charged polymers exactly balancing the surface charge. Thus, in that case, the number of polyions does not vary as we change the separation [7–9].

In order to mimic the full equilibrium situation, one has to invoke more elaborate simulation techniques, allowing the slit concentration of polymers to adjust according to a bulk chemical potential. This route is taken in grand canonical Monte Carlo simulations, where particles are attempted to be created or destroyed, leading to an equilibrium density determined by the input chemical potential [12,13]. However, dealing with polymers, one quite quickly runs into problems, due to a very low bulk exchange acceptance. With a biased insertion technique [14–16], we can simulate surface forces in systems containing neutral hard sphere polymer solutions in contact with repulsive and attractive surfaces [17]. After a slight modification, this technique can also be used for insertions and deletions of short polyelectrolyte chains (plus their counterions) [18]. The method works properly for short chains with up to about 15 monomers per chain. Beyond this degree of polymerization, the method becomes computationally intractable. One should keep in mind that inserting a 15-mer, requires an insertion of 30 charged species at one go.

2.3. The isotension ensemble

There exist alternative methods, to calculate equilibrium forces in confined polymer solutions.

The starting point of our approach is to perform simulations within the *isotension ensemble*, where fluctuations of the surface area account for the correct equilibrium density. Analogous with isobaric–isothermal simulations, we set an external pressure $P_{\parallel}$, acting in the direction *parallel* to the surfaces. It is defined as:

$$P_{\parallel} = -\frac{1}{h}\left(\frac{\partial A}{\partial S}\right)_{T,N_p,h}. \tag{7}$$