

# Charged colloids, polyelectrolytes and biomolecules viewed as strongly coupled Coulomb systems\*

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## Abstract

A brief review is given on recent studies of charged soft matter solutions, as modelled by the ‘primitive’ approach of strongly coupled Coulomb systems, where the solvent just enters as a dielectric background. These include charged colloids, biological macromolecules such as proteins and DNA, polyelectrolytes and polyelectrolyte stars. Also some original results are presented on colloid–polyelectrolyte complex formation near walls and on the anomalous fluid structure of polyelectrolyte stars as a function of increasing concentration.

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## 1. Introduction

When dissolved in a polar solvent, mesoscopically sized colloidal particles and biological macromolecules typically get charged due to the dissociation of ion groups at the particle surfaces into the solution. They leave a highly charged object which can be called a ‘macroion’ or ‘polyion’. Addition of salt ions to the solution tailors the degree of screening in the Coulomb system. Since the solvent approximately only enters via its dielectric constant, the interaction between the particles is mainly governed by Coulomb’s law, such that an ensemble of large highly charged particles together with the microscopic counter- and salt ions represents a strongly coupled Coulomb system *par excellence*. Such polyionic solutions are different from dusty plasmas due to the presence of the solvent that limits large temperature variations. The major advantages of solutions of mesoscopically sized polyions lie in the facts that (i) the solvent allows for quick thermalization and equilibration and (ii) the properties of the macroparticles can be tuned and tailored by using different preparation schemes in

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solution. Therefore, spherical charged colloids are excellent realizations of standard models of charged mixtures known from statistical mechanics. Due to the presence of microscopic and mesoscopic ions, two different length scales and large charge ratios are involved which make the mixture strongly asymmetric.

The standard model is the so-called primitive approach to strongly asymmetric electrolytes where the interaction between the different species is modelled by a combination of excluded volume (hard core) and Coulomb interactions. The latter are reduced by a factor  $1/\epsilon$  from the bare Coulomb law, where  $\epsilon$  denotes the dielectric constant of the solvent. The aim of this paper is twofold: first we shall review some recent investigations within the ‘primitive model’ which are mainly based on direct computer simulation studies. Primitive modellings of different systems such as, e.g., charged colloids, flexible polyelectrolyte chains and charged biomolecules (proteins, DNA) will also be described. The systems treated in this paper are sketched in figure 1. In particular, results for the effective interactions, i.e., the mean-force between the macroions—averaged about the degrees of freedom of the microions—will be analysed. Here we focus on more recent results, a more general review describing the basic concepts can be found, e.g., in [1–5]. The second goal of the paper is to present some new results, in particular for colloid–polyelectrolyte complexes and the fluid structure of polyelectrolyte stars at finite concentration.

The paper is organized as follows: section 2 is devoted to charged colloids where the macroparticle charge is smeared over a spherical surface. Then, in section 3, the effect of discrete charge patterns is discussed with emphasis on proteins and parallel DNA strands. Complexes of charged colloids and polyelectrolytes are briefly described in section 4. Finally polyelectrolyte stars with a ‘porcupine-like’ architecture are treated in section 5. Some conclusions and open problems are summarized in section 6.

## 2. Charged colloidal suspensions

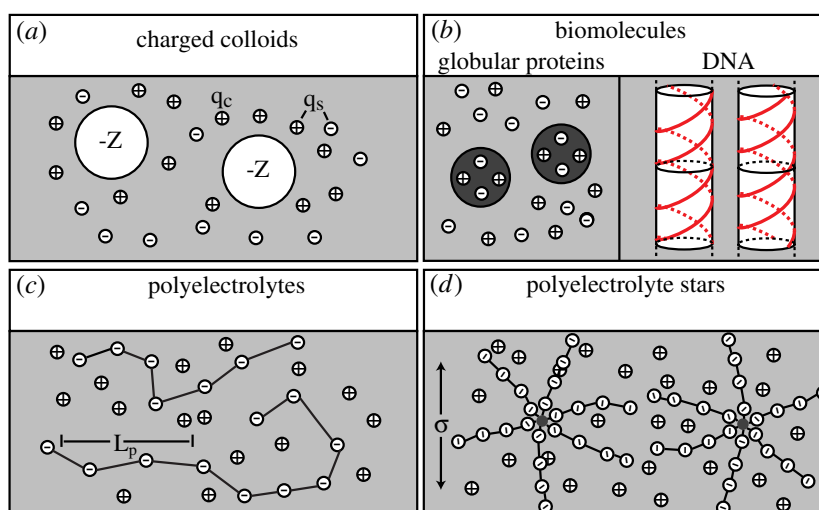
Charged spherical colloids have long been a test bed for the primitive model of strongly asymmetric electrolytes. The colloids are modelled as charged hard spheres of diameter  $D$  with their charge  $Z$  homogeneously smeared over the spherical surface, which is equivalent to setting a point charge in the centre of the sphere, see figure 1. The microscopic counter- and salt ions are small spheres with charges  $q_c$  and  $\pm q_s$ . The key question is whether—in a salt-free solution—the effective force between two such like-charge macroions is repulsive or attractive. Linear Debye–Hückel screening theory certainly predicts a repulsion of screened Coulomb form with an effective pair potential

$$V(r) = \frac{Z^2 \exp(-\kappa(r - D))}{\epsilon r (1 + \frac{\kappa D}{2})^2} \quad (1)$$

where the inverse Debye–Hückel length is

$$\kappa = \sqrt{\frac{4\pi}{\epsilon k_B T} \sum_i q_i^2 \rho_i} \quad (2)$$

with the sum running over every microionic species of charge  $q_i$  and number density  $\rho_i$ . In (1)  $r$  is the centre-to-centre separation between two macroions. The derivation of (1) is only justified in the weak coupling regime. For stronger coupling, it has been shown that the exponentially screened form of the interaction is still valid provided the charge  $Z$  and the Debye–Hückel inverse screening length  $\kappa$  are suitably renormalized [1, 6]. Nonlinear Poisson–Boltzmann theory also results in mutual repulsion [7, 8]. For strong Coulomb coupling, however, counterion correlations, which are neglected in the Poisson–Boltzmann



**Figure 1.** Sketch of the primitive model as applied to different systems: (a) charged colloids: the macroions carry a point charge  $Z$  in their centre, their microscopic counterions possess a charge  $q_c$  and the microscopic salt ions have a charge  $\pm q_s$ , (b) biological macromolecules: two globular proteins with a discrete charge pattern are shown together with their counterions on the left and two parallel DNA molecules with a double-helical charge pattern are shown on the right, (c) linear polyelectrolyte chains in solution with their counterions (the persistence length  $L_p$  is sketched as well), (d) two polyelectrolyte stars (porcupines) in solution with their counterions,  $\sigma$  denoting the corona diameter. The continuous solvent is shown as a grey background.

approach, become important and these can give rise to short-range attractions. The attraction typically sets in when most of the counterions are in a small shell around the oppositely charged colloidal surfaces, resulting in a very strong screening. While computer simulations have demonstrated convincing evidence for attraction stemming from the crucially important counterion correlations, a simple intuitive version of the physical mechanism underlying the onset of attraction is still not completely understood. The key role of counterion Wigner-like lattices on the colloidal surfaces has been pointed out [9, 10]. Attraction has also been attributed to counterion depletion between the macroions [11]. Different colloidal net charges as induced by metastable counterion adsorption were also put forward in [12]. For a recent review of simulation results and a discussion of theoretical treatments we refer the reader to [1–3, 13]. In the case of strongly coupled counterions there is an analogy to charged particle bilayers which have been studied in a completely different context [14, 15].

### 3. Biological macromolecules: influence of charge patterns

If one gets down to sub-nanometre length scales, details of the charge distribution on the surfaces of the macroparticles play a role. The assumption of a homogeneously smeared charge characterizing the traditional primitive model of charged colloids becomes questionable. In particular, this is relevant for globular protein solutions, in which the proteins are characterized by charged patches on their surface.

A systematic study of how the discreteness of the surface charge influences the effective forces [16, 17] reveals that important qualitative effects are missed by a continuously smeared charge if the colloidal radius is on the nanometre scale such that the Coulomb coupling between surface charge and counterion is getting large (corresponding to protein solutions). For discrete

surface charges a nonmonotonicity in the sign of the forces and a nonmonotonicity of the second osmotic virial coefficient of the proteins as a function of added salt concentration were obtained in accordance with experimental data. The nonmonotonicity vanishes for smeared charges. It has to be seen whether this effect maintains its stability for more realistic charge patterns including dipole moments [18].

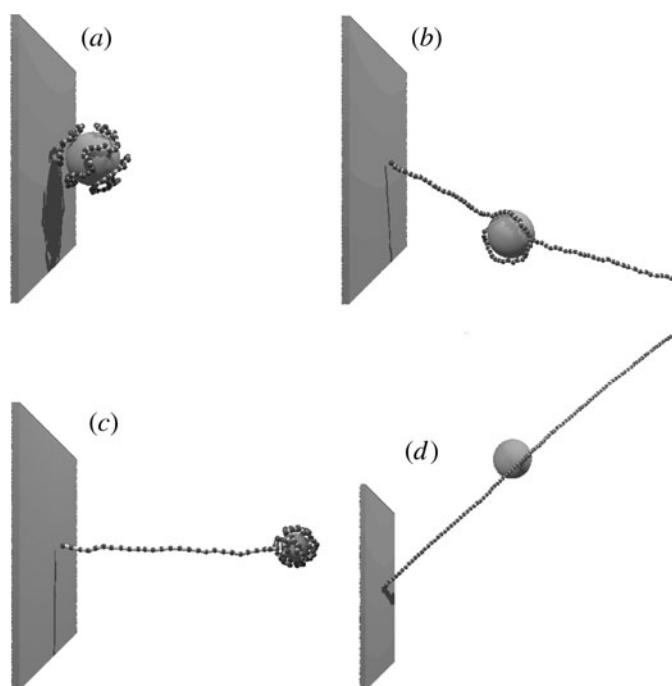
Another biological situation with a nontrivial charge pattern arises for the interaction between two parallel DNA strands. DNA molecules are characterized by a double helix of phosphate charges shown as a continuous line charge in figure 1(b). The charge pattern may also be affected by condensation of specific counterions into the major and minor grooves between the phosphate charges. Linear screening theory for the effective interaction between two parallel DNA molecules has been developed [19] showing that such a helical charge pattern with both phosphate and counterions gives rise to an electrostatic zipper-like attraction in DNA aggregates [20]. Computer simulations of the primitive model [21] confirm in principle the linearized screening theory provided the parameters are suitably renormalized. The full phase diagram for aggregates of many parallel DNA molecules was obtained recently [22] and the stability of various orientational orderings on triangular and rhombic lattices was predicted.

#### 4. Linear polyelectrolytes and colloid–polyelectrolyte complexes

Polyelectrolytes are charged polymers [23], the simplest architecture being a linear chain, see figure 1 again. The physics of polyelectrolytes is dictated by Coulomb interactions and the primitive model together with a finite-extension-nonlinear-elastic interaction between neighbouring charged monomers along the chain has been invoked in many simulation studies. Among the goals are a microscopic understanding of single-chain properties. Two questions are how the persistence length  $L_p$  of a polyelectrolyte chain scales with added salt concentration [24, 25] and how the radius of gyration  $R_g$  of the polyelectrolyte coil behaves for very large Coulomb coupling as, e.g., realized for divalent and trivalent counterions. For the latter case, a polymer collapse has been found in simulations [26–29] and in theoretical approaches [30].

If a polyelectrolyte is added to an oppositely charged spherical colloid, the Coulomb attraction will lead to the formation of *colloid–polyelectrolyte complexes*. Depending on the size and charge of the sphere, the stiffness of the polyelectrolyte chain, and the salt concentration, many different types of complexes are conceivable. The study of complex formation is a very active field of current approach. Many computer simulations and phenomenological theories have been put forward, some relevant references are collected in [31]. At the same time experimental studies give insight into DNA complexations, see e.g. [32]. Here we present simulation data based on the primitive model (similar to that used in [33]) for complex formation in the case where one end of the polyelectrolyte is attached on a planar wall. This is of importance for colloids near polyelectrolyte brushes grafted on a surface. Four different simulation snapshots are given in figure 2, showing different types of possible conformations for different polyelectrolyte persistence lengths (or stiffnesses). Experimentally the stiffness can be tuned by addition of salt to the solution.

For a very small chain stiffness, the chain will wrap around the colloid in order to experience the mutual Coulomb attraction in an optimal way. This implies that the colloid will be pulled close to the wall (see figure 2(a)). In the opposite limit of very strong stiffness (figure 2(d)), the polyelectrolyte is almost completely stretched perpendicularly to the wall, so that its end segment is a distance  $L$  from the wall, where  $L$  is the full contour length of the polyelectrolyte chain. In this limit, the Coulomb interactions are small as compared to the bending energy. Assuming a completely stretched chain, the colloid will come to the middle

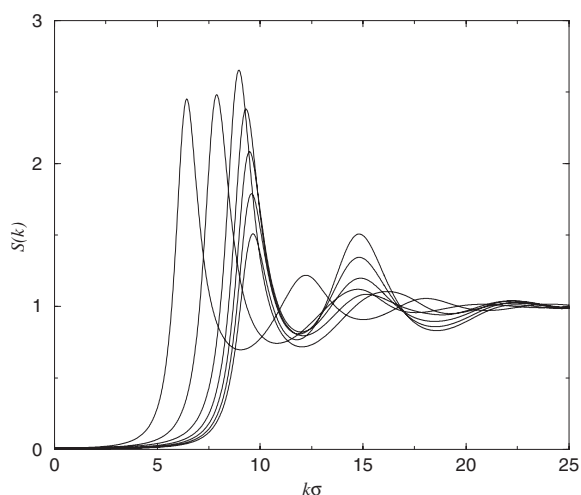


**Figure 2.** Computer simulation snapshots of a polyelectrolyte–colloid complex near a hard planar wall for different chain stiffnesses. One end of the polyelectrolyte is attached to the surface of the wall. The chain stiffness is increasing from (a) to (d). (a) The polyelectrolyte is completely wrapped around the colloid and the complex is adsorbed to the wall. (b) Two-tail configuration: only a part of the chain is wrapped around the colloid and two rigid tails are stretched away. (c) One-tail configuration: same as (b) but only one rigid tail is stretched away. (d) The polyelectrolyte is completely stretched and the colloid sticks at the middle of the chain on average.

of the chain with a central distance  $L/2$  to the wall, in order to optimize the Coulomb energy. Between these two extremes, the so-called two-tail (figure 2(b)) or one-tail configurations (figure 2(c)) are observed [34]. Here part of the PE is still adsorbed on the colloid while one or two rigid parts are stretched away from the macroion to lower the bending energy and so minimize the total energy. The lengths of the tails and thus the position of the macroion can be tailored by changing the system parameters. The further lesson to be learned is that the colloid distance to the wall can be tuned by increasing the salt concentration.

## 5. Polyelectrolyte stars

If  $f$  linear polyelectrolytes are attached to a common centre, a star-like architecture arises, see again figure 1. If the Coulomb coupling between the charged monomers and counterions is not too large so that strong recondensation of the latter can be ruled out, the polyelectrolyte chains are stretched due to the mutual Coulomb repulsion of the monomers. This leads to ‘porcupine’-like conformations of the polyelectrolyte star, with a corona diameter  $\sigma$  measuring the spatial extent of the monomers around the centre. In this limit, the effective interaction between two such objects has been investigated recently by computer simulation and phenomenological theory [35, 36]. Though Coulomb forces are dominating, the leading contribution to the interaction was found to be the *entropy* of the counterions trapped inside the two corona of the two stars [37]. This immediately gives a nice analogy to the structure of foams which was



**Figure 3.** Structure factor  $S(k)$  from polyelectrolyte star solutions of arm number  $f = 15$  and a fraction  $\alpha = 1/3$  of charged monomers as a function of the dimensionless wave vector  $k\sigma$ . The solution densities are, from left to right:  $\rho\sigma^3 = 0.8, 1.6, 2.4, 3.2, 4.0, 4.8, 5.6$ . Note the overlap density is  $\rho^*\sigma^3 = 6/\pi$ .

put forward by Kamien and co-workers [38]. The effective pair interaction energy exhibits a very soft repulsion which even stays finite (many  $k_B T$ ) if the two stars completely overlap. Although the physics is completely different, the softness of the interaction is similar to the case of *neutral* stars [39, 40]. Therefore, it is no surprise that the phase diagram (e.g. as a function of the arm number  $f$  and the star number density  $\rho$ ) is different from that of hard spheres or the one-component plasma but similar in spirit to that of neutral stars [41, 42]. Indeed, a reentrant–melting transition and the stability of an exotic crystal lattice can be confirmed by lattice sum calculations [43] including body-centred-orthogonal and diamond phases.

The softness of the effective interactions leads to unusual fluid structure as well. The fluid structure factor  $S(q)$  which measures correlations of particle density waves of the star centres is shown in figure 3 for different number densities  $\rho$  at fixed arm number  $f = 15$ . The data shown in figure 3 were obtained using the effective pair interaction potential proposed in [35] and the hypernetted chain approximation. The structure factor  $S(k)$  exhibits a first peak at a wave vector  $k \approx 2\pi\rho^{1/3}$ . Below the overlap concentration  $\rho^* = 6/\pi\sigma^3$ , the peak height increases with rising concentration indicating larger correlations for higher concentrations. This is normal behaviour in fluids governed by a repulsive pair potential. In striking contrast, however, the peak height *decreases* if the concentration is raised beyond  $\rho^*$ . This anomalous behaviour reflects the fact that for  $\rho > \rho^*$  particles feel neighbouring coronae and experience the softness of the effective interaction. This is qualitatively similar to the case of neutral star polymers [44].

## 6. Conclusions and open problems

In conclusion, there are many relevant applications in the field of soft matter and biological physics in which strong Coulomb interactions play an essential role. The underlying physical mechanisms are thus governed by Coulomb interactions. Examples include counterion-mediated attraction between equally charged macroions, non-monotonic variations of the

effective interaction with added salt concentration (as discussed in the case of protein solutions), zipper-like attractions between DNA molecules, complex formation of colloids and polyelectrolytes and very soft forces between star-like polyelectrolytes. For length scales below a nanometre, however, specificity of chemical details and discrete solvent effects [45], which are ignored in the primitive model, will become important.

We close by mentioning some open questions in the field of charged soft matter: first it would be interesting to study the complex formation between a colloid and a polyelectrolyte star. This is in particular interesting for small colloidal particles which may serve as carriers of pharmaceuticals. A microscopic understanding of how a small colloid is wrapped or coated by a polyelectrolyte star could have important applications for drug delivery. Second, the crossover in criticality for molten salts with a moderate asymmetry [46, 47] to that of strongly asymmetric charged colloids should be worked out in greater detail, see e.g. [48]. Finally, the interfaces between strongly asymmetric electrolytes (in particular the density distribution of the counterions across the interfaces) should be studied. There are some data for molten salts [49] which need to be extended to the asymmetric case of charged colloids.

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