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Current Opinion in Colloid & Interface Science xx (2006) xxx – xxx
Current Opinion in COLLOID and INTERFACE SCIENCE
www.elsevier.com/locate/cocis

Polyelectrolyte bridging interactions between charged macromolecules

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Abstract

Polyelectrolyte chains confined by oppositely charged macroions can significantly modify the interactions between them. This polyelectrolyte mediated interaction depends on various parameters characterizing the polyelectrolyte as well as the surface of the macroion and can be either repulsive or attractive. Though polymers are mostly used to stabilize various colloidal systems they can just as well induce flocculation either by depletion interaction or by bridging. In the case of charged polymers we refer to this additional attractive interaction as *polyelectrolyte bridging*. This review will focus on equilibrium properties of polyelectrolyte mediated attraction between macroions, its theoretical underpinnings and its phenomenology.

Keywords: Polyelectrolytes; Bridging interaction; Colloidal stability

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1. Introduction

The addition of polyelectrolytes to the bathing solution demands a thorough generalization of the DLVO theory of macromolecular interactions, especially its electrostatic part, that has to take into account the connectivity between charged segments along the polymer chain [1]. This connectivity can often lead to a very peculiar interaction, where long charged polymers can mediate interactions between macroions of opposite charge. The term *bridging interactions* is usually applied to this situation where a single chain can adsorb to different, two or more, macroions and via its connectivity mediate attractive interactions between them. If the chain is charged and adsorption is mediated *via* coulomb interactions we refer to this interaction as *polyelectrolyte bridging* interaction. For polyelectrolyte chains grafted to the surfaces at high enough grafting density, repulsive polyelectrolyte brush interactions between the surfaces replace polyelectrolyte bridging. These interactions will not be part of this review. Different theoretical approaches elucidated some of the aspects of the polyelectrolyte bridging interactions but in many cases it is difficult to dissociate the bridging interactions from electrostatic multipole interactions or strong coupling electrostatic effects [1]. Our review will mostly, though not exclusively, focus on theoretical aspects of polyelectrolyte bridging since the experimental situation has been recently thoroughly reviewed by Claesson et al. [2].

2. Self-consistent fields and beyond

Theoretical work provided a clear mesoscopic picture of the bridging interaction between macroscopic surfaces and elucidates the effects of salt and non-electrostatic excluded volume effects on the strength and range of this interaction [3–7]. Since it is based on sometimes severe model or formal restrictions there is no single theoretical approach that is able to account for all experimentally observed details or to explore in comparable details all the regions of the parameter phase space. Different approaches thus usually address different regions of the parameter space. Recent and earlier developments in the self-consistent field theory and variational theory of polyelectrolyte mediated bridging interactions were reviewed extensively in Ref. [8].

Charged interfaces with charged polymers were first treated in the seminal work of Muthukumar [9]. A further step was taken when the self-consistent mean-field polymer theory was applied to the problem of polyelectrolyte mediated interactions, starting from the work of van Opheusden [10] and later of Varoqui [11]. A

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doi:10.1016/j.cocis.2006.08.001

mean-field theory, akin to the usual Poisson–Boltzmann theory of electrostatic interactions in colloidal systems, that treats both the polyelectrolyte chain density field and the local electrostratic potential on the same self-consistent level has been proposed for confined polyelectrolytes and applied successfully to the problem of polyelectrolyte mediated interactions between charged surfaces in Ref. [3]. In this approach polyelectrolyte mediated macromolecular interactions and electrostatic interactions mediated by other mobile ionic species (such as simple salt ions) are strongly coupled, which results in a rather complicated picture of the bridging interaction. What is clear is that bimodal polyelectrolyte chain density profiles between macromolecular interfaces, exhibiting two maxima in vicinity of the bounding charged surfaces, lead to chain-mediated attractions between them that usually decays exponentially with separation between macromolecular surfaces. These bridging interactions stem from the fact that the chain is partially adsorbed to both surfaces and the remaining part in between provides an entropic–elastic force between them (see Fig. 1). Some aspects of this picture can be understood by simply replacing the polyelectrolytes by "grafted" ions that interact with the grafting wall via a one-dimensional potential [12]. The mean-field approach to polyelectrolyte bridging interactions has later been properly generalized [6,13] to include also non-coulombic interactions, such as the effect of excluded volume interactions between polymer segments [14,15]. In addition the effects of van der Waals interactions between polymer segments and the surfaces has been shown to modify the properties of polyelectrolyte bridging substantially [16]. Introducing also the effects of polymer segment adsorption to the surfaces [17] allows for an analysis of the polyelectrolyte brush repulsion as well as bridging attraction. These additional non-coulombic interactions make the phase space of bridging attraction even more complicated with different regimes where electrostatic, bridging, van der Waals or steric forces dominate. If there have been many varied attempts to include non-coulombic interactions in the formulation of bridging attraction, they were nevertheless all confined to the self-consistent field *ansatz*. Few attempts have been made to go beyond this approximation. One of them was based on expanding the partition function around the self-consistent field extremum by including the Gaussian fluctuations around the saddle-point [18] and led to a Casimir-like interaction mediated by polyelectrolyte chains.

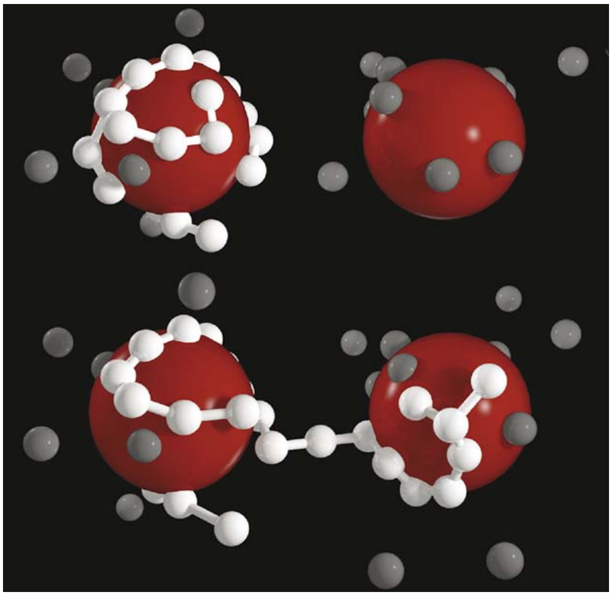

Fig. 1. A schematic representation of polyelectrolyte bridging: upper figure — polyelectrolyte chain (white monomers) is adsorbed onto a single macroion (red). Lower figure — polyelectrolyte chain (white monomers) is adsorbed onto both macroions (red) creating polyelectrolyte bridging configurations that lead to attractive bridging interactions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The self-consistent mean-field theory was successfully applied not only to planar interfaces but also to small, like-charged spherical macroions neutralized by an oppositely charged polyelectrolyte chain [19]. In this context it is *formally* closely related to electron-mediated chemical bond interactions between ionized atoms [5]. Though it appears that the problem of polyelectrolyte adsorption to small macroions is well described by the self-consistent mean-field theory, this approach is not well suited for the analysis of polyelectrolyte mediate interactions between small macroions. A different formulation based on a variational *ansatz* [20] with free [21] or grafted [22] polyelectrolyte chains was found to be more convenient in this particular case. It is based on a Gaussian variational *ansatz* for the effective Hamiltonian of the chain and allows for an elegant and straightforward evaluation of the polyelectrolyte mediated interactions in the geometry where self-consistent field theory would be more difficult to solve since it involves solutions of a Schrödinger-like differential equation in complicated geometries.

All the works listed above were concerned exclusively with the polyelectrolyte mediated interaction between two charged macroions. An attempt to treat many-body effects in macromolecular arrays where polyelectrolyte chains can mediate collective bridging interactions between many macroions was made in Ref. [23]. The bridging interaction in this case appears to be longer-ranged than in the case of only two confining surfaces and in fact decays algebraically rather than exponentially with separation between macroions. Coupling between salt and bridging effects can even lead to non-monotonic pressure between interacting macromolecular surfaces and thus to phase transitions between collapsed and expanded phases [24]. This transition could be responsible for the collapse in the systems like DNA-polyelectrolyte complexes as studied experimentally in Ref. [25]. Interestingly enough, for macromolecular colloidal crystals with intervening polyelectrolytes the problem of bridging interactions can be shown to be analogous to the problem of electrons in crystal lattices [23].

An interesting and important connection between strong coupling electrostatics [1], that can also induce attractive interactions between nominally similarly charged bodies due to correlation effects, and bridging interaction for stiff polymers was noted in [26]. The approach to polyelectrolyte bridging interaction in this work is based on the correlation corrected density functional theory [27], itself a variant of the polyelectrolyte density functional theory introduced in Refs. [28,29]. At intermediate chain stiffness the polyelectrolyte chain gives rise to weak but longer ranged attraction, if compared to the case of flexible

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polyelectrolytes discussed above. In the limit of infinitely stiff chains the bridging attraction itself is lost, but the system exhibits strong coupling correlation attraction [1] at small intersurface separations. A continuity of states thus appears to exist between bridging and strong coupling electrostatic interactions.

On the level of statistical mechanics of liquids, alternative theoretical approaches to polyelectrolyte bridging in colloidal systems (such as in mixtures of like-charged colloids and flexible polymers in solution), can be formulated, as in Ref. [30]. The presence of hydrophobic sites on partly charged polymer chains induces steric repulsion and bridging attraction between colloids. In this case bridging is rather due to short range hydrophobic/van der Waals interactions.

3. Computer simulations

Simulation results on confined polyelectrolytes lend further support for the qualitative underpinnings of the bridging interaction between macroscopic surfaces, as revealed by the self-consistent field method, starting from the seminal work of the Lund group [4]. An application of the density functional analysis to this problem was also successfully pioneered by this group. Monte Carlo simulations revealed a short range attractive interaction between two equally charged surfaces neutralized by polycounterions that corresponds to exponentially decaying bridging interactions in the self-consistent field approach. The attractions were identified as due to entropic bridging mechanism [4] and were found to be significantly larger then the corresponding van der Waals interactions [31]. Polyelectrolyte bridging is in fact not very different from the bridging seen in short range wall–polymer interactions [32]. The coupling between polyelectrolyte counterions and simple salt ions in bridging interaction was investigated via Monte Carlo simulations and direct experiments [33]. It was found that addition of salt enhances the repulsive component of the interaction partly due to directly screened electrostatic repulsions and partly due to brush repulsions between adsorbed polycounterions.

Monte Carlo simulations of polyelectrolyte bridging interactions in the case of single and many polyelectrolyte chains in the presence of two small, oppositely charged macroions [5] also corroborate results stemming from simple self-consistent mean-field and variational theories. They clearly point to important finite size effects since a polyelectrolyte chain of finite length can bridge the separation between two macroions only up to a certain maximal separation, which depends on the conformational entropy-electrostatic energy compensation of the chain. Polyelectrolyte bridging simulations in the presence of additional salt ions point to a complex interplay between electrostatic repulsion, chain entropy and polyelectrolyte bridging interactions [21] that can be to some extent rationalized via self-consistent field and variational approaches.

Strong coupling between electrostatic and steric effects has been addressed on the self-consistent mean-field level in Ref. [14] but the simulation results strongly point to the conclusion that this coupling can lead to non-monotonic behavior of the bridging interaction pressure on separation between planar surfaces [28]. This non-monotonic effect cannot be addressed by simple self-consistent mean-field theories but demands additional steric and correlation terms that lead to non-monotonic density profiles [7]. In simulation studies the non-monotonicity of the polyelectrolyte bridging interaction pressure does not scale with the polyelectrolyte net charge indicating that the polyelectrolytes pack as cylindrical objects. These conclusions are consistent with some experimental studies of confined polyelectrolytes in freestanding films produced from aqueous solutions containing cationic surfactant and the polybase poly(ethylene imine) or the polycation poly(DADMAC) [34,35] that show stepwise thinning. The size of the step correlates with the size of the bulk polyelectrolyte correlation length.

Monte Carlo simulations have also been used to assess the importance and efficiency of bridging interactions in the case of medium size polyanion collapse in the presence of compacting polycations [36]. The polyanion chain undergoes a sudden collapse as a function of the condensing agent concentration and of the number of charges on the molecules. Further increase of the concentration gives also an increase of the degree of compaction. The compaction was found to be associated with the polycations promoting bridging between different sites of the polyanion [37]. Monte Carlo simulations have been also instrumental in understanding the effects of polyelectrolyte bridging used in neutralization of surfactant aggregates by mixed polymeric and monovalent counterions. The simulations qualitatively reproduce all experimentally observable trends in cetyltrimethylammonium (CTA(+)) with short (30 repeating units) polyacrylate (PA(−)) counterions, and show that the dominating source of attraction between the aggregates is polyion bridging [38]. Molecular dynamics and Monte Carlo methods have also been recently used to investigate the properties of systems like polyelectrolyte-polyampholyte complexes and effects like polyampholyte induced repulsion between charged surfaces, as reported in Refs. [39–41].

4. Experimentally observed or inferred polyelectrolyte bridging

Polyelectrolyte bridging interactions have been observed directly or inferred indirectly from measurements of colloidal interactions in various systems. Surface force apparatus and atomic force microscopy have provided direct data on the separation dependence of total interaction between macroscopic surfaces with polyelectrolyte chains either grafted or in chemical equilibrium with a bulk solution starting from the work of Luckham and Klein on poly-L-lysine covered mica surfaces [42]. Many experimental aspects of the polyelectrolyte-surface mediated interactions have been thoroughly reviewed by Claesson *et al.* [2].

Polyelectrolyte mediated interactions of a bridging type were inferred from a series of detailed experiments by Abraham and coworkers [43,44]. In the case of polyacrylic acid (PAA) between mica surfaces, divalent counterions ($CaCl_2$,$MgCl_2$ and $BaCl_3$) are needed to induce attractions between nominally equally (negatively) charged mica surface and PAA. Long range bridging attractions showed up indirectly as a jump into a primary minimum located at small intersurface separations ~ 10 nm, followed

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by a repulsive regime closer in. The range of polymer-mediated interactions can usually be correlated with the size of the chain but can sometimes appear to be a lot longer [45] as in the case of gelatin-coated surfaces studied by AFM. In the experiments of Abraham's group [43,44] the attractive regime disappears at high enough concentrations of PAA (50 ppm), leaving long range repulsion in its stead. Polyelectrolyte mediated interactions in the case of PAA are very different from those observed with hydrophobically anchored polyelectrolytes [46]. Copolymers of neutral acrylamide and negatively charged acrylic acid (AMAC) can be synthesised at three different charge densities [44]. The medium and high charge density (40% and 70% charge density) polyelectrolytes induce long range bridging attractions between two silica surfaces, whereas in the case of low charge density polyelectrolye only repulsion is observed. The range of polymer-mediated interactions can be correlated with the size of the chain. The self-consistent-field analysis of polyelectrolyte bridging interaction as described in the previous section, can *qualitatively* explain the dependencies of the bridging attraction on polymer concentration, even more, it can *quantitatively* explain some aspects of the electrostatic interactions in the system as a function of the polymer charge density [44].

There are many experiments in other colloidal systems where the presence of polyelectrolyte bridging interactions can be inferred either directly by measuring the forces between macroscopic surfaces – such as flame-polished glass surfaces – in solutions of a branched cationic polyelectrolyte, polyethylenimine (PEI) [47] or indirectly by observing the flocculation of colloidal suspensions, as in the case of cationic polyacrylamide and silica nanoparticle systems [48]. Polyelectrolyte bridging interaction has been also used in irreversible self-assembly of magnetic nanowires that opens up the way to "macrocolloidal chemistry" [49]. Polyelectrolyte bridging interaction cannot only induce attractions between macroions but can sometimes even change the structure of the (softer) macroions. Such is the case of dilute lamellar L_α phase formed by the nonionic surfactant triethylene glycol monodecyl ether (C10E3) in water in the presence of cationic polyelectrolyte poly(diallyldimethylammonium chloride) that induces formation of strongly undulated bilayer structures with repeat distances as large as 200 nm [50]. Polyelectrolyte bridging can be relevant also in biological contexts such as lysozyme in aqueous environment where bridging interaction promotes the protein-polyelectrolyte cluster formation [51].

A fundamental role of polyelectrolyte bridging has been recently invoked in the context of interactions between nucleosomal core particles (NCPs) that make up the fundamental units of chromatin [52,1]. The anomalous (non-monotonic) behavior of the second virial coefficient of reconstituted NCPs in aqueous solutions as a function of salt was taken as an indication of short ranged salt-dependent attractions between NCPs [53]. In addition to direct second virial coefficient measurements, fluorescence microscopy and atomic force microscopy studies also point to the existence of short ranged attraction between reconstituted NCPs in solution that lead to a transition between dense and dispersed states [54]. The hypothesis that this short ranged attractions inferred from the second virial coefficient measurements are specifically due to polyelectrolyte bridging interaction mediated by histone protein N-tails was based on the salt dependent conformational changes of NCPs [55] and was put forth in Ref. [53]. The N-tails consist of eight disordered N-termini of the histone core proteins, composed of between 15 and 44 positively charged amino acids. The bridging effect was simulated by an empirical form for the bridging potential. Experimentally it was observed that added salt concentration has a pronounced effect on the conformation of the N-tails of the NCP [55] and that trypsinization (chemical removal) of the N-tails eliminates the effects of molecular attractions in the second virial coefficient completely [56].

The first attempt to calculate *explicitly* the bridging interaction potential between two NCPs with polyelectrolyte tails was made in Ref. [22]. Though it was found that polyelectrolyte tails clearly lead to strong bridging attraction, this was not enough to explain the experimentally observed non-monotonic behavior of the second virial coefficient found in NCPs. Interactions between two macroions with oppositely charged adsorbed polyelectrolytes have been discussed also by Boroudjerdi [57,1]. The attraction in this case, which does lead to a non-monotonic dependence of the second virial coefficient on the added salt, is not due to N-tail polyelectrolyte bridging but rather to multipole interactions between two patterned macroion surfaces. These charge patterns are due to histone-core (positively charged) adsorbed stiff DNA (negatively charged). The charge patterning or patchiness attraction can be formulated in terms of higher electrostatic multipoles of the inhomogeneous charge distribution on NCPs and can be seen in other systems as well [58]. The connection between charge patterning of spherical colloids vs. short and long range bridging interactions has been explored theoretically in Ref. [59]. These studies imply that the N-tail bridging itself is not essential for the experimentally observed behavior of the second virial coefficient of NCPs, and that patterning effects brought about by wrapped DNA might be the culprit.

Simulation of macroions with grafted polyelectrolyte tails apparently resolved the theoretical quandary by explicitly showing how bridging interaction can indeed lead to non-monotonicity in the second virial coefficient as a function of added monovalent salt. Schiessel *et al.* [60,61] claim that their simulation results, based on a simple mesoscopic model for an NCP with explicit N-tails and screened Debye–Hückel interactions, can clearly differentiate between charge patterning effects and N-tail bridging. They have separately evaluated the contribution of N-tail bridging and the contribution of patterned charge to the interactions and shown that the bridging is stronger and that it is thus indeed the N-tail bridging that unequivocally drives the observed behavior of the second virial coefficient. Molecular dynamics simulations with explicit counterions and salt ions have been performed by Korolev *et al.* [62]. The size, charge and distribution of the N-tails relative to the histone core were built to mimick real NCPs. The authors have been able to study the effects of monovalent as well as multivalent counterions that are strongly coupled to all the other charges in the system. They were also able to study more detailed mechanisms of the histone N-tail–DNA interactions and dynamics by performing all-atom molecular dynamics simulations (including water), comprised of three DNA 22-mers and 14 short fragments of the H4 histone tail (amino acids 5–12) carrying three positive charges on lysine(+) interacting with DNA. These all-atom simulations essentially confirm the conclusions reached on the basis of coarse grained models. The N-tail polyelectrolyte bridging interactions between nucleosomal core particles appear to be the most important case of polyelectrolyte bridging in biological context observed to date.

5. Conclusions and future directions

Though we certainly possess qualitative understanding of the main features of polyelectrolyte bridging interactions, the quantitative connection with experiments is not as well established and is relatively sparse. Comparisons between experiments on charged copolymers and self-consistent field theory of polyelectrolytes [44] point to the conclusion that the theory can indeed capture main features of polyelectrolyte bridging. On the other hand, detailed simulations [61] establish exactly the opposite picture between the NCP second virial coefficient experiments and variational theory of polyelectrolyte bridging. One reason for this might be due to the fact that theoretical mesoscopic descriptions of polyelectrolyte bridging, which take into account the chain connectivity, treat the electrostatic interaction on the low-coupling level. Simulation and density functional results [26] however expose the close connection between bridging and strong-coupling electrostatics, a line of reasoning worth exploring in finer detail.

Acknowledgement

This research was supported in part by the National Science Foundation under Grant No. PHY99-07949 and by the Agency for Research and Development of Slovenia under Grant P1-0055(C).

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