Electrostatics of rigid polyelectrolytes

Gerard C.L. Wong

Materials Science and Engineering Dept., Physics Dept., Bioengineering Dept., University of Illinois at Urbana-Champaign, United States

Available online 16 January 2007

Abstract

The organization of rigid biological polyelectrolytes by multivalent ions and macroions are important for many fundamental problems in biology and biomedicine, such as cytoskeletal regulation and antimicrobial sequestration in cystic fibrosis. These polyelectrolytes have been used as model systems for understanding electrostatics in complex fluids. Here, we review some recent results in theory, simulations, and experiments. © 2007 Elsevier Ltd. All rights reserved.

Electrostatics is important in biology because all nucleic acids and virtually all proteins and membranes are charged. Electrostatic interactions in water however are qualitatively different from those in a vacuum or a dielectric. The starting point for understanding these interactions is usually mean-field theories like the Poisson–Boltzmann (PB) formalism and their approximations, which are routinely employed in colloid science and computational biology. It can for example be used to computationally estimate the distribution of counterions around realistic models of biological macromolecules. This approximate approach, however, systematically ignores counterion correlations and finite ion sizes. (Recent work suggests that a partial cancellation between these two effects result in approximate agreement with experiments [1••].) Within the PB description, like-charged objects such as polyelectrolytes always repel, in accord with intuition.

In systems with strong electrostatic interactions (ex: high surface charge densities, multivalent ions), interactions between polyelectrolytes are controlled by the organization and dynamics of the condensed ions surrounding the polyelectrolyte. For example, using the hypernetted chain approximation, Kjellander and Marcelja [2] found that attractions can occur between like-charged surfaces in the presence of multivalent ions if the surface charge densities are *high* enough, and attraction between like-charged hexagonally ordered DNA was observed in a series of pioneering Monte Carlo simulations [3,4••]. It is generally agreed that condensation of polyelec-

trolytes by multivalent ions or macroions is important for many fundamental problems in biology and biomedicine. One well-known series of examples is nucleic acid packaging in viruses, bacteria, chromosomes, and artificial gene delivery systems [5• 6 7•8•• 9• 10• 11 12• 13•• 14• 15•] (Fig. 1).

Correlations between 'territorially-bound' counterions near polyelectrolytes can produce attractions that dominate monopolar repulsion between the polyelectrolytes. When the distance between two like-charged polyelectrolytes is large compared to the ion size, correlated thermal fluctuations of the condensed ion clouds can result in an attraction (see for example, [16,17•]). Recently, it has been suggested that if the two macroions have the same sign but different magnitudes of charge, it is possible to get an additional polarization attraction that is stronger than van der Waals interactions, analogous to the attraction between two conducting spheres with the same sign at different potentials [18]. At closer distances, spatial correlations between the ions on the polyelectrolyte surfaces become important, and an elegant picture of two interacting Wigner crystals was proposed [19•• 20••]. In the last 10 years, theoretical investigations have focused on the electrostatic behavior of highly-charged polyelectrolytes that cannot be explained by mean-fields, such as overcharging, the collapse behavior of the polyelectrolyte itself, as well as the existence and form of multivalent ion induced like-charge attraction, using approaches such as density functional theories, integral equations, field theoretical calculations, as well as others. A number of excellent reviews with comprehensive references have been published [21•• 22•• 23•• 24••]. In the following sections, we review

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E-mail address: gclwong@uiuc.edu.
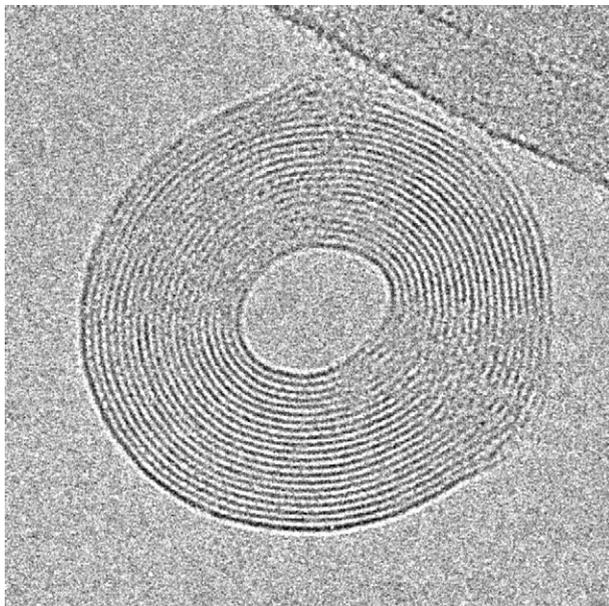
Fig. 1. Cryoelectron micrograph of a λ-DNA toroid condensed with cobalt hexammine show 2.4 nm fringes, corresponding to the periodicity of DNA packing (data from N. V. Hud and K. H. Downing, PNAS 98 14925–14930).

recent work on the structure, interactions, and phase behavior of primarily rigid polyelectrolytes.

1. Rigid polyelectrolytes

Anionic rigid biopolymers have been recently used as experimental systems for polyelectrolyte electrostatics. Due to their large persistence lengths (>μm), they can be thought of as idealized charged rods, and are well-suited for comparison with theory. For example, the addition of divalent cations to a solution of anionic F-actin filaments will drive the ordering of close-packed bundles of twisted filaments [25]. In the case of microtubules, a polymorphism of bundle structures can be formed via multivalent ions. Hexagonal bundles with control-lable diameters are formed via interactions with trivalent and higher valence ions, whereas 'living necklace' bundles with linear, branched, and looped morphologies are formed with divalent ions [26] (Fig. 2).

From a purely observational viewpoint, polyelectrolyte chains or rods attract one another and precipitate out of solution as the multivalent salt concentration exceeds a critical value, but as the salt concentration is increased beyond a second critical value, the condensed polyelectrolytes redissolve into solution (Fig. 3). One
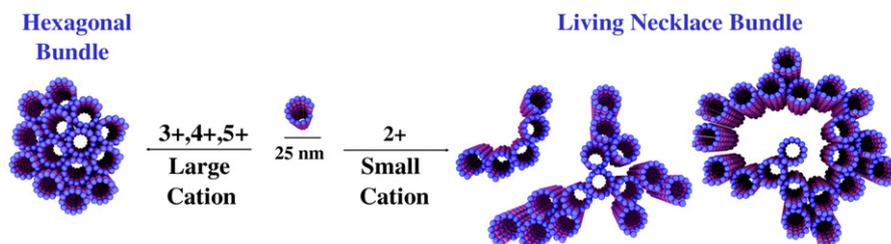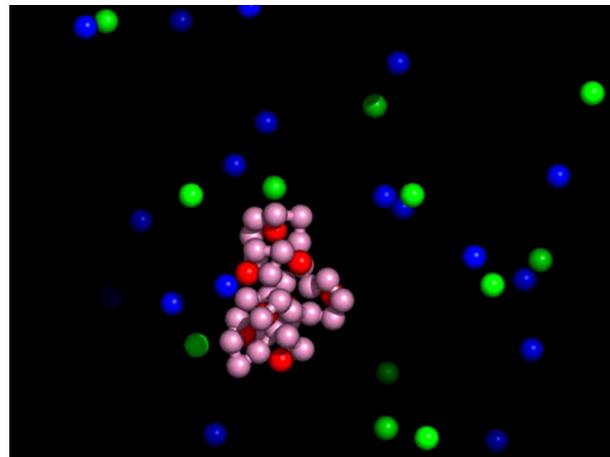
Fig. 3. Representation of a fully collapsed polyelectrolyte chain from molecular dynamics simulations. The choice of parameters represents sodium polystyrene sulfonate. Every pink monomer carries one elementary charge. Green ions are the original neutralizing monovalent counterions from the polyelectrolyte chain. Red and blue ions from externally added salt are the tetravalent counterions and monovalent coions respectively. Clearly, the tetravalent counterions have completely replaced the original monovalent counterions, and link together different parts of the chain. This picture of the condensed polyelectrolyte corresponds to the most compact structure at the threshold for charge inversion. (Figure courtesy of E. Luijten, from simulation study described in Ref. [31]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

compelling recent example is the work of Murayama et al. in which the elastic response of single DNA molecules were measured at different spermidine concentrations, and the existence of a lower and upper critical cation concentration was verified [27]. Charge inversion of polyelectrolyte chains via counterion overcompensation after initial polyelectrolyte precip-itation has been proposed as an explanation for these generic 'reentrant' effects at high salt [21,28]. (Such charge inversion has been recently directly observed for surfaces in the presence of multivalent ions [29]) Alternately, a two-state model for polyelectrolytes (collapsed or extended) that does not necessarily involve overcharging has also been proposed, in which a sensitive dependence on ion size is predicted [30], which was not in the original overcharging models. A recent computer simulation demonstrated that multivalent counterions can overcharge the polyelectrolyte charge in the high salt 're-expansion' regime; however, the occurrence of overcharging depends on the ion size via coion interactions [31].

A number of interesting investigations have been recently done on how ion size and shape influences polyelectrolyte phase

Fig. 2. Condensing ions of different valences generate microtubule bundles of different structures, from hexagonal bundles to open 'living necklace' bundles. (Adapted from Ref. [26]).

behavior. Ermoshkin and de la Cruz investigated the competition between gelation and phase segregation in the presence of multivalent ion linkers [32•], and found that gelation tends to be suppressed due to electrostatic repulsions between crosslinked charged chains: dilute polyelectrolyte solutions macroscopically phase segregate, while gels can form in semi-dilute solutions only if the ion size is smaller than both the Bjerrum length and the distance between charged monomers. This is consistent with the empirical observation that ions with larger hydrated sizes are less 'multivalent', and require larger threshold concentrations before inducing polyelectrolyte condensation. Ion size effects, however, are notoriously difficult to isolate experimentally. In addition to the possibility of specific binding, the importance of ionic dispersion potentials in generating ion-specific Hofmeister effects has recently been described for a wide range of systems [33••]. Using a family of homologous diamine ions, 'dumbbell'-shaped molecules with two cationic amine (+1) groups connected by a spacer of variable length, it was experimentally shown that the small divalent diamines condense M13 virus polyelectrolyte rods while the larger divalent diamines cannot. Moreover, the addition of a single CH_2 group to the spacer can enforce a transition between condensing and non-condensing behavior [34•]. A rough empirical criterion for condensation using these prototypical 'dumbbell' ionic linkers was proposed, but clearly a rigorous microscopic understanding is still lacking.

2. Phase behavior of polyelectrolytes

Counterion-induced attractions strongly impinge on polyelectrolyte phase behavior. For example, the mechanisms described above for multivalent ion induced polyelectrolyte attraction are all relatively short-ranged, while the imperfectly compensated polyelectrolyte rods are mutually repulsive at long-range. The competition between long-range electrostatic repulsion and short-range attractions can drive the formation of a rich polymorphism of structures. As a function of increasing divalent ion concentration, the global organization of cytoskeletal F-actin rods can convert between different liquid crystalline phases with different symmetries and packing densities. F-actin rods in isotropic or nematic phases will both organize into a lamellar liquid crystalline network phase of crosslinked rafts before fully condensing into bundles composed of close-packed F-actin rods [35•]. Interestingly, this liquid crystalline network phase can exist at physiological concentrations of divalent ions, which suggests that it may play a role in cytoskeletal organization.

The physics of multi-axial liquid crystalline gels and networks have been engaged theoretically in a number of studies [36•• 37–40]. In the presence of strong linkers such as multivalent ions that can form crosslinks between polyelectrolyte rods, where it is possible to effectively maintain a high-density of repulsive rods, the repulsive interactions responsible for the orientational behavior are expected to be strong since the rods forced into proximity via crosslinking. Bruinsma extended the Onsager theory of nematic liquid crystals to rod-like polyelectrolytes crosslinked by multivalent ions, and found that a range of exotic multi-axial liquid crystalline phases can exist near regions of phase coexistence between the isotropic phase and dense bundle phase [38] (Fig. 4). In addition to cubatics, which require perpendicular crossing, non-perpendicular crossings are possible due to repulsions between multiple ion linkers at a single rod crossings. Moreover, Borukhov and Bruinsma examined a system of rigid rods and perpendicular 'π/2'
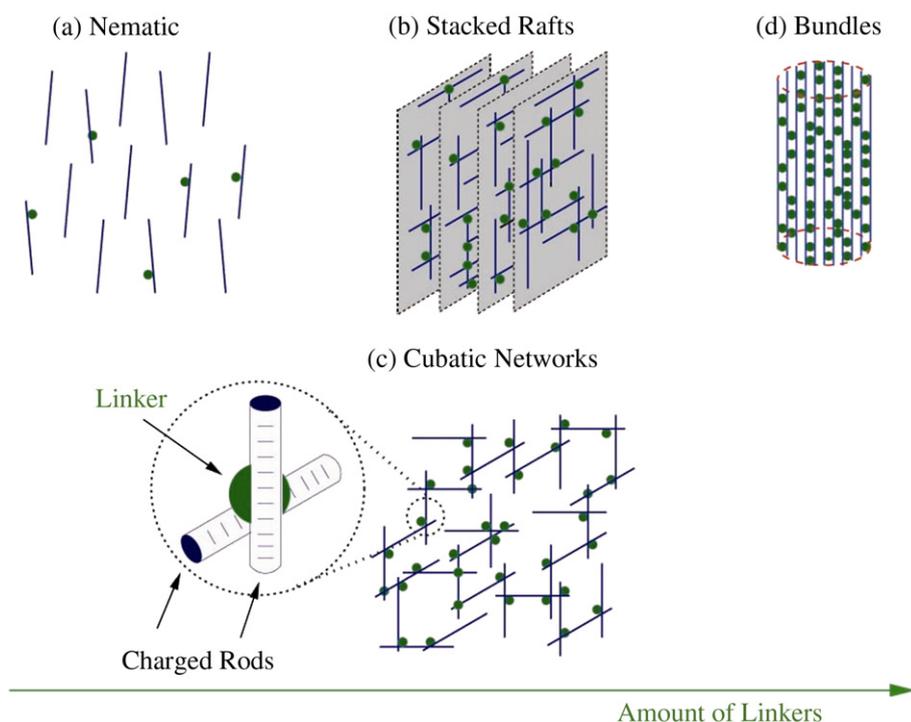
Fig. 4. Linkers such as multivalent ions or proteins can modify the effective interaction between rod-like cytoskeletal polymers and lead to a rich polymorphism of ordered phases, including nematics, cubatics, stacked rafts, and bundles. (Figure courtesy of I. Borukhov, adapted from Refs. [37,39]).

crosslinkers using Onsager excluded volume theory, and found a long-ranged anisotropic depletion attraction between the linkers that leads to a 'raft instability' [39]. For low linker concentrations and binding energy, excluded volume effects prevent crosslinking, and simple nematic results. For high linker concentrations, a transition to a liquid crystalline gel is predicted. At intermediate linker concentrations, however, depletion interactions can drive the formation of raft-like ribbons composed of crosslinked rods [39]. The sequence of experimentally observed phases with increasing multivalent salt concentration, from isolated rods to aggregated networks of rods to aggregated bundles of rods, was recently confirmed in a molecular dynamics simulation [41•]. Interestingly, it was found that monovalent ions enhance aggregation near the threshold of multivalent ion driven polyelectrolyte condensation, by reducing the repulsive contribution to the effective interaction through counterion screening. In contrast, at high multivalent ion concentrations, monovalent ions have the opposite effect, and decrease the effective attraction by unbinding multivalent ions from the polyelectrolyte rods and forcing them to stay in solution via interactions with monovalent coions. These ideas have been extended to a generalized model of linkers and charged rods in order to describe the equilibrium phase behavior and structural polymorphism in the cytoskeleton. Instead of the classic sol–gel type transition described by percolation models widely employed to describe the actin-linker system, the existence of competing interactions (such as electrostatic repulsion, steric repulsions, and actin-linker attraction) leads to a taxonomy of phase diagrams, each dominated by different types of actin organization, such as networks and/or bundles [37].

Since counterions play a central role in the generation of inter-polyelectrolyte forces, it is important to be able to probe their spatial distribution, correlations, and dynamics. In the last few years, progress has been made in this area. Das et al. use anomalous small angle x-ray scattering to measure counterions condensed onto a 25 bp dsDNA, and deconvoluted the ion contribution from the overall scattering signal [42•]. It was found that nonlinear Poisson–Boltzmann calculations yield quantitative agreement with the anomalous scattering measurements. Similarly, Andresen et al. measured the distribution of different competing cations in a mixed ion cloud around DNA and found that the normalized distribution of each cation remains constant at different mixing ratios [43•].

3. Role of counterions

Although experiments show unambiguously that an attractive interaction exists, there has been little done on measuring actual counterion correlations, which are necessary for generating attractions. The organization of divalent Ba ions on actin filaments was studied using synchrotron x-ray diffraction [25•]. Interestingly, the counterions do not form a lattice that simply follows actin's helical symmetry; rather, they organize into one-dimensional (1-D) counterion density waves (CDW) parallel to the actin filaments. Each monomer has a heterogeneous charge distribution, which is repeated along the symmetry a 13/6 helix, or 13 monomers in 6 full helical turns. The 1-D counterion

density wave is coupled to torsional deformations of the oppositely charged actin polyelectrolyte, so that attractions are optimized via charge alignment with the counterion domains. It will be interesting to see how this counterion organization is modified under different conditions. For example, it has been shown that the structure of a counterion lattice within a condensed polyelectrolyte rod phase undergoes a series of shearing transitions as the spacing between the rods decreases [44•]. This general theme of a coupled mode between counterion density changes and polyelectrolyte distortions can also be seen in recent work on DNA. Kornyshev and Leikin developed a theory of interactions between DNA with explicitly defined helical charge patterns [45••]. It was proposed that an 'electrostatic zipper' can form when multivalent cations adsorb in the major groove of one DNA chain, and interact with the protrusive anionic ridges of the sugar-phosphate backbone on an adjacent DNA chain. Within this theoretical framework, it was shown that counterion-induced aggregation of DNA can be accompanied by significant torsional deformations of the DNA helix, in order to maintain registry between opposing DNA [46], similar to the F-actin case above. The physics of these polyelectrolyte-ion systems have been recently mapped onto a diverse range of statistical mechanical problems. For example, columnar self-assembled systems of helical DNA have been compared to a variant of the XY model, in which the role of spin is played by the azimuthal orientation of the molecules [47]. Recently, the problem of counterion ordering on a frustrated columnar hexagonal lattice of polyelectrolytes can be mapped onto a $T=0$ quantum phase transition in an array of Josephson junctions [48•].
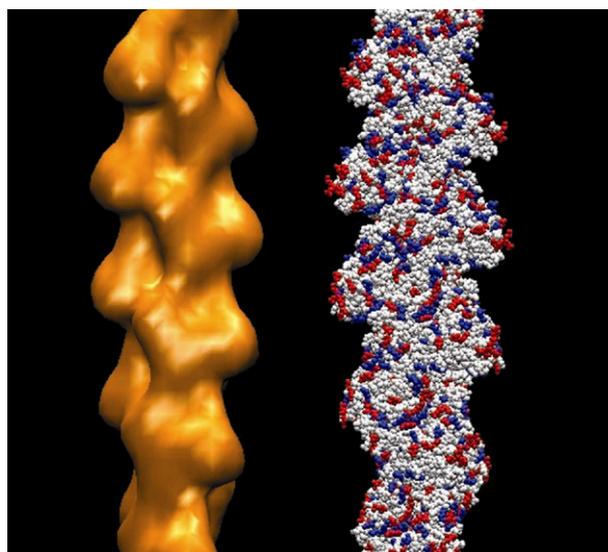
Fig. 5. The charge distribution on the surface of biological polyelectrolytes is highly heterogeneous. This shows two representation of F-actin. On the high-resolution representation (right), anionic residues are colored red; cationic residues are blue, and all others are white. The heterogeneous charge distribution can significantly modulate the counterion and coion distributions. A liquid-like layer of ions coats the heterogeneous F-actin surface and mediates attraction between F-actin rods (adapted from Ref. [49,••]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

The collective dynamics of counterions that mediate binding between F-actin in aqueous solution has recently been directly measured using high-resolution inelastic x-ray scattering [49••]. A new acoustic phonon mode was observed, and suggests the existence of a correlated liquid-like phase of counterions. The dynamics of ions interacting with their 'cages' of nearest neighbors can be inferred from the widths of Brillouin peaks at large wave-vectors, which allow direct experimental access to inter-ion correlations. An examination of the spatial charge heterogeneity on the surface of F-actin suggests that the ions are hierarchically organized: they modulate their density according to charge density variations of the F-actin surface. High-density counterion domains are observed, with a density comparable to that of highest local charge densities on F-actin. At small length-scales within the domains, counterions exhibit liquid-like correlations and dynamics. The measured speed of sound and collective relaxation rates in the liquid-like domains agree well with simple model calculations.

4. Conclusions and outlook

New concepts and new tools have inspired a recent renascence of interest in 'wet' electrostatics, and much has been learned from the intense level of activity. Rather than point to the issues that remain 'unresolved', I believe it is more useful to speculate on what must be developed in this field before it can significantly impact or influence other fields. The need to address formally the role of heterogeneity comes to mind, since most charged objects have charges of both signs, arranged in various patches and topographies. In such cases, coions and their correlations will likely also play a significant role (Fig. 5). Electrodynamics of complex fluids is a largely unexplored field with many opportunities [50•]. However, in order to take the current understanding to the next level, we need to know the structure and dynamics of water, and how they are ultimately expressed in a dielectric function that depends on system size. This last proposal is of course is not new, and is in fact the fundamental challenge in an entirely different field.

Acknowledgement

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