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Download date: 18. Jun. 2025

Surface forces in electrolytes containing polyions

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Abstract

Studies of interactions between surfaces immersed in a solution containing oppositely charged polyions are reviewed. Experimental as well as theoretical progress is discussed, focusing on underlying molecular mechanisms.

Introduction

This review will focus on interactions between colloidal particles, or macroscopic surfaces, in the presence of polyelectrolytes. It should be mentioned that several other reviews have been devoted to this, or a very similar, topic. [1–6] Let us start our discussion by a brief recapitulation of polymer mediated interactions from a more general perspective, removing the constraint that the polymers are charged. An interesting aspect of polymer-induced interactions is that the forces can be mediated by the molecules themselves. There is a number of alternative ways in which polymers can be used to control interactions between colloidal particles, or surfaces. One option is to graft one end of the polymers onto the particle surfaces. In a good solvent, this will generate repulsive

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particle interactions, on account of the steric repulsion that results as the polymer layers are compressed when two such particles approach. However, as the solvent gets poorer, which often can be regulated by changing the temperature or adding salt, these interactions may turn attractive, often resulting in flocculation, or the formation of a gel.[7] Ungrafted and non-adsorbing polymers tend to generate depletion attractions between the particles. If these "free" (ungrafted) polymers instead adsorb at the particle surfaces, the scenario is a bit more complex. Equilibrium interactions then tend to be overall attractive, with a free energy minimum stemming from the entropic increase that results when adsorbed chains are able to bridge across to a neighbouring particle. However, the attraction is generally short-ranged, and there is often a considerable free energy barrier at larger separations. In other words, such a dispersion may in practice be apparently (kinetically) stabilized by polymer addition. This is reminiscent to the barriers provided by electrostatic repulsion for charged particles (at low salt). Non-equilibrium phenomena are relevant also to the very interactions that the polymer give rise to. We shall discuss this in more detail below, but for now we note that finite configurational relaxation times, as well as diffusion limitations, may lead to polymer-mediated interactions that differ from those at true equilibrium. If so, it should be noted that fully relaxed states by definition have a lower free energy than their non-equilibrium correspondence. Provided forces are integrated from a common free energy state, such as two separated and equilibrated surfaces, non-equilibrium states will lead to more repulsive interactions[8]

Interactions between charged surfaces in polyelectrolyte solutions

Now, we switch focus to the specific case of polyelectrolytes, i.e. solutions containing charged polymers. In addition to the "molecule-mediated" interactions discussed above, Coulomb interactions ("through space") will also be important in such solutions. The electrostatic interactions can of course be regulated by the addition of salt, changes to the pH etc. The line charge density, LCD, along the polymer chains is another variable that has an impact on surface forces in these

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systems. This leads to a rich plethora of possible interactions, which complicates matters but also increases the options to optimize the interactions for a specific purpose. In order to limit the scope somewhat, we will in this review restrict ourselves to cases where the polymers are dissolved, i.e. they are *not* covalently grafted onto any surface. Moreover, we will disregard hydrodynamic interactions, and assume that the surfaces (or colloidal particles) are charged, with a sign opposite to that of the polyions.

Overcharging

Paramount to the resulting force that polyions give rise to between such surfaces is the amount of polymer that is adsorbed at a single surface or, even more importantly, the amount of charge that is adsorbed. If the LCD of the polyions is high, they will almost certainly adsorb strongly enough to overcompensate the nominal surface charge, provided that there is enough polymer in the bulk solution.[9,10] In other words, in the presence of a true (essentially infinite) bulk solution, one would have to keep the bulk polymer concentration at exceptionally low values in order to prevent such "overcharging". By overcharging, we mean that if one measures the electrostatic potential Ψ as a function of the normal distance z to the surface, then $\Psi(z)$ will change sign for some value of z. The reason is that the polyions correlate so as to reduce their mutual repulsion, which allows a high packing at the surface, without a strong penalty in terms of Coulomb repulsion. In cases were such overcharging takes place, one anticipates a double-layer repulsion between overcharged surfaces, which can be long-ranged at low salt.[11,12] Note that this is an electrostatic correlation effect, and as such it will not require additional attractive van der Waals interactions. Furthermore, mean-field theories will generally fail to capture this effect.[13–16] Overcharging will thus tend to stabilize a corresponding colloidal dispersion. A similar stabilization mechanism is present if the added amount of high-LCD polyions is insufficient to neutralize the particles[a]. These considerations imply that, at least from an electrostatic point of view, we expect minimum stability when the added polyion charge exactly matches the total particle charge. This has indeed been confirmed

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[a]In other words, the total particle charge exceeds the total polymer charge in the system.

experimentally.[4,17–22] Note also that this is not a polymer-specific effect, and similar observations are found if the polyions are replaced by highly charged dendrimers, or by simple multivalent ions.[4,12,23–25] The sensitivity to the amount of added polyion or dendrimer tends to be greater at low ionic strengths.

At low LCD levels, overcharging may not occur, and the polyions may even adsorb at an amount which is insufficient to neutralize the surface charge. In contrast to cases with high LCD, these conditions may generate purely repulsive interactions, presumably brought about by steric repulsion between polymer layers that are electrostatically "grafted" to the surfaces at the charged positions along the chains.[22,26] It should be noted, however, that for low LCD polyions, electrostatics is obviously less dominating, which makes difficult to establish general behaviours, i.e. non-electrostatic monomer-specific properties can have a relatively strong influence.

Ion correlations

At perfect neutralization, particle flocculation is generally promoted by attractive van der Waals (vdW) interactions (primarily dispersion) but there is at least one other mechanism at play. The overall charge-neutralized surfaces are not necessarily homogeneous, and if they are not, one would anticipate an attractive interaction, due to the Boltzmann-weighted bias between charged patches at opposing surfaces. Such "patch attractions" was suggested more than 40 years ago,[27,28] and have been further scrutinized in subsequent works.[4,6,21,23,29–32] They and have also been proposed as a mechanism underlying some surface force measurements of "hydrophobic" interactions.[33–35] In principle, they may be viewed as multipole interactions, and as such, they are actually, at long range, somewhat related to the vdW class of forces. We will nevertheless treat them on a separate footing. It should be noted that the patch attraction can be considered as a special case of a broader concept called "ion correlations".[36] The latter stems from the simple fact that like-charged species tend to avoid each other, resulting in anti-correlations, sometimes denoted as "Coulomb holes". These are neglected in mean-field treatments, such as the Poisson-Boltzmann theory, and can be of profound influence in many systems. Relevant correlation-driven phenomena include overcharg-

ing by multivalent ions[9] and attractions between like-charged surfaces,[36,37] in the presence of such ions. The description of patches, while conceptually useful, can sometimes be a bit misleading. A frequently occurring illustration pictures a scenario where each chain occupies a circular "blob", which correlates with other blobs. However, simulations as well as theory beyond mean-field[16] suggest that adsorbed highly charged polymers at low ionic strength tends to adopt very flat configurations. This observation finds strong experimental support.[11,22,38,39] Furthermore, at least in the presence of a proper (essentially infinite) bulk solution, they usually saturate the surface whereupon there is a considerable extent of chain mixing. In other words, by spreading out the monomers, a more complete surface coverage is achieved, than a corresponding scenario where the each chain forms a (roughly) circular blob of its own. Configurational entropy also favours chain mixing.

The polymer configurations on two such opposing and approaching surfaces will of course correlate so as to generate an overall attraction, so the concept of "patch attraction" can indeed provide a useful mental picture, but it should keep in mind that the "patches" in reality might be be geometrically rather complicated - cf. Figure 1. Nevertheless, we shall here use the broader concept of "ion correlations", noting that "patch attractions" constitutes a special case, in which the charges are assumed (or constrained) to move on a surface.

Bridging

In addition to ion correlations, bridging attractions[4,40–44] can in principle assist flocculation. For high LCD polymers at low ionic strengths, such bridges are most likely rare, except at very short separations, due to the the concomitant high electrostatic cost. Borkovec *et al.* established experimental support for this conjecture, via a statistical analysis of measured retraction forces using a colloidal probe technique.[5,39] Specifically, they studied interactions between positively charged amidine latex particles in the presence of highly charged poly (styrene sulphonate), under conditions close to perfect surface charge neutralization. Upon stretching one or several bridges, the bridging chains finally lose their grip of the adjacent surface and coil back. This leads to characteristic jumps in the (retraction) force profile. Only a small fraction of the measured retraction

force curves displayed this characteristic, suggesting that this provides a minor contribution to the overall force in these systems. Instead, the authors propose that the observed attractions are due to ion (patch) correlations.[5] In addition to a high LCD, strong chain rigidity also tends to diminish the overall influence of bridging attractions.[45] On the other hand, if the LCD is low and the chains are relatively flexible, significant bridging attraction is quite feasible, especially at high salt concentrations. This was corroborated by Yoon and Deng,[46] who compared flocculation and re-flocculation in clay suspensions, in the presence of polymers with different LCD:s. Assuming that the neutral polymer poly (ethylene oxide) (PEO) adsorbs at the clay particle surfaces (in the presence of the cofactor PFR (phenol formaldehyde resin)), one would anticipate that the observed flocculation is primarily caused by polymer bridging. Yoon and Deng also found that bridging-assisted flocs resisted shear to a higher extent than those generated by ion correlations (high LCD polymers). On the other hand, after redispersion (by shear), the PEO/PFR system showed no signs to flocculate, which the high-LCD polymer systems did. It should be noted that simulations by Dahlgren *et al.*[11] did establish attractive bridging-dominated interactions that exceeded typical van der Waals attractions up to about 8 nm, even at low ionic strength. This would seem to contradict our statement above, but it should be emphasized that they only found such long-ranged interactions for weakly charged chains, and in the mentioned case, the average separation between charges along the chain was 2.5 nm, i.e. the range of the reported bridging attraction was about three bond lengths (the charges were connected by harmonic springs).

Polymer length

Overall, high-LCD polymers with a low degree of polymerization tends to be very efficient flocculators, when added in an appropriate (close to charge-neutralizing) amount.[19,47,48] Practical examples include water treatment, where the goal is to remove organic particles. The latter tends to be negatively charged close to neutral pH, and an established coagulant is short-chain Poly (diallylmethylammonium chloride) (PDADMAC). One reason why short polyions flocculate efficiently could be that equilibrium conditions are attained much faster than with long polymers. The ap-

proach to equilibrium can be even slower in a polydisperse sample, especially if the bulk contains a more than charge-neutralizing amount of charge. The initial adsorption will then be dominated by fast-diffusing short polyions. At full equilibrium, the surface should be enriched by long chains, due to cooperativity effects [b]. However, the process of displacing short polyions with longer is often very slow. An even higher free energy barrier to complete equilibrium will result if the short chains overcharge the surface. Non-equilibrium effects can be quite important in many systems of practical relevance, and another aspect to consider is the heterogeneous polymer concentration that inevitably results from polymer addition. This may lead to an inhomogeneous distribution of adsorbed polymers in the dispersion.

The practical use short high-LCD polyions to generate rapid flocculation can seem to at odds with findings by Bauer *et al.*, who established that long-chain polycations lead to "better" flocculation properties. However, this is probably related to somewhat different target properties, and Bauer *et al.* focused on required polycation concentrations, and sediment volume fraction, rather than kinetics.

Addition of simple salt

As mentioned above, the range of the electrostatic part of polymer-induced interactions can be regulated by the addition of salt. However, there are several other side effects to consider. First, it should be noted that the polymer adsorption itself usually will respond to salt addition, and this will of course also have an impact on the corresponding surface forces. Considerable efforts have been devoted to the variation of polyion adsorption upon the addition of salt,[49–59] but the outcome has been remarkably scattered, and there seems to be no clear consensus on the matter. As simple monovalent salt is added, the electrostatic attraction to the surface decrease, but so does the electrostatic repulsion between adsorbed species. Hence, the response is non-trivial, and a non-monotonic dependence is commonly observed. Although it is strongly related to surface interactions, the sub-

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[b]By saturating the surface with long polymers, there will be a smaller total entropic penalty than if many short chains are adsorbed.

ject is broad enough to warrant a separate review. Hence, we here will refrain from an in-depth analysis. Many experimental techniques to measure adsorption rely on a relatively substantial adsorbed amount. While this can be achieved by utilizing polyions with a low LCD, interpretations are often complicated by the fact that the adsorption of such polymers usually has a substantial, or even dominating, non-electrostatic component. This could be one of the reasons underlying the apparent contradiction between different adsorption experiments. Another complication is titration, of surfaces as well as polyions. Note that the charge in such cases generally will change as salt is added.

As already mentioned, high-LCD polyions normally generates an "overcharged" surface, and at low salt, interactions at long range tends to be dominated by an electrostatic double-layer repulsion.[12,15,16,20,22,32,39,60–62] Consequently, addition of salt will diminish the range of this repulsion. We emphasize that the overcharging is a correlation effect, and will not be theoretically captured by mean-field approaches, such as standard versions of Scheutjens-Fleer[63] (sometimes denoted "self-consistent field") or polyelectrolyte Poisson-Boltzmann[41] theories. In fact, already 1992, van de Steeg and Cohen-Stuart showed that the former theory will not predict overcharging, under "electrosorption" conditions, i.e. in the absence of a non-electrostatic adsorption potential.[64] They furthermore demonstrated that at a constant surface charge density, the mean-field theory will predict a monotonic decay of the adsorbed amount, upon salt addition. Both of these observations are in stark contrast to predictions by a theory that takes ion correlations into account, or by simulation methods (the latter are essentially exact, for a given model system).

Density functional theory, DFT, has the advantage that approximations of ion correlations can be added or removed, allowing effects of correlations to be scrutinized.[14–16] In Figure 2, we illustrated how the long-ranged electrostatic repulsion, originating from overcharging, disappears if the correlation approximation is removed, leaving a pure mean-field treatment. Parameters were taken from one of the "electrosorption" models investigated in ref.[58] We also see in Figure 2 how the free energy barrier, as expected, drops as simple salt is added to the solution.

If the polyions carry a low LCD, adding salt can lead to complete or partial desorption. Fur-

thermore, any remaining adsorbed layer will be thicker than at low salt, which will increase the range of a steric repulsion between adsorbed layer (see more on steric effects below).

Surface force measurements

There have been many attempts to quantify and rationalize surface forces in polyelectrolyte solutions. On the experimental side, direct force measurements using the Surface Force Apparatus (SFA) and the Atomic Force Microscope (AFM) have provided useful insights.[1,11,17,18,22,65] For instance, Poptoshev et al.[18] demonstrated how an extremely low polyelectrolyte concentration can lead to purely attractive interactions. Referring to our discussion above, this is an expected outcome, in cases were the bulk concentration is so low that the polyion adsorption merely neutralizes the bare surface charge. An increase of the polymer dosage lead to a free energy barrier, commensurate with the expected overcharging. Poptoshev et al. suggested that the observed purely attractive, and long-ranged, interaction resulted from attractive bridge forces. This is partly at odds with conclusions from other subsequent studies, as noted above. Maurdev et al.[20] used the SFA to study how interactions between mica surfaces in the presence of a titrating polyelectrolyte (poly(2-vinylpyridine)) responds to changes to the pH of the solution. They proposed that below and close to the pK_a of the polyion, there is a separation regime at which bridging attraction occurs. A possible alternative interpretation is that ion correlations provide an important attractive component.

An important aspect to consider when analyzing data from AFM or SFA measurements in polyelectrolyte solutions, with surfaces carrying a charge with a sign opposite to that of the polyions, is that there are considerable non-equilibrium effects. Specifically, the interactions will usually display strong hysteresis effects, with forces on approach differing quite dramatically - often even qualitatively - from those found when the surfaces are pulled apart (retraction). With such large surfaces, the so-called Derjaguin Approximation (DA)[66] should be essentially exact, which means that the measured force per radius is proportional to the interaction free energy per area between flat surfaces. Since the free energy is a state function, equilibrium forces upon approach and re-

traction will be identical. Since the measured ones are not, it would be of interest to establish a rule of thumb for which of the observed forces (approach or retraction) that tends to agree better with the true equilibrium force. Unfortunately, such a rule of thumb does not seem to exist. One mechanism underlying the observed hysteresis is likely related to polymer diffusion not being fast enough to ensure chemical equilibrium between the confined space and the surrounding bulk solution. A process that may be even slower is configurational relaxation of adsorbed chains. Consider, for instance, intertwined polymer layers in a compressed state. As the surfaces are pulled apart, many of the polymers in these layers will have to undergo a complicated and slow process to reach configurational equilibrium, with an opposite process on approach. The latter hysteresis effect is most likely rather general, and will apply also for polymer-covered colloidal particles in dispersion. The study by Yoon *et al.*, discussed above,[46] supports this notion. On the other hand, unless the particles are very large, polyion diffusion limitations will be considerably smaller than in SFA measurements, and smaller that in typical AFM setups (save the version of AFM where two colloidal spheres are utilized). Surface force measurements do provide valuable and fundamental information about these systems, but it wise to keep in mind some of their limitations [c].

Steric repulsion

If the LCD is high, and/or the surface charge density is low, the chains will form a less dense layer at the surface. At very short range, this will, on approach, generate a steep steric repulsion at short range, as the polymer layers start to overlap.[11,20,32] At low LCD, for weakly charged surfaces and/or at high levels of salt, the polymers layers are naturally thicker, and the steric repulsion tends to be less steep, but extend to larger separations.[22,67]

Adhesion

Hysteresis effects are often particularly pronounced if polymer layers are pushed into overlap on approach, in which case one usually (in a good solvent) will observe a steric repulsion. Relax-

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[c]Hydrodynamic interactions can sometimes also play a role, especially at short separations, but they are not further discussed in this review.

ing the chains at contact (overlapping layers) leads to the formation of bridges, and entangled chains.[22,39] Upon pulling the surfaces away from each other, an strong attraction is often detected as these chains become stretched, and display slow dynamics of chain disentanglement.

Notes on equilibrium problems

Above mentioned equilibrium problems could perhaps be alleviated by studying interactions in the presence of polyions with a low degree of polymerization. By comparing force hysteresis effects obtained with progressively increasing polymer length, one could in principle gain more quantitative knowledge about these effects. Note that true equilibrium might require quite short chains, or even just oligomers. Remarkably enough, there seems to be no such investigations reported in the literature.

Theoretical approaches

Several theoretical studies have been performed, to scrutinize surface interactions in polyelectrolyte solutions. Lyklema and Fleer[68] noted the possibility of ion correlation attractions at perfect neutralization, but without quantitative attempts. Theoretical analyses of bridging by a single chain, or with polyions as counterions to the charged surfaces have already been mentioned.[40–44] Böhmer et al.[69] used a lattice approach to investigate interactions between charged surfaces in the presence of titrating chains, under conditions of restricted equilibrium, i.e. with a constant amount of polymers between the surfaces at all separations (no diffusion to or from a surrounding bulk). They adopted a rather complicated model, in which the dielectric response was allowed to vary in a way dictated by the relative occupancy of various components in each lattice layer. They found significant bridging attractions at high surface charge densities. Borukhov et al.[70] adopted a continuum mean-field approach to investigate the interaction between two surfaces at constant potential, in the presence of a polyelectrolyte solution. They established an almost completely attractive interaction, although they did mention the existence of a very weak repulsion at long range. The latter results from a small overcharging. The latter was most likely rather severely underestimated

due to the lack of ion correlations. As expected, Borukhov *et al.* found a strong and long-ranged repulsion under conditions of restricted equilibrium, as obtained by keeping the amount of confined chains constant as the surfaces were pushed together from a large separation. This might be a relevant way to model AFM/SFA "approach" measurements. Performing a similar theoretical restriction as the surfaces are moved apart, often leads to a considerable hysteresis,[61,71] in qualitative agreement with AFM/SFA experiments. There have been recent attempts to account for the effects of ion correlations in these systems. Forsman and Nordholm[15] adopted several different levels of description to study pair interactions between charged spherical particles, immersed in a polyelectrolyte solution, with added simple salt. Simulations as well as an ion correlation-corrected classical polymer density functional theory were used, and by direct comparisons the latter was shown to be remarkably accurate. By adding simple salt, the repulsion stemming from overcharged particles could be reduced, resulting in an essentially monotonic and long-ranged attraction. Simulation studies in planar geometries,[12,60] employing various techniques to ensure bulk equilibrium (constant chemical potential) as the surface separation is varied, have confirmed the free energy barrier that overcharging generates, as well as an attractive regime, usually dominated by ion correlations, at short range. At high polymer concentrations, a different correlation effect may occur, namely electrostatic packing, sometimes denoted "stratification".[12] This provides an oscillatory component to the overall interaction curve. In agreement with our previous discussion, simulations have demonstrated that a triblock structure of the polyions (or a lower LCD of the chain), in which the central part contains neutral monomers, will lead to a smaller degree of overcharging.[61] Furthermore, with a neutral mid block the energetic cost of forming bridges is reduced. Both mechanisms favour an overall attractive interaction, although non-equilibrium effects might be problematic if this is a desirable outcome.

Summary and conclusions

Collected research efforts during the past few decades have lead to a substantial increase to our grasp of molecular mechanisms and expected outcomes in these systems. On the other hand, the complexity, and the overwhelming number of relevant parameters that govern the behaviour in these systems have far from reached a complete understanding. Non-equilibrium effects are notoriously difficult to investigate in a systematic and reproducible manner, and it is often difficult to build an unambiguous theoretical model for such systems. Yet, these effects are certainly interesting, and have considerable practical relevance. Another aspect that often is relevant, but difficult to quantify, is contributions from specific interactions, stemming from hydrogen bonding, hydrophobic interactions, ion-specific adsorption etc. These constitute a considerable theoretical challenge, since they in principle require an explicit solvent representation, or even a quantum-mechanical description. However, describing polyelectrolyte-mediated interactions with such detailed models are in most cases prevented by computational restrictions, despite decades of rapid hardware developments. Still, a systematic coarse-graining approach might prove helpful, and we can anticipate progress in this area in the near future. Experimental progress is of course also desirable, and a very useful complement to SFA/AFM studies would be approaches that measures the interaction between colloidal particles. For instance, Murakami *et al.*[72] have recently studied the interaction between silica particles with grafted polyions, using optical tweezers. We expect, and hope for additional studies using this, and similar techniques. Furthermore, there are reasons to expect new experimental tools to be developed, providing complementary and valuable information about these fascinating systems.

Acknowledgement

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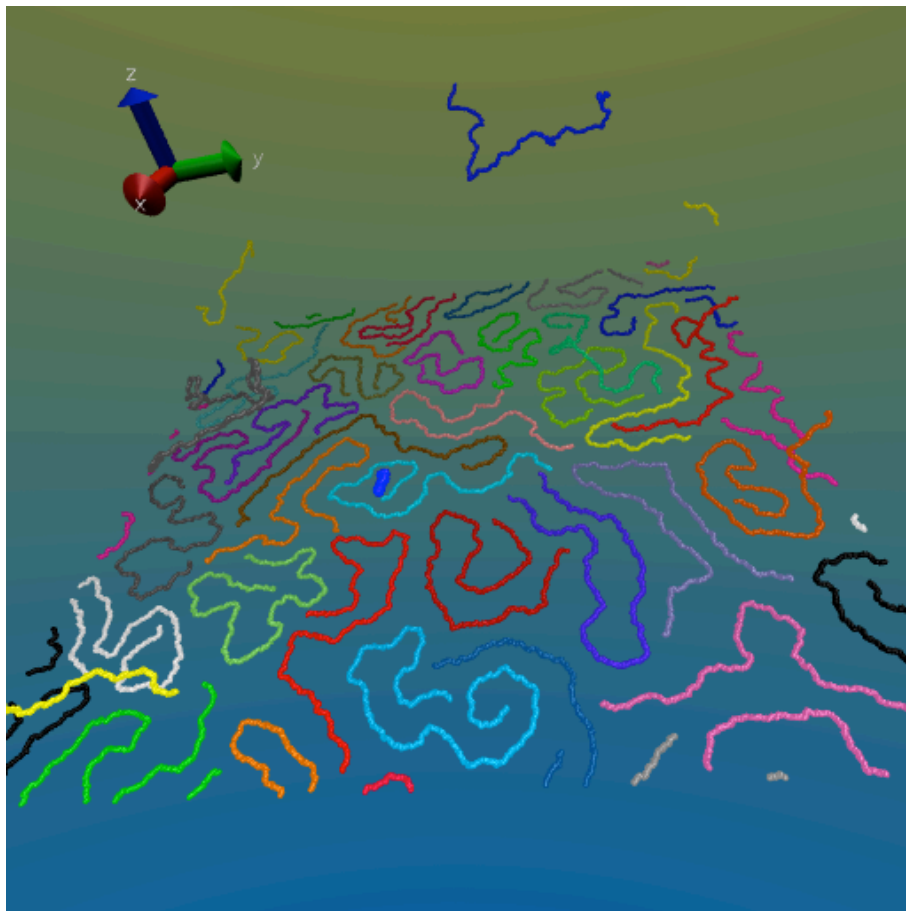
Figures

Figure 1: Snapshot from a simulation of highly charged 640-mers (each monomer carries a unit charge), adsorbing at an oppositely charged flat surface. Details of the simulations can be found in ref.[16]
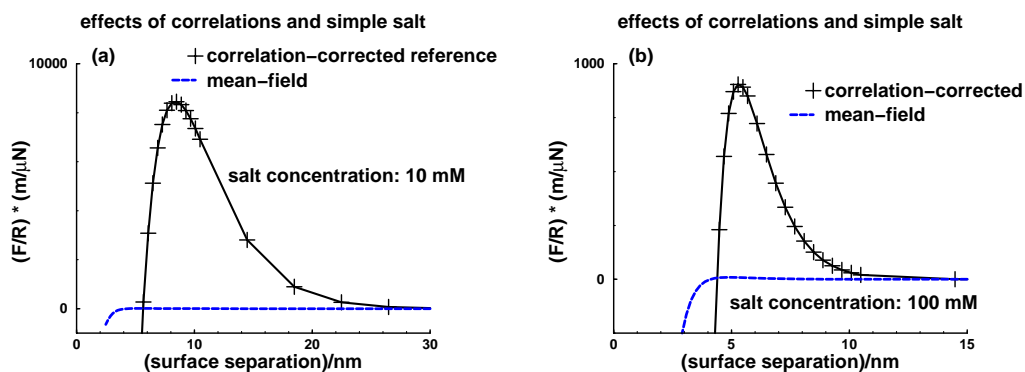
Figure 2: DFT predictions of interactions between charged surfaces, in the presence of highly charged linear chains, but without any non-electrostatic adsorption potential. See ref.[58] for more details (the chain model is illustrated in Figure 4 of that reference.).
(a) Concentration of simple monovalent salt: 10 mM
(b) Concentration of simple monovalent salt: 100 mM