FAST TRACK COMMUNICATION

Complexation and overcharging of polyelectrolyte stars and charged colloids

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Received 3 June 2012, in final form 27 June 2012
Published 18 July 2012
Online at stacks.iop.org/JPhysCM/24/322101

Abstract
We examine the complexation behavior of polyelectrolyte stars on oppositely charged colloidal particles with similar sizes by means of computer simulations employing the molecular dynamics approach. In particular the overcharging phenomenon is considered and its dependence on the charge and functionality of the stars. The complexes thus formed are a realization of inverse patchy particles (Bianchi et al 2011 Soft Matter 7 8313) for which both the number of patches and the total charge can be tuned.

Advances made in chemical synthesis techniques in the last few decades have resulted in many new materials. Whereas polymeric systems originally used to consist mainly of long chain-like molecules of relatively simple repeated units with some additional cross-linker material to stabilize the compounds, they now form an essential building block in many novel substances such as polymer brushes [1–4], coated colloidal particles [5–7], and many more. Not only the hierarchical structure, but also the implementation of different functionalized groups and/or charged sites led to the discovery of new properties and types of behavior.

A good example of this is for instance microgels, which are macroions that change their size by adsorbing water under minor changes in temperature, pH or other external stimuli [8]. Since such a swelling affects the refractive index of these particles in suspension, this transition is sometimes even visible as it can change the solution from a transparent to a milky white appearance [9]. The volumetric transition of these type of particles can, among other applications, be exploited to create micro-lenses [10] or manufacture a photonic sensor for glucose [11].

A different phenomenon that has received a considerable amount of interest and is investigated by simulation, theoretical and experimental methods is that of the complexation of colloidal spheres with polyelectrolyte (PE) chains [12–14], which is an important process with both biological and technological relevances, e.g. polyelectrolyte-mediated protein adsorption [15, 16], responsive interfaces [17], and the control of charge transfer [18].

On the simulative aspect of the problem it should be noted that most work has focused on the interaction between one colloid and a large PE-chain, as well as the corresponding co- and counter-ions and added salt. For instance the work by Podgornik et al [19] where the effective interaction between charged spherical aggregates mediated by oppositely charged polyelectrolyte chains was investigated, revealed that, depending on the relative charges and the length of the PE-chain, either a short range, entropic bridging can be formed by multiple chains or a longer range, energetic bridge in the case of a single PE-chain that needs to balance the overall charge of several colloids. Johnson and Linse [20, 21] investigated the dependence of the morphology of a long PE-chain with various macroions and found non-monotonic behavior in the extension of the polyelectrolyte on increasing the number of complexed macroions, attaining a minimum at approximately the neutral complex. In a later study the dependence on the rigidity of the chain was included by Akinchina and Linse [22]. Messina et al [23] considered the adsorption of oppositely charged PE-chains on a charged sphere finding a layer-by-layer structure.
The theoretical approaches focus mostly on a single colloid and a PE-chain and are based on variational free-energy calculations, taking into account electrostatic interactions and chain connectivity and sometimes rigidity. With complementary methods such as self-consistent field theory, Poisson–Boltzmann and scaling theories by for instance Gurovitch and Sens [24], Park et al [25], and Mateescu et al [26], not only the phenomenon of overcharging has been investigated [27], but also the effects of chain rigidity and salinity on the morphology by Netz and Joanny [28] and Kunze and Netz [29].

A substantial number of experimental investigations have been made, see for instance the work of Borkovec and coworkers [27] and references therein), which indicate that the complexation of polyelectrolytes on latex spheres is irreversible for low salt concentrations [30], has a minimum in the stability ratio at the iso-electric point [31], and that overscreening is a rather common phenomenon [27]. It is this latter behavior on which we will focus in this work.

Closely related to polyelectrolyte–colloid complexation, is the phenomenon of overcharging, which can occur in systems that are comprised of two or more charged compounds. The system we will consider here is one formed by a mixture of spherical colloidal particles and polyelectrolyte star-polymers in an aqueous solution. Colloidal spheres can be manufactured such that they behave as almost hard-sphere-like particles, with or without a nearly homogeneous surface charge. PE-stars on the other hand are formed by grafting suitable polymer chains on a relatively small core [32, 33]. By controlling both the functionality, i.e. the number of polymer chains attached to the core, as well as the length of the arms, the softness of PE-stars can be fine tuned. In addition, the polymer chains can be manipulated to contain ionizable groups that are responsive to the pH of the solvent in which they are immersed.

When the surface charge density of the colloid is opposite to the charge of the PE-stars, both components experience a mutual attractive electrostatic force. For entropic reasons, it is beneficial for the co- and counter-ions of either species to dissolve in the solvent. As a result, the colloidal particles and PE-stars will form complexes or aggregates. How many macromolecules of either compound are found within a single complex will depend on the relative size and relative total charge of the colloidal particles and the PE-stars.

Naively, one would expect that a complex would strive to be electrically neutral. However, we find that in the case of colloidal particles that are larger than the PE-stars, more of the latter can be adsorbed on the surface of the former than necessary for negating the charge of the colloid. In fact, the total charge of the colloid–star complex can be of the same order of magnitude but opposite sign to that of the individual colloidal particles. It is this phenomenon, in which the electric charge of a colloidal particle is overcompensated by oppositely charged PE-stars, that is known as overcharging and can, for instance, be measured by electrophoretic mobility experiments. Here we will examine the process, however, on the more microscopic scale by means of molecular dynamic simulations.

Computer simulations are a tool that enables us to obtain a more fundamental understanding of the behavior of complicated systems on a molecular or atomic level. There are clear disadvantages to simulation techniques, such as the limiting real-time a system can be followed. Depending on the accuracy required and the system size, this time can range from nano- to milliseconds. Also the system size, i.e. the number of particles that is simulated, is of concern, since systems that are too small create various types of artifacts and large systems cannot be simulated for a sufficiently long time. The main advantage of simulations, however, is that at each time it is exactly known where particles are on the level of individual atoms or basic molecular groups. Such information, which is usually not available in the experiments, can help us to shed some light on some of the phenomena that are observed.

The model we employ to study the complexation behavior of PE-stars on oppositely charged colloids is coarse-grained, i.e. it contains only the essential features of the experimental system. The PE-stars are formed by a central core to which \( f \) identical, polymer chains of length \( N \) are bounded [33]. The monomeric units in the chains are assumed to be identical and exert a short range repulsive force on each other, modeled by the Weeks–Chandler–Andersen (WCA) or shifted Lennard-Jones potential\(^\text{1}\)

\[
\nu_{\text{WCA}}(r) = \begin{cases} 
4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + \frac{1}{4} \right] & r \leq 2^{1/6}\sigma \\
0 & r > 2^{1/6}\sigma,
\end{cases}
\]

where \( \sigma = 2.5 \text{ Å} \) represents the effective diameter of the particles. The energy scale \( \varepsilon \) is fixed via the Boltzmann constant \( k_B \) by the chosen temperature \( T = 1.2\varepsilon/k_B \) [33]. Sequential monomers within the chain have an additional interaction in order to maintain connectivity. These bonds are modeled by the standard finite extension nonlinear elastic (FENE) potential [34]

\[
\nu_{\text{FENE}}(r) = \begin{cases} 
\frac{1}{2}k_{\text{FENE}} \left( \frac{R_0}{\sigma} \right)^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] & r \leq R_0 \\
\infty & r > R_0,
\end{cases}
\]

where \( k_{\text{FENE}} = 7\varepsilon \) is a spring constant that restrains the maximum distance between connected monomers of less than \( R_0 = 2\sigma \). In order to avoid possible divergencies in the interactions between chains in the vicinity of the core, the latter is modeled by a somewhat larger sphere with a hard-core radius \( R_d = 2\sigma \). This larger size of the core with respect to the monomers within the chain is reflected by a modified core–monomer interaction given by

\[
\nu_{\text{WCA}}(r) = \begin{cases} 
\infty & r \leq R_d \\
\nu_{\text{WCA}}(r - R_d) & r > R_d.
\end{cases}
\]
Figure 1. Typical snapshots from the simulations at a salt concentration 0.077 M. (a), (b) For two PE-stars with $f = 6$, (c), (d) three PE-stars with $f = 4$. Iso-electric complexes are shown on the left in (a) and (c), the overcharged complexes on the right in (b) and (d).

and a corrected interaction between the first monomer of each polymer chain that guarantees the connectivity of the core to its arms

$$v_{\text{FENE}}^c(r) = \begin{cases} \infty & r \leq R_d \\ v_{\text{FENE}}(r - R_d) & r > R_d. \end{cases}$$

(4)

Note that the arms are not attached to the core at fixed positions, but are free to rearrange themselves around the surface of the core.

A fraction $\alpha$ of the monomeric units along the chains carry a monovalent charge $+e$. They are distributed equally, and in a periodic fashion, over the different arms of the PE-stars. In order to guarantee charge-neutrality, the charged monomers are compensated by the same number of counter-ions with an electric charge $-e$, but in every other way behave as the monomeric units. The Coulomb interactions between charges are given by

$$\beta v_{\text{Col}}(r) = \lambda_B \frac{Z_i Z_j}{r},$$

(5)

with $Z_i$ the valence of a particle ($Z_i = \pm 1$ for the monomeric units or free ions), $\beta = (k_B T)^{-1}$ the inverse temperature, and $\lambda_B = 7.1$ Å is the value of the Bjerrum length. The latter value corresponds roughly to water at room temperature and is a realistic value for polyelectrolytes such as hydrophilic poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane-sulfonate) [35].

Colloidal particles are modeled in the same fashion as the core of a PE-star, i.e. a hard core with radius $R_{\text{Col}}$ and a short range repulsive interaction from the colloidal surface by means of the WCA potential (3). In addition to that, the colloids are charged with a homogeneous surface charge density which results in a coulombic interaction (5) with total charge $Q_{\text{Col}}$.

In order to facilitate the analysis of the colloid–star complex as well as to improve the computational efficiency, we focus on the formation of a single complex consisting of only one spherical colloid with radius $R_{\text{Col}} = 25\sigma$ and total charge $Q_{\text{Col}} = -120e$. The colloidal particle is allowed to form a complex with either two stars with functionality $f = 6$ or three stars with $f = 4$. The number of monomers within each of the polymer arms of the PE-stars are chosen to be $L = 60$. By assuming $\alpha = 1/6$ or $\alpha = 1/3$, we control the level of protonation of the polymer chains. Since the total number of monomers in both types of complex (two $f = 6$ or three $f = 4$ stars adsorbed on a colloid) are the same, the former case with $\alpha = 1/6$ corresponds to the iso-electric system in which an electrically neutral complex is formed, whereas in the latter case the colloid is overcharged by 100%. Note that this only refers to the direct charges of the colloid and stars and does not contain strongly bound co- and/or counter-ions. In each of the four situations $(f, \alpha)$ an additional salinity is introduced up to a concentration of 0.077 M.

Representative snapshots for each of the four different complexes for the highest salt concentration (0.077 M) simulated in this work are shown in figure 1. They suggest that the PE-stars in a complex attempt to maximize their mutual distance, while remaining adsorbed on the surface of the colloid. In the case of two PE-stars this results in diametrically
opposite positions with respect to the center of the colloid, whereas in the case of three stars an almost equilateral triangular configuration around the center of the colloid is formed. In addition, it can be seen that not necessarily all arms belonging to the same PE-star are adsorbed. In particular for the higher functionality stars \( f = 6 \) shown here, one arm is fully immersed in the solvent. These characteristic arrangements of the stars on the colloidal surface are in full agreement with the patch decoration in the model for inverse patchy particles by Bianchi et al [36].

In figure 2 the polymeric-monomer density profiles are shown with respect to the center of the colloidal particle for different salinities. The profiles with the highest peaks correspond to the simulations with no added salt. The absence of salt, results in almost no screening of the electrostatic interactions and therefore leads to a stronger adsorption of the PE-stars on the colloid. By adding salt the height of the peak in these profiles diminishes and, at the same time, the maximum is shifted to larger distances from the colloid. In addition to this, the width of the distribution is also increased. These changes are caused by a more efficient screening by the salt of the colloidal charge, which changes the internal structure of the PE-star from relatively rigid polymer chains in the absence of salt to arms that are more floppy and loosely bound to the surface for higher salinities, which can also be observed in the snapshots presented in figure 1.

Comparing the monomer density profiles of the different systems, it also appears that the iso-electric complexes reveal a somewhat wider distribution than those of the overcharged case. This is more clearly visible in figure 3, where a direct comparison at equal salt concentration is made. Although this might seem counterintuitive, the explanation is found in the fact that in the overcharged complexes one or several polymer arms are no longer adsorbed at the surface, but remain free in solution, and are only part of the complex by their connectivity in the PE-star to those arms that are adsorbed. This effect occurs in the case of stars with higher functionality enhanced by the mutual repulsive interactions between arms belonging to the same PE-star.

An alternative fashion to visualize that the stars are adsorbed less strongly on the colloid on increasing the salinity is shown in figure 4(b). It depicts the average distance \( D \) of the central core of a PE-star to the center of the colloid as a function of the salt concentration. Figure 4(a) shows the same behavior for systems of smaller complexes, formed by a colloid in combination with stars with the same functionality and fraction of charges, \( f \) and \( \alpha \) respectively, as well as the same number of stars. In this case, however, the colloidal particle has a total charge \( Q_{\text{Col}} = -60e \), radius \( R_{\text{Col}} = 15\sigma \), and the PE-stars have only \( L = 30 \) monomers per arm. In either case, a growing distance with increasing salt concentration is revealed, where some deviations from an approximately linear behavior can be observed. This non-monotonicity is brought about by morphological changes in the adsorption of individual PE-stars, i.e. by a partial or full detachment of the number of adsorbed polymer arms on the colloidal surface. This is to some extent also visible in figure 2 by the relatively sudden changes in the profiles observed on only minor increases in the salt concentration, as is, for example, the case in going from 0.006 to 0.013 M salt concentration in figure 2(a). In addition, it can be seen that the distance of the core to the colloidal center does not appear to depend strongly on the type of complex characterized by a \((f, \alpha)\)-combination.
Figure 3. Monomer density profiles with respect to the center of the colloid for (a) 0 M, (b) 0.026 M, and (c) 0.077 M salt concentration.

Figure 4. Average distance $D$ between star-core and colloid as a function of the salt concentration. (a) $Q_{\text{Col}} = -60e$, $L = 30$, $R_{\text{Col}} = 15\sigma$; (b) $Q_{\text{Col}} = -120e$, $L = 60$, $R_{\text{Col}} = 25\sigma$.

Although the monomer density profiles for the iso-electric or overcharged situations are not too distinct from one another, there is an important difference in the distribution of charges. The charges within the polymer obviously will, provided they are appropriately scaled, almost coincide with the monomer density profiles due to their regular distribution within the PE-star. Figure 5 shows the charge density distributions as well as the cumulative charge of all charged monomers and ions in the absence of salt and for a 0.026 M salt concentration. In the case of the iso-electric complexes the charge density remains positive, whereas in the overcharged case there is an overshoot to negative values. This is more clearly visible in the cumulative representation, where the total mobile charges in a spherical region are shown to go beyond the value of $120e$ that is required to compensate the negative charge of the colloid. This surplus is caused by the electric double layer formed by co- and counter-ions. In order to optimally neutralize the colloidal charge a positive charge density layer is formed by free co-ions and charged monomers within the PE-stars near the colloidal surface. The charged groups in the arms of the PE-stars that are not or only partially adsorbed at the colloidal surface, lead to an excess of positive charge at further distances, which in turn is neutralized by negative counter-ions that for entropic reasons form a surrounding, second and much wider layer.

We have shown here a simple model system that already allows us to perceive the complexity in complexation behavior of mixtures of charged colloidal particles and PE-stars. Although the electrostatic interactions are crucial in the process, it is entropy that lies at the basis of the adsorption of the stars on the colloidal surface, i.e. the entropic gain of the co- and counter-ions by being able to explore the total available volume overshadows the entropic loss of the internal degrees of freedom in the PE-stars due to the vicinity of the colloidal surface. We have by no means presented a complete description of the process of overcharging. By focusing on two types of stars of different functionality and a relative density ratio that allows us to form only a neutral or fully overcharged complex, we merely illustrate some of the trends. The fashion in which the PE-stars adsorb for instance, depends on their functionality. Contrary to the low functionality stars, the higher functionality stars will not
adsorb with all their arms on the colloid because of the internal Coulomb interactions between the arms. In addition, it is to be expected that even more PE-stars could adsorb on the colloid resulting in an even more overcharged complex. The reason for this lies in the observation that a non-negligible part of the colloidal surface is not covered by adsorbed PE-stars and that fully adsorbed stars could detach some of their arms from the surface in favor of (partially) adsorbing other PE-stars, thus raising the amount of overcharging of the complex. What the actual maximum load will be is difficult to predict, but clearly will depend on all quantities, i.e. functionality, the length of the arms, and the overall charge of the PE-stars, as well as the size and charge of the colloidal particle. Although a more complete analysis falls outside the scope of the present work and will be left for further studies, it does demonstrate the potential of these types of complexes to become a realization of the inverse patchy particle model as developed by Bianchi et al [36], in which the number of patches formed by the adsorbed PE-stars, their decoration over the colloidal surface, and their interaction can be tuned by means of the relative sizes, charges, and functionality.

This work has been supported by the Deutsche Forschungsgemeinschaft.

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Figure 5. Charge density profiles (a) and (b), and cumulative charge (c) and (d) with respect to the center of the colloid. Figures on the left, (a) and (c), correspond to a salt concentration 0 M, and on the right, (b) and (d), are for 0.026 M.
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