Collapse of Spherical Polyelectrolyte Brushes in the Presence of Multivalent Counterions

Yu Mei,[1] Karlheinz Lauterbach,[1] Martin Hoffmann,[1] Oleg V. Borisov,[2] Matthias Ballauff,[1] and Arben Jusufi[1,*]

[1]*Physikalische Chemie I, University of Bayreuth, 95440 Bayreuth, Germany*
[2]*Laboratoire de Physico-Chimie des Polymères (CNRS-UPPA), 64053 Pau cedex 09, France*

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We consider the interaction of multivalent counterions with spherical polyelectrolyte brushes (SPB). The SPB result if linear polyelectrolyte (PE) chains (contour length: 60 nm) are densely grafted to colloidal spheres of 116 nm in diameter. Dispersed in water, the surface layer consisting of chains of the strong PE poly(styrene sulfonic acid) (PSS) will swell. We demonstrate that successive addition of trivalent ions (La^{3+}) leads to a collapse in which the surface layer is shrinking drastically. All findings are discussed on the base of a theoretical mean-field approach using the Donnan equilibrium. The ion exchange and a strong binding of trivalent ions by PE chains is followed up by a drop in the osmotic pressure inside the brush. This reduction is the driving force for the collapse. The strong ion-chain correlation is discussed with results obtained from molecular dynamics simulations.

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Polyelectrolyte brushes are systems in which polyelectrolyte chains are attached densely to a planar or curved surface. The term brush denotes a system in which the grafting density σ as expressed by the number of grafted chains per unit area is high enough so that neighboring chains strongly interact and are stretched away from the surface. Attaching long polyelectrolyte chains to colloidal core particles leads to spherical polyelectrolyte brushes (SPBs) shown schematically in Fig. 1 [1,2]. Pincus as well as Birshtein, Borisov, and Zhulina were the first to show that the counterions are confined within such polyelectrolyte brush [3,4]. The high number of charges present in the brush will lead to a strong repulsive interaction between the attached chains if the ionic strength in the system is low. This is in full agreement with all experimental data available so far [2,5–8].

A major point of interest is the investigation of phase transitions in these systems. In particular, the density profile of planar polyelectrolyte brushes for different solvent quality and grafting density has been widely discussed by analytical methods as well as by computer simulations [4,9]. Furthermore, previous work has demonstrated that multivalent counterions which are strongly correlated to the macroion [10] can reduce tremendously the stiffness of polyelectrolyte chains, such as DNA strands, reaching even collapsed configurations [11–15]. Recently, Santangelo and Lau have calculated counterion fluctuation effects on planar polyelectrolyte brushes [16]. They showed that classical Poisson-Boltzmann theories combined with fluctuation terms lead to a collapse transition of the brush height with increasing ion valency: the fluctuation terms become important for strongly charged polyelectrolytes and for multivalent counterions. However, no quantitative experimental check of these predictions is available so far.

Here we present for the first time a systematic experimental study of a collapse of a polyelectrolyte brush in presence of multivalent ions. By comparing these results with mean-field theory, we show that the marked reduction of the osmotic pressure within the brush layer in conjunction with the strong preferential adsorption of the higher-valent counterions leads to the collapse. Correlation and fluctuation effects which are expected to be relevant for multivalent ions are shown to be of secondary importance for the observed collapse.

The SPBs used in this study carry long chains of the strong polyelectrolyte poly(styrene sulfonic acid) [1]. The colloidal core of the particles consist of poly(styrene), see Fig. 1. Dispersed in water the surface layer consisting of such a polyelectrolyte brush will swell. The core particles are practically monodisperse and the hydrodynamic radius R_H determined by dynamic light scattering (DLS) is related to the brush height L through $R_H = R + L$, where R denotes the radius of the core particles. All systems investigated here have been fully characterized with regard to their structural parameters, namely, the contour length $L_c = 60$ nm of the grafted chains, the radius $R = 58$ nm of the core particles, and the grafting density $\sigma = 0.064\ \text{nm}^{-2}$ giving the number of chains per unit area. The SPBs are immersed in a solution of lanthanum and sodium-chloride ions with a varying concentration ratio

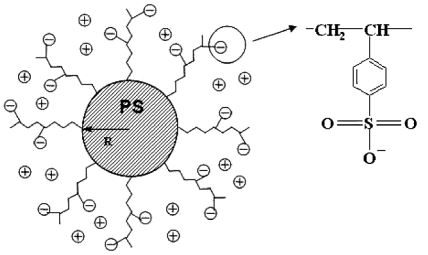

FIG. 1. Schematic representation of the spherical polyelectrolyte brush investigated in this study. Anionic polyelectrolyte chains are grafted to colloidal particles (radius: R) made from solid poly(styrene).

$\Phi = c_{\mathrm{La}^{3+}}/c_{\mathrm{Na}^{+}}$. However, for a given set of ratios Φ we keep the ionic strength constant. The thickness of the brush layer L was obtained through $L = R_H - R$, where the hydrodynamic radius R_H was determined using a Peters ALV 4000 light scattering goniometer [2].

The theoretical model used here for comparison with experimental results is based on the Alexander–de Gennes approach [17,18]. We consider a single SPB within a cell volume with radius R_W corresponding to the brush density in the experimental sample. In our model we used two fitting parameters: the radius R_W and the number of osmotically active ions in the brush. The brush thickness L results from a balance of the chain retraction of the flexible polyelectrolyte chains modeled as Gaussian and the osmotic pressure forces of the counterions. Hence, the elastic and the excluded volume Flory-type contributions read:

$$F_{\mathrm{ch}} = -\frac{3kTfL}{Na^2} + v_0 kT(fN)^2 \frac{9(R+L)^2}{8\pi[(R+L)^3 - R^3]^2}, \quad (1)$$

with $f = 4\pi\sigma R^2 \approx 2700$ being the chain number and $N = 240$ being the degree of polymerization. The monomer length a is set to 0.25 nm [8,9]; kT is the thermal energy and the excluded volume parameter is assumed to be $v_0 \approx a^3$.

The osmotic pressure forces of the confined and free ions, with the concentrations, c_x^i and c_x^o, respectively ($x = \mathrm{La}^{3+}, \mathrm{Na}^{+}, \mathrm{Cl}^{-}$) are $F_p = \Delta\Pi 4\pi(R+L)^2$, with the ideal osmotic pressure $\Delta\Pi = (c_x^i - c_x^o)kT$. Combining these equations with Eq. (1) yields the equilibrium brush thickness L. The concentrations appearing in $\Delta\Pi$ are calculated by taking into account the Donnan equilibrium via

$$\frac{c^i_{\mathrm{La}^{3+}}}{c^o_{\mathrm{La}^{3+}}} = \left(\frac{c^i_{\mathrm{Na}^{+}}}{c^o_{\mathrm{Na}^{+}}}\right)^3 = \left(\frac{c^o_{\mathrm{Cl}^{-}}}{c^i_{\mathrm{Cl}^{-}}}\right)^3. \quad (2)$$

In addition, there are the neutralization conditions inside and outside of the brush $3c^i_{\mathrm{La}^{3+}} + c^i_{\mathrm{Na}^{+}} = c^i_{\mathrm{Cl}^{-}} + c^i_m$ and $3c^o_{\mathrm{La}^{3+}} + c^o_{\mathrm{Na}^{+}} = c^o_{\mathrm{Cl}^{-}}$, respectively. $c^i_m = fN/V_{\mathrm{in}}$ is the charged monomer concentration inside the brush volume $V_{\mathrm{in}} = 4\pi[(R+L)^3 - R^3]/3$. Equation (2) and the neutralization conditions together with the experimentally given ionic strength $I = (1/2)\sum_x q_x^2 c_x$ have to be solved numerically at each concentration ratio Φ. q_x is the valency of ion x.

Obviously any electrostatic correlation and fluctuation effects have been neglected. Recently Yin *et al.* calculated all ion virial contributions of a polyelectrolyte network using molecular dynamics simulations [19]. Their results show that the pressure virial contributions due to electrostatics is almost completely cancelled by the virial part due to counterion excluded volume terms. Since the physical behaviors of the counterions in a polyelectrolyte network are similar to polyelectrolyte brushes in terms of their correlation to the chains and their osmotic activity, in particular, in the collapsed state, we apply these results to our system. Therefore, we neglected electrostatic contributions and the excluded volume terms of the counterions in our mean-field model.

In order to investigate the osmotic activity of the counterions we performed molecular dynamics simulations of a SPB. The simulation model is very similar to that of starlike polyelectrolyte stars published recently [20]; the details will be discussed elsewhere. A single SPB was simulated with explicit counterions without added salt. The parameters of the completely dissociated brush are $R = 6a$, $f = 40$, and $N = 30$. The simulations were equilibrated for 500 000 time steps; the desired quantities were produced during further 250 000 steps. Although the model-SPB is much smaller than the real one the essential physical effects are captured. In Fig. 2 we show two important quantities for the case $\Phi = 1$. The first quantity is the pair correlation function among counterions and monomers. Clearly, the correlation of the trivalent counterions is much stronger than that of the monovalent ones. The strong binding of the former ions affects also their mobility which is quantified by the mean-square displacement (MSD) $\langle \Delta r^2 \rangle$ shown in the inset. The mobility of the trivalent counterions is much smaller than that of the monovalent ones. For comparison reasons, the MSD of the monomers is also shown (dotted line in the inset). From the slope of the MSD we obtain the self-diffusion coefficient D_0 of the particles expressed in Lennard-Jones units τ and a, denoting the time and length scale, respectively [20]. The diffusion coefficient of the trivalent ones is bigger than that of the monomer beads. However, it is still in the same order of magnitude although the monomers naturally possess a small diffusion due to their chain configuration. In contrast, the monovalent counterions show to exhibit a diffusion of 1 order of magnitude higher than the monomers. We conclude from these results that the trivalent counterions are osmotically deactivated due to their strong binding at the chains. It justifies our theoretical mean-field approach for the further considerations.

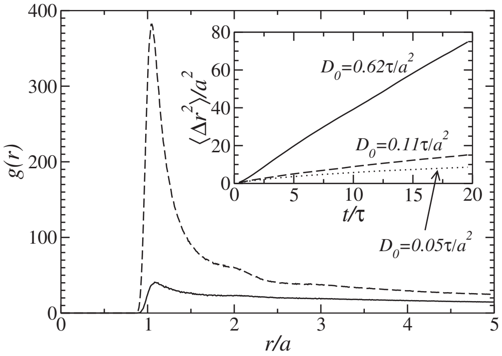

FIG. 2. Pair correlation function $g(r)$ between monomers and monovalent counterions (solid line) and trivalent ones (dashed line). Inset: MSD $\langle \Delta r^2 \rangle$ of monovalent counterions (solid line), trivalent ones (dashed line), and monomers (dotted line). The diffusion coefficients D_0 are obtained from the slope of the lines above 7.5τ, where τ denotes the Lennard-Jones time scale [20].

A central step of the further analysis is the calculation of the partition of the different ions between the brush layer and the solution in which the particles are immersed. We do not assume that the solution provides an infinitely large reservoir for the particles. Rather, we place each particle in the center of a Wigner cell of volume $V_{\mathrm{out}} = 4\pi R_w^3/3$. The parameter η describing the volume fraction $V_{\mathrm{in}}/V_{\mathrm{out}}$ is not negligibly small but of appreciable magnitude in each case studied here. The total concentrations of each ion type occurring in I and Φ is then $c_x = \eta c_x^i + c_x^o$. Note that the force balances of F_{ch} in Eq. (1) and the osmotic pressure force F_p have to be solved simultaneously with the Donnan equation [Eq. (2)] together with the neutralization conditions.

The introduction of a Wigner-Seitz cell is necessary for a correct description of the collapse for the following reasons: the brush collects all La^{3+} ions from the surrounding until it becomes saturated. At the same time at low fraction Φ virtually no La^{3+} ions are outside of the brush. Hence, the finite salt reservoir in the solution can be depleted from the lanthanum concentration which must be taken into account. In most theoretical treatments a constant bulk density of ions outside of the brush is assumed, corresponding to an infinite salt reservoir [21]. This would lead to collapse already at very low concentration ratios around $\Phi \approx 10^{-9}$.

Figure 3 shows the relative thickness L/L_c of the brush layer in presence of a mixture of Na^+ and trivalent La^{3+} counterions (Φ). Parameter is the overall ionic strength I of added salt. At lowest ratios Φ the reduced thickness L/L_c remains more or less constant, in particular, at low ionic strength. For higher Φ a marked shrinking is observed which is most pronounced for a ratio $\Phi > 0.01$. The collapsed state reached for all I is found to be the same. For low ionic strengths I the suspension remains stable at this point. However, higher I are followed by coagulation of the particles. The coagulation of the particles points to an effective attraction between the particles which is not described by the mean-field approach, of course.

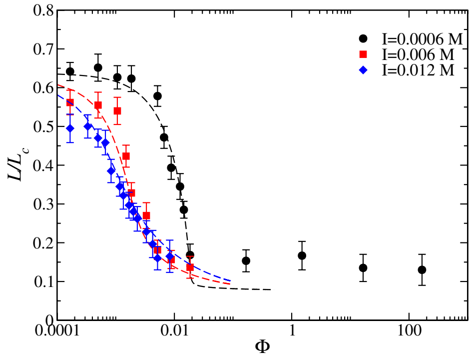

FIG. 3 (color online). Relative brush thickness L/L_c of the spherical polyelectrolyte brush in presence of a mixture of monovalent (Na^+) and trivalent (La^{3+}) counterions. Parameter of the different sets of data is the overall ionic strength I. At $I = 0.006$ M and 0.012 M, coagulation occurs. The lines are theoretical predictions. See text for further explanation.

Qualitatively, the strong shrinking of the brush layer upon addition of trivalent counterions must be traced back to the significant lowering of the osmotic pressure within the brush layer. In average three monovalent counterions are replaced by one La^{3+} ion, thus reducing the osmotic pressure by a factor of ca. 3. A key point is the enrichment of the trivalent ions in the brush layer on the expense of the monovalent ions. The ion exchange process is determined by the Donnan effect. This is shown by the fact that our theoretical model fits the experimental data very well. The deviations at low Φ are within 10%–15%; the discrepancies at high Φ are discussed below. Only two parameters enter into the fit: the number of ions which are osmotically active inside the brush and the cell radius R_W. For the first parameter we assume in our model that only 80% of the confined Na^+ ions and no La^{3+} ions contribute to the osmotic pressure $\Delta\Pi$. Therefore, $c^i_{\mathrm{Na}^+}$ occurring via $\Delta\Pi$ in the osmotic pressure force F_p has to be multiplied with 0.8 and $c^i_{\mathrm{La}^{3+}}$ is omitted. Note that we kept this parameter constant for all our comparisons with the experimental results. In our picture the Na^+ ions, although mostly condensed to the chains, still exhibit an entropic contribution since they are localized around the chains but can glide along them [22]. Hence, reducing the chain length costs entropic energy. In contrast the La^{3+} ions are strongly correlated to charged monomers. Since the chains are flexible at one end they can wrap locally around the La^{3+} ions. Hence, the La^{3+} ions hardly move along the chains yielding a significant loss of translational degree of freedom; their entropic contribution is negligible. This picture is confirmed by our simulation results discussed above. We stress that these considerations are not in contradiction to the analysis of the interaction energy between two planar brushes or two starlike polyelectrolytes. Here it is important to subtract the condensed counterions before calculating the osmotic pressure [6,22]. In these cases there is no change in the entropic energy of the condensed counterions, since the chains retract from each other by keeping their length constant. The second parameter which has to be adjusted is the cell radius R_W. We used $R_W = 2000$ nm at $I = 0.0006$ M and $I = 0.012$ M. At $I = 0.006$ M we set $R_W = 1875$ nm. These values are close to the experimental calculation which yields 1675 nm.

The collapse depends also on the number density of the SPB that determines the concentration c_m of the charged monomers in the solution. Figure 4 shows that with decreasing brush density the collapse begins at lower Φ. The neutralization of the brush by La^{3+} ions is achieved earlier at fixed ionic strength ($I = 0.0006$ M) since there are less monomer charges in the system. Accordingly, the cell radius is increased to $R_W = 3625$ nm (experimental value). The shift of the collapse is reflected by the parameter $\zeta = 3c_{\mathrm{La}^{3+}}/c_m$, which gives a degree of saturation of the brushes by La^{3+} ions at $\Phi = 0.0001$; a value of $\zeta = 1$

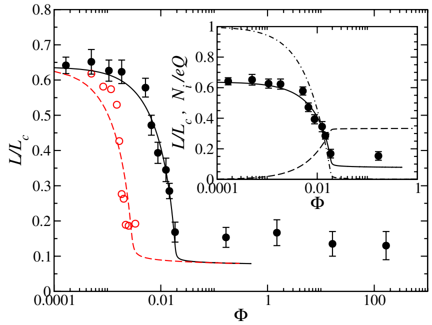

FIG. 4 (color online). Relative brush thickness L/L_c of the system LQ8 in presence of a mixture of monovalent (Na^+) and trivalent (La^{3+}) counterions. The ionic strength is set to $I = 0.0006$ M. Parameter of the different sets of data is the brush concentration c_{SPB} in the experimental sample in weight ppm. The filled circles are results for $c_{SPB} = 55$ wt ppm corresponding to $\zeta = 0.0164$, and the open circles are for $c_{SPB} = 5.5$ wt ppm ($\zeta = 0.164$). The parameter $\zeta = 3c_{La^{3+}}/c_m$ gives the degree of saturation of charged monomers by La^{3+} ions at $\Phi = 0.0001$. The lines are theoretical calculations. The inset shows the strong ion exchange: the filled circles denote L/L_c (solid line: theory) at $c_{SPB} = 55$ wt ppm. The calculated relative numbers of confined counterions N_i/eQ are shown [i: Na^+ (dashed-dotted line), La^{3+} (dashed line); $eQ = 648\,000$: numbers of charged monomers per brush].

means a complete saturation at $\Phi = 0.0001$. The shift of the crossover regime of the brush thickness to lower values of Φ is also according to the Donnan equilibrium reflected in Fig. 3 if the ionic strength is increased: higher ionic strength increases the degree of saturation ζ, enhancing it closer to complete saturation of the brushes by La^{3+} ions.

The inset of Fig. 4 demonstrates that the collapse of the brush thickness L/L_c is accompanied by a decay of the number of confined Na^+ ions [normalized to the brush charge $Q = 648\,000e$ (e: elementary charge)]. Simultaneously, the number of confined La^{3+} ions increases until the brush is saturated at $\Phi \approx 0.02$. The theoretical predictions using a finite salt reservoir, as it is in the experimental setup, describe the collapse very well. Slight discrepancies occur in the relative brush thickness after the collapse is reached. Here, at higher La^{3+} concentration in the system, correlation and fluctuation effects might play a role, or specific ion effects, which cannot be covered by our mean-field model.

Data obtained on SPB can furnish an important piece of further information: if the steric stabilization breaks down, the particles will start to coagulate. Moreover, if coagulation starts even when L has diminished only partially, there must be an attractive force between the particles. In this way the SPB can be compared with data obtained on planar brushes by the surface force apparatus. Recently, Tirrell and co-workers demonstrated that multivalent ions lead to attraction between planar polyelectrolyte brushes indeed [23].

In conclusion, we demonstrated that the observed brush collapse in presence of trivalent ions is of purely entropic nature. It is not driven by any screening or fluctuation effect. The exchange of monovalent counterions by trivalent ones leads to a collapsed chain configuration. This is due to a reduction of the osmotic pressure caused by this ion exchange. Moreover, our simulation results point to a strong binding of the La^{3+} ions to the polyelectrolyte chains which reduces the osmotic activity of the trivalent ions. This strong binding virtually neutralizes the trivalent counterions. As a consequence, we could show for the first time that the collapse of polyelectrolyte brushes in presence of trivalent ions can be described very well within the mean-field approach. Only at higher La^{3+} concentrations, corresponding to high ionic strength or ion fractions Φ, correlation and fluctuation effects may become important. This can be seen from the aggregation which occurs in the collapsed state at ionic strengths $I = 0.006$ M and above. Other phenomena as, e.g., ion bridging, will be studied in a forthcoming Letter in which we present more results of molecular dynamics simulations of SPBs.

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*Email address: arben.jusufi@uni-bayreuth.de

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