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Measurement of long-ranged steric forces between polyelectrolyte layers physisorbed from 1 M NaCl

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The colloidal probe technique (CPT) is used to measure distance-dependent interaction forces between polyelectrolyte layers physisorbed from 1 M NaCl solution in salt solutions between 0.1 mM and 1 M. Both linear polycations (poly(allylamine)hydrochloride, poly-l-lysine) and linear polyanions (poly(styrene-sulfonate)) are used. The repulsive interaction energies in the range between 10^{-7} and 10^{-4} $\mathrm{J/m^2}$ are described by the theory of Alexander and de Gennes for surfaces covered with neutral anchored polymers. However, the brush thickness scales with molecular area and salt concentration with a power of $-1/3$ as known from a salted brush and reaches approximately 50% of the contour length in diluted solutions. The findings are confirmed by CPT images using a gold layer as height reference.

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Polyelectrolytes (PEs) are used in a multitude of traditional applications (e.g., as wet and dry strength additives, as flocculating or dispersing agents), but also in basic research in connection with material and the life sciences (PE multilayers made by sequential adsorption of alternately charged polyions for optics, electronics, membranes, etc.) [1–6]. Therefore, to understand the conformation of adsorbed PEs as well as surface interactions is of major importance. However, in most of these cases PEs adsorb onto surfaces from salt solutions of intermediate or high ionic strength. The first measurement of forces acting between PE layers (physisorbed from such solutions) dates back to the pioneering work of Luckham and Klein with the surface forces apparatus (SFA), which showed steric forces due to compression of polymer chains extending into solution [7]. Yet, on first approach, an irreversible compression of the layers occurred, which rendered the quantification of the experiments difficult. In the following years, research focused on adsorption from salt-free solution which leads to flat adsorption (called flat PE layer below) accompanied by surface charge overcompensation, as has been established theoretically [8,9] and experimentally [10–12]. On increasing the salt concentration in the deposition solution (which is the biological and technological more important case) more PE is adsorbed, but it is not known how the increase in surface coverage influences the PE conformation. To avoid the irreversible compression of the polymer chains, it is necessary to reduce the applied force.

Method. Here the colloidal probe technique (CPT) is used to investigate the forces between PE-coated surfaces in salt solutions between 0.1 mM and 1 M NaCl, with the polyelectrolyte layers adsorbed from 1 M NaCl solution. As polyelectrolytes cationic poly(allylamine)hydrochloride (PAH, 70 kDa, contour length L_C=220 nm) and poly-l-lysine (PLL, 300 kDa, L_C=350 nm) and anionic poly(styrenesulfonate) (PSS, 350 kDa, L_C=425 nm) are used, the latter on surfaces which are positively charged by chemisorption of 3-aminopropyldimethyl-ethoxysilane. All chemicals were used as received from Sigma Aldrich. The PE solutions were prepared by solving 1 M NaCl and 3 mM PE monomers in Milli-Q water (Millipore, Billerica, MA). After adsorption (1 h at 30 °C) the surfaces were transferred in a wet state into the fluid cell of our commercial DI Multimode atomic force microscope (AFM) with Nanoscope IIIa Controller (Santa Barbara, CA). The force measurements were performed in PE-free NaCl solutions of different ionic strengths: starting at 1 M, then diluting down to 1 mM (PSS, PAH) respectively 0.1 mM (PLL), and enriching again to 1 M. Force curves were recorded not later than five minutes after change of the solution.

The setup used for CPT on PE coated $\mathrm{SiO_2}$ surfaces is shown in the inset of Fig. 1(a) and described in detail elsewhere [13]. Silica spheres (Bangs Laboratories, Fishers, IN; radius R=3 μm) were glued onto soft springs (spring constant k=0.01–0.1 N/m) (cantilevers OBL and NP0 from Veeco, Dourdan, France, and CSC-12 from MicroMasch, Tallinn, Estonia). Spring constants were determined using the methods of Butt *et al.* and Sader *et al.* [14]. During one experiment we recorded at least 150 force curves for each salt concentration at different positions on the surface, with one approach-separation cycle per 10 s. In all more than 12 000 force curves were recorded.

Results. For all PEs we measure repulsive forces which exhibit exponential decay at intermediate surface separations. Flat PE layers show a similar decay which is caused by electrostatic double-layer forces and whose decay length λ^{-1} corresponds to the Debye length κ^{-1}. For a monovalent aqueous salt solution κ^{-1} is given by $\kappa^{-1}=0.304\ \mathrm{nm}/\sqrt{I}$, where I denotes the ion concentration [15].

In our measurements the decay length always exceeds κ^{-1} and hence these forces cannot be explained in the framework of the Derjaguin-Landau-Verwey-Overbeck (DLVO) theory which was used in the past to describe forces between flat PE layers. The presence of these long-ranged forces leads to the conclusion that some parts of the PE dangle into the solution and that therefore the PE layer exhibits a nonflat conformation.

We applied the theory of Alexander and de Gennes (AdG) which describes the steric force acting between two end-grafted neutral polymer brushes and which was successfully applied to adsorbed polymer layers [16]. AdG force profiles are characterized by the average distance between two graft-

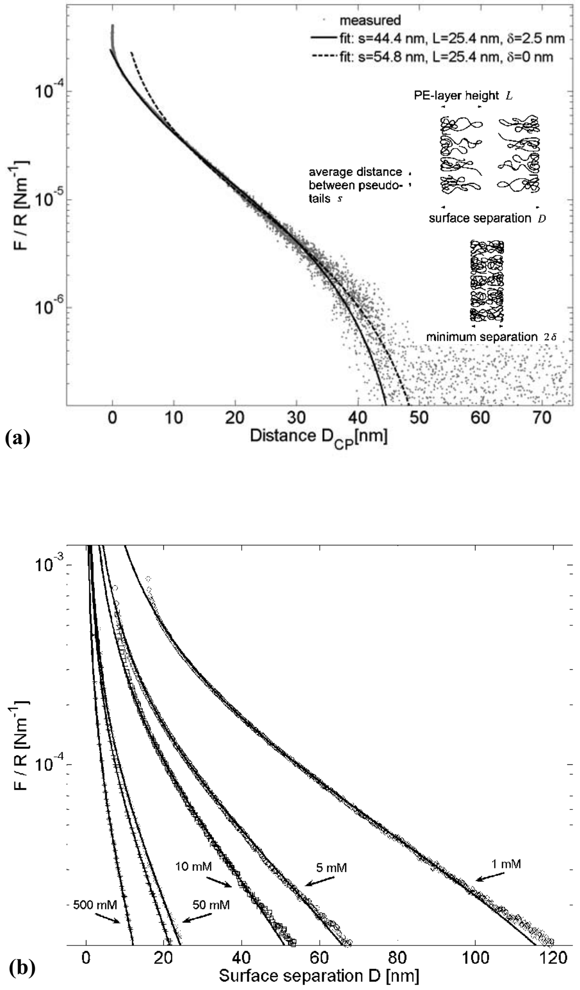

FIG. 1. (a) Measured force between two PLL layers physisorbed from 1 M NaCl solution in 5 mM NaCl (gray dots, obtained by averaging over 1500 approach curves) and fit to the theory of Alexander and de Gennes, Eq. (1), with (solid line) and without (dashed line) the displacement parameter δ. At small separations, the gray dots coincide and appear as a gray line. The inset shows a scheme of the experimental setup, together with the parameter assignment. (b) Distance-dependent forces between two PAH layers physisorbed from 1 M NaCl and measured in aqueous solutions with different ionic strength. The fits (solid lines) yield the brush length L; the average separation between pseudotails, s; and the separation between the silica and film surfaces, D [cf. inset to 1(a)].

ing points s and the height of the polyelectrolyte layer L and are given by

$$\frac{F(D)}{2\pi R} = \frac{8k_bTL}{35s^3}\left[7\left(\frac{2L}{D}\right)^{5/4} + 5\left(\frac{D}{2L}\right)^{7/4} - 12\right], \qquad (1)$$

where D denotes the surface separation, R the colloidal probe (CP) radius, and k_bT the thermal energy.

Equation (1) exhibits an exponential decay at intermediate surface separations ($0.2 \leq D/L \leq 0.9$) that can be described by [15]

$$\frac{F(D)}{2\pi R} \approx \frac{100k_bTL}{s^3}e^{-(\pi/L)D}. \qquad (2)$$

We obtained L by fitting the exponential function, Eq. (2), to the force at intermediate surface separations and s by a least-mean-squares (LMS) fit of Eq. (1) to the whole data.

Discussion. In AFM force measurements the surface separation D_{CP} is determined from the point of contact of both surfaces, which is the contact of both PE layers in our case. Contact is reached if the displacements of cantilever and piezo are equal (called constant compliance). However, D in Eq. (1) denotes the distance between the substrate surfaces and not between the solution-polyelectrolyte interfaces D_{CP} [see inset of Fig. 1(a)]. Obviously the PE layers can only be compressed to a height δ, because otherwise both substrates would touch and squeeze the PE out of the contact area, leading to irreproducible approach-separation cycles. Hence the discrepancy between D and D_{CP} is given by $D=D_{CP}+2\delta$. Furthermore, reaching $D_{CP}=0$ ($D=2\delta$) the PE layer cannot be compressed any further and the force profile will show a vertical slope and deviate from Eq. (1).

Figure 1(a) compares two fits of Eq. (1) with δ fixed to zero and δ regarded as free parameter. For $\delta=0$ one can conclude that at short separations the force profile will be overestimated by Eq. (1) by at least one order of magnitude, whereas a shift of 2δ results in an excellent agreement between Eq. (1) and the experimental data.

Equation (2) connects the decay length of the exponential part of the force profile with the thickness of an AdG brush. Using Fig. 1(a) one can notice that the force between both surfaces vanishes at a distance that corresponds to $2L$, where L was obtained as above. Hence in the following we will interpret L as the thickness of one PE layer. This interpretation is confirmed by ellipsometric measurements (data not shown).

The measurements show that chains of the layer dangle into solution leading to steric forces. The question is whether these chains are connected (i.e., networks) or are independent of each other (i.e., brushes). We assume that the chains are not connected and form a brushlike conformation.

(i) As we will show in the next section it is possible to reversible swell and shrink the layer. The force measurements show that the PE layer adopts its equilibrium conformation within 5 min after a change of the solution. In the case of a network, bonds would have to break and newly form within this time scale, which is highly unlikely.

(ii) We recorded tapping-mode images of PSS layers with sharp tips ($R \approx 20$ nm) and with CPs at different ionic strengths. It was not possible to image any changes in the layer conformation with a sharp tip as the tip moves to the substrate surface between the chains. However, as we will show in the last section, it is possible to image the swelling and shrinking of the PE layer by using a CP as a tip. Both points indicate that connections between the chains are unlikely and that the steric interaction is created by single chains protruding into the solution. However, Eq. (1) contains the parameter s, which measures the average distance between two grafting points for end-grafted brushes. As the interaction between brushes is created by the tails and not by the grafting points and as AdG brushes exhibit one tail per grafting point, one can conclude that s in fact measures the average distance between adjacent tails. Hence it is reasonable to say that in our measurements the parameter s corresponds to an average distance between neighboring tails or loops (subsumed as pseudotails below [17]).

Note that for all measurements it was not necessary to add electrostatic forces to describe the force profiles. It has to be concluded that the polyelectrolyte chains protruding into solution are surrounded by their counterions and do not produce a net surface charge. A similar feature was experimentally found and theoretically described for PE brushes, where all counter-ions are incorporated into the brush, leading to brush neutralization [18,19].

Power laws. Theoretical and experimental studies showed that two different regimes can be distinguished for PE brushes [19]. The *osmotic brush regime* is reached if the salt concentration in the bulk solution I is negligible compared to the monomer concentration in the brush I_{mono}. Increasing I until $I \geq I_{\mathrm{mono}}$ is fulfilled leads to the *salted brush regime*. Here the brush thickness L is proportional to $L \propto (I\, s^2)^{\alpha}$ with scaling exponent $\alpha = -1/3$. This behavior is explained with a balance between electrostatic forces (which stretch the chain because of the excess of counterions neutralizing the chain) and elastic forces (which oppose this stretching). Increasing I decreases the imbalance between the counterion concentration in the brush and in the subphase; therefore, the osmotic pressure is reduced and L shrinks.

Figure 1(b) shows force profiles of PAH-coated surfaces measured at different ionic strengths and fits to Eq. (1). Again good agreement between Eq. (1) and the data is achieved. Furthermore, the forces get more long ranged as I is decreased, which indicates a swelling of the PE layer. In Fig. 2 we plot the logarithm $\log_{10}(L)$ over $\log_{10}(I\, s^2)$ for all measurements and include regression lines obtained by a LMS fit to the data points. The slope of the regression lines equals $-1/3$ within 15% in every case which supports the idea that the PE layer behaves like a brush. Furthermore, the inset of Fig. 2 shows that PE layers physisorbed from 1 M NaCl behave qualitatively and quantitatively different from flat PE layers (physisorbed from salt-free solutions).

However, unexpected is the finding that adsorption in 1 M NaCl leads to PE layers that are several orders of magnitude thicker than layers of flatly adsorbed PEs. In dilute solutions the thickness can reach one-half of the contour length, a stretching never observed for brushes from neutral polymers [15,16], but for PE brushes [10]. These strong stretching forces can only be explained by counter-ions that are incorporated into the brush to screen the chain charges. This mechanism leads to the scaling exponent α derived for PE brushes.

From Fig. 3 one can infer that s is almost a constant and increases by less than 50% if the salt concentration is decreased from 1 M to 1 mM. This leads to the conclusion that the stretching of the chains is accompanied by only minor structural rearrangements of the PE layer.

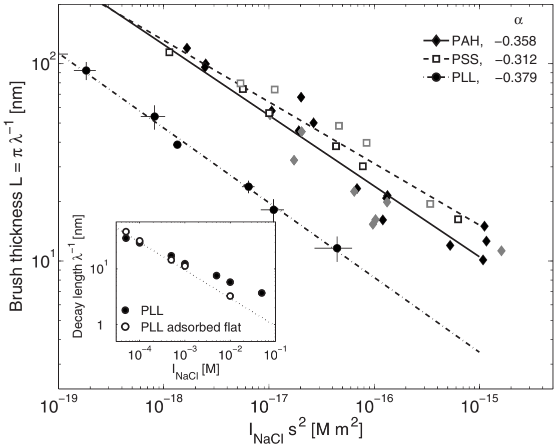

FIG. 2. Polyelectrolyte brush thickness L as function of the product of molecular area and ionic strength. The straight lines are power laws; the respective exponents are given in the legend. The black (gray) symbols correspond to measurements performed while lowering (raising) the salt concentration. The error bars of the PLL thickness represent twice the standard deviation. The inset shows the measured decay lengths between PLL layers physisorbed from aqueous solutions containing 1 M NaCl (solid circles) and no salt (open circles). The Debye length κ^{-1} according to DLVO theory is also shown (dotted line).

To check the swelling and shrinking of the PE layer for hysteretic effects we decreased and increased the salt concentration by factors of 2 and 5 over three decades. Considering the data from all experiments and the experimental resolution we have no indication that swelling-shrinking hysteresis occurs. Thus we infer that swelling and shrinking of the layer is reversible on the time scale of our experiment (<5 min). From the assumption that one PE chain is located in the unit volume Ls^2 one can cross check the condition for the salted brush, $I > I_{\mathrm{mono}}$. It is found to be valid for PAH above 10 mM, for PSS above 57 mM, and for PLL above 310 mM. The far too high value for PLL suggests that within the unit volume only a fraction and not a whole PLL chain is located. Also the decrease of the chain charge due to binding of the counter-ions is neglected, which was found to be substantial [8,18,19].

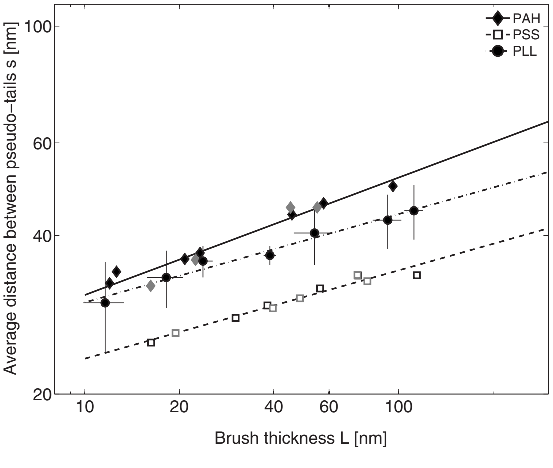

FIG. 3. Average distance between pseudotails, s, as function of brush thickness L. The shrinking and swelling is accompanied by minor structural rearrangements which are fully reversible if 5 min equilibration time after changing the solutions was allowed (same symbols as in Fig. 2).

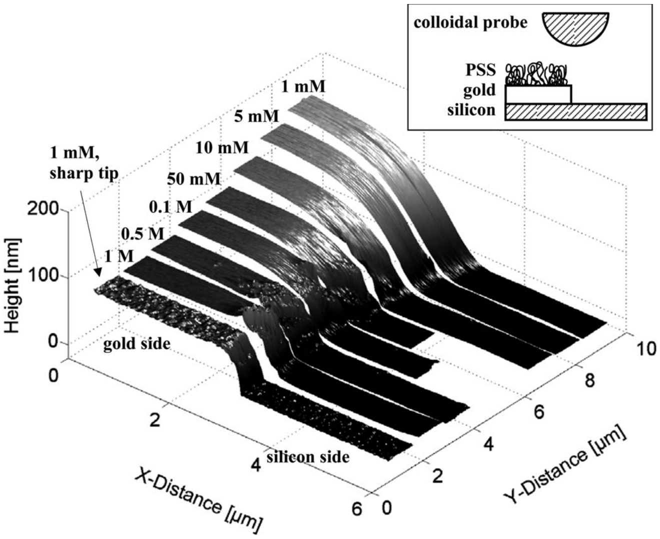

FIG. 4. Tapping-mode images of a surface-functionalized gold step (50 nm high) with physisorbed PSS at different ionic strengths as indicated imaged with CP tips ($R=3$ μm). With sharp tips ($R<20$ nm) the brushes cannot be resolved. Therefore the step height is independent of the ionic concentration and only one representative image obtained with a sharp tip is shown.

Gold step. We constructed a 50-nm gold step onto a silicon wafer by evaporation of gold [20] and subsequent silanization and adsorption of PSS onto the gold side of the step (cf. inset of Fig. 4). Thereby we were able to absolutely measure the PSS-layer thickness by performing tapping-mode (TM) imaging of the gold step at different ionic strengths and to compare the force profiles of the PE-coated side with the uncoated side. To achieve reproducible results TM images were recorded, keeping the imaging parameters (i.e., driving amplitude and setpoint) constant.

Figure 4 shows TM height profiles of the gold step at different ionic strengths measured with a CP ($R=3$ μm) as tip. Force curves measured on both sides of the step confirm that long-ranged steric forces occur only on the gold side of the step whereas electrostatic double-layer forces with a Debye length κ^{-1} can be measured on the silicon side. Therefore a change in the step height is mainly caused by swelling or shrinking of the PSS layer.

Conclusion. The colloidal probe technique is an appropriate method to measure small interaction energies; good accuracy can be obtained by averaging over at least 50 force curves. To measure smaller interaction energies reliably, very soft springs and improved statistics are necessary. With that approach we investigated the surface forces between layers from natural and artificial linear polyelectrolytes, which were physisorbed from 1 M NaCl solutions. Qualitatively, all systems show the same behavior: repulsive steric interactions known from brushes consisting of neutral polymers. However, the PE-layer thickness shows the scaling of a salted brush (power-law dependence on the product of molecular area and salt concentration, $\alpha\approx-1/3$, fairly constant grafting density, extreme stretching) with led us to the conclusion that linear polyelectrolytes adsorb in the presence of high salt concentrations in brushlike structures. How the conformation of the polyelectrolyte layer changes when an oppositely charged multiion is adsorbed on top of it is the next challenge.

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