

## Density Profile of Polyelectrolyte Brushes

Y. Mir,<sup>2</sup> P. Auroy,<sup>1</sup> and L. Auvray<sup>2</sup>

<sup>1</sup>*Institut Curie URA 448 du Centre National de la Recherche Scientifique, Section de Recherche, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*

<sup>2</sup>*Laboratoire Léon-Brillouin, Centre National de la Recherche Scientifique-CEA, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-Sur-Yvette Cedex, France*

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Using small angle neutron scattering techniques, we have determined the interfacial density profile of polyelectrolyte brushes. We show that in pure water the density profile has a Gaussian shape whose characteristic length appears to be a decreasing function of the grafting density. Upon the addition of salt, the layers shrink but never collapse. Even at very high ionic strength, the chains remain stretched and the density profile is eventually parabolic.

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We report in this Letter the main results of an experimental study we have carried out on polyelectrolyte brushes. These are polymer layers (at a solid-liquid interface, in our case) where the chains, carrying a significant number of ionizing groups, are anchored by one end on a flat surface. Furthermore, the density of grafting (or the number of chains per unit area) is high enough to induce interchain correlations.

This system has attracted a lot of attention from the theoreticians, not only because it is a variant of the famous and now classical problem of polymer brushes [1] but also because it has been thought that, in this restricted geometry, the behavior of charged chains would be more easily understandable. With charged brushes, one could thus test the basics of the theory of polyelectrolytes, which remains to some extent puzzling. On the other hand, from a technological point of view, it has been pointed out that these polyelectrolyte brushes might be useful in preventing the flocculation of water-dispersed colloids induced by an increase of salt concentration.

Despite all these appealing features, experiments on these charged brushes are so far very scarce, because of the extreme difficulty of preparing the samples. Indeed, the electrostatic repulsions are so strong in pure water that they do not allow the chains to build a dense interface. Thus, if one uses block copolymers, with one block charged and the other (the anchor) neutral or water insoluble, one must add a lot of salt to screen these electrostatic interactions [2]. But even if one succeeds in attaching some chains in this way, the grafting density is never high and furthermore some strange effects are observed, e.g., hysteresis during measurement of forces between two curved surfaces [3]. In our case, we have followed a completely different strategy to make polyelectrolyte brushes: we first prepare a dense neutral brush of polystyrene by covalently grafting the polymer in an organic solvent, and then we perform a chemical reaction (sulfonation) directly onto the interface to convert the chains into polyelectrolytes [poly(styrene sulfonate

sodium salt)—PSS-Na]. This original synthesis route has enabled us to determine the density profile of such highly charged polyelectrolyte brushes in pure water, and also as a function of the concentration of added salt (from 0 to 5M in NaCl). In particular, we clearly show that even in 5M NaCl the chains remain stretched like neutral polymers of a dense brush in good solvent.

Throughout this paper, only two samples will be considered: They differ most importantly in their grafting density. Both have been obtained as explained above: a (neutral) PS brush is prepared using porous silica as the solid substrate [4]. The perdeuterated PS chains have been anionically synthesized, and they carry at one end a reactive group (monochloro- or trichlorosilane) which reacts with the surface of the silica in organic solvents (benzene). The conditions for grafting are as follows: solvent carefully dried benzene; typical polymer concentration 60%; temperature 90 °C; time 24 h, and controlled atmosphere (vessel sealed under argon). We then rinse the sample to remove all the chains which have not reacted. Finally, the grafted chains are converted *in situ* into PSS-Na by a sulfonation reaction [5] adapted from Ref. [5]. We used a fourfold excess of the 1.5/1 complex of SO<sub>3</sub>/triethylphosphate, in carefully dried dichloroethane, for 30 min, at a temperature of -20 °C. These conditions have been optimized in order to minimize the degrafting of the polymer which can occur with this kind of aggressive chemistry. We end up with two polyelectrolyte brushes, called, respectively, Md and Hd, referring to their grafting density, which have an equal degree of substitution  $f = 0.64$  (determined by elemental analysis), an approximately equal number of segments ( $N = 611$  for Md and  $N = 580$  for Hd) and a distance between grafting points  $D$  equal to 43 Å for Md and 28 Å for Hd [determined according to Eq. (2)—see below]. Hd is thus 2.4-fold more dense than Md. As checked by elemental analysis, no sulfone crosslinks have been detected. We assume that the distribution of charges along the backbone is homogeneous.

The density profile of the interface  $\phi(z)$ , in aqueous salt solutions, has been determined by the small angle neutron scattering (SANS) technique, described [6] previously. All the spectra have been obtained under the contrast match condition where the scattering length density of the liquid is adjusted to be the same as that of the substrate. For each sample, observed in a given aqueous solution, the signal due to the bare silica immersed in the same solution is subtracted. We divide then the resulting signal by the signal of water which is used to normalize the detector. We end up with the intensity  $I(q)$  vs  $q$  which is solely due to the polymer interface because of the condition of contrast match.  $I(q)$  reduces [6] to

$$I(q) = \kappa^2 q^{-2} \left| \int_0^{+\infty} \phi(z) e^{iqz} dz \right|^2, \quad (1)$$

where  $\kappa$  is just a contrast term, exactly known. In Eq. (1), no contribution from the correlations of density fluctuations has been introduced because experimentally such correlations become significant only at much higher  $q$ . At very small  $q$ , Eq. (1) becomes

$$I(q) = \kappa^2 \gamma^2 q^{-2} \left( 1 - \frac{q^2 h^2}{\alpha} \right), \quad (2)$$

where  $\gamma$  is the amount of polymer per unit area [ $\gamma = \int \phi(z) dz$ ],  $h$  is the typical thickness of the interface, and  $\alpha$  is a numerical constant depending on the actual shape of  $\phi(z)$ . Therefore a plot of  $q^2 I(q)$  vs  $q^2$  (analogous to a Guinier plot, but for  $2d$  interfaces) allows us to determine  $\gamma$  (hence the grafting density  $\sigma$ ) independently of any model.

To determine the density profile, we use in this study a heuristic function for  $\phi(z)$ :

$$H_m(z) = \phi_s \frac{1 - \text{erf}[m(z/h - 1)]}{1 + \text{erf}[m]} + d \delta(z), \quad (3)$$

where  $m$ ,  $h$  (in  $\text{\AA}$ ),  $\phi_s$ , and  $d$  (in  $\text{\AA}$ ) are adjustable parameters whose values are determined by fitting the spectra with this generalized error function according to Eq. (1).  $\phi_s$  is the surface fraction occupied by the polymer [ $\phi_s = \phi(z=0)$ ];  $h$ , which is the position of the inflection point in the density profile, is a measure of the layer thickness. The parameter  $m$  has no physical meaning, but allows us to account for density profiles whose shape evolves continuously from gently sloped (small  $m$ ; Gaussianlike) to very steep ( $m = \infty$ ; step function). The last term in Eq. (3),  $d \delta(z)$ , is a correction (given the  $q$  range we have used) which accounts for the deviation of the spectra from the Porod law at  $q > 0.02 \text{ \AA}^{-1}$ . Experimentally, it is always of the order of  $10 \text{ \AA}$ .  $d$  cannot be interpreted unambiguously, but it is likely related to the presence of a small depletion (or adsorption, depending on the sign of  $d$ ) layer close to the surface. It might be also due to correlations inside the interface which become important only at higher  $q$ .

It turns out that this generalized error function accounts very well for our data (see Fig. 1). Thus it is possible to discuss changes in the spectra in terms of a structural change of the interface, since the number of adjustable parameters is kept constant and the quality of the fit is equally good for all the data shown in this paper [7].

In pure water (Fig. 2), it appears that the density profile is rather gently sloped for both samples and extends very far from the surface. If we compare the experimental results to a Gaussian, it turns out that the agreement is very good; we cannot make the distinction. This Gaussian shape was predicted by Zhulina, Borisov, and Birshtein [8] but has never been observed up to now. Nevertheless, one striking feature which was not anticipated and which appears very clearly in Fig. 2 is that the mean thickness of the interface  $L$  depends on the grafting density  $\sigma$ : it seems to be a decreasing function of  $\sigma$ , whereas theory [8,9] predicted  $L \approx \sigma^0$ . We recall also that for a neutral brush in a good solvent  $L$  is an increasing function of  $\sigma$ :  $L \approx \sigma^{1/3}$ . If we calculate  $L$  [defined as  $2 \int z \phi(z) dz / \int \phi(z) dz$ ], we find  $L_{\text{Hd}} = 482 \text{ \AA}$  and  $L_{\text{Md}} = 754 \text{ \AA}$ , while according to the theory of Zhulina we would predict  $L_{\text{Hd}} = 510 \text{ \AA}$  and  $L_{\text{Md}} = 538 \text{ \AA}$  (no adjustable parameters). Quantitatively, the agreement is satisfactory, but as pointed out before there is a significant difference between the two experimental values, much larger than that expected from the theory. What can be the explanation for this discrepancy? Since so far we have not carried out an exhaustive study, we are not sure that this discrepancy should be ascribed to the grafting density. It might be due to artifacts: The distribution of charges might be very different for the two samples (perhaps homogeneous for Md and inhomogeneous, as in a block copolymer, for Hd). It might be also that the Hd sample contains a small number of crosslinks (undetectable by elemental analysis), and that would keep the Hd layer from stretching. But it might also be that the theory is not fully right.

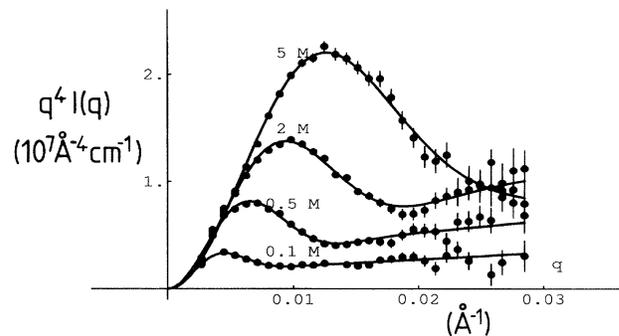


FIG. 1. Scattering intensity in the Porod plot [ $q^4 I(q)$  vs  $q$ ] for the sample Md at various NaCl concentrations. The solid lines are the corresponding results of the fit using the generalized error function, as described in the text.

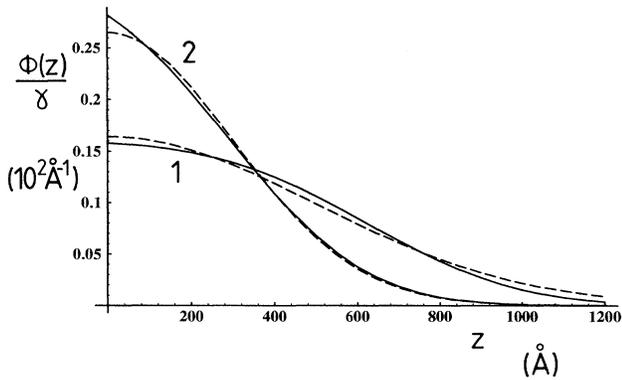


FIG. 2. Normalized density profile  $\phi(z)/\gamma[\gamma = \int \phi(z) dz]$  in pure water for the Md sample (1) and Hd sample (2). The solid lines correspond to the results of the fits using the generalized error function; dashed lines result from Gaussian fits.

What happens to the density profile if we add some salt? The results are summarized in Figs. 3(a) and 3(b). We can see that for both samples the polymer layer shrinks. The mean thickness decreases while the density close to the wall increases. But this effect is much more pronounced for the medium grafting density sample than for the high grafting density one. If we look in

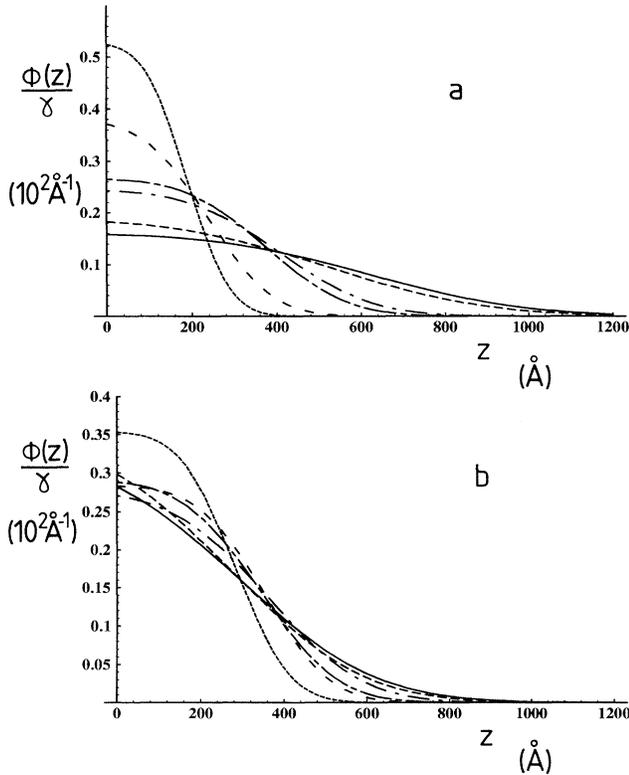


FIG. 3. Normalized density profile for the Md sample (a) and Hd sample (b) for various salt concentrations : — 0M, - - - 0.1M, · · · 0.5M, — — 1M, - - - 2M, and · · · · · 5M.

detail at the shape of  $\phi(z)$ , we can see that it does not markedly change for the Md interface:  $m$  remains roughly constant for all the salt concentrations; only  $h$  and  $\phi_s$  in Eq. (3) vary significantly (by a factor of 3) but not the product  $h\phi_s$ . The Hd interface exhibits rather different behavior, almost opposite:  $\phi_s$  and  $h$  are nearly constant (maximum variation of 25%) but  $m$  varies now by a factor of 3. Thus it seems that at medium grafting density the polyelectrolyte brush is quite sensitive to the addition of salt: The screening of the electrostatic interaction is very effective, and the stretching of the chains is released to some extent. But at high grafting density this cannot work: The inner concentration of counterions is so high ( $\approx 1.3M$ ) that the addition of salt in the bulk can influence only the outer edge of the layer [where  $\phi(z)$  goes to 0]; the main modification concerns now the shape of the interface.

Finally, we emphasize that neither interface ever collapses, even at 5M in NaCl which is close to the saturation limit. The average concentration  $\bar{\phi}$  (defined as the ratio  $\gamma/L$ ) is 0.19 for Md and 0.29 for Hd in 5M NaCl, while in a poor solvent for a neutral brush we find  $\bar{\phi} \approx 0.9$  regardless of the grafting density (Fig. 4). Moreover, if we compare the density profile of sample Hd for the charged brush in 5M NaCl with that of its neutral precursor (which has the same grafting density) in a good solvent, we find very similar curves (not shown). The data, in all cases (even for the Md sample at 5M NaCl), can be fitted satisfactorily by a parabolic form (modified by an exponential tail [4(b)]; see Fig. 4. This tells us that even at 5M in NaCl the polyelectrolyte chains remain stretched [10]. This had never been proven experimentally and was heretofore only a conjecture [8,9]. This effect can be understood if we realize that strong screening of the long range Coulomb repulsion results in an effective short range excluded volume interaction. This might have interesting consequences for the stabilization of hydrosols: A suspension of colloidal particles protected by

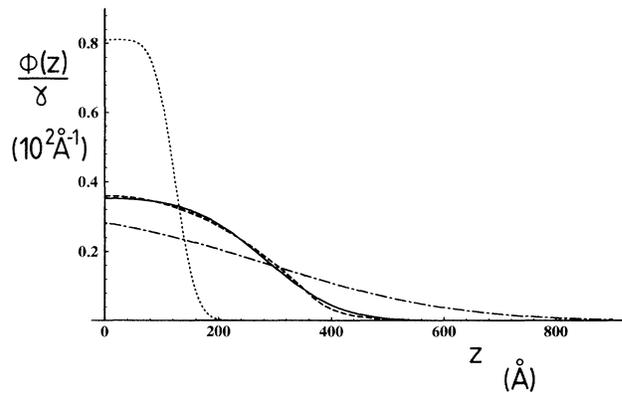


FIG. 4. Comparison between a polyelectrolyte brush (sample Hd) in pure water (dashed-dotted line) in 5M NaCl (solid line), and its neutral precursor in a poor solvent, methanol (dotted line). The dashed line corresponds to the fit with a parabola.

such dense polyelectrolyte brushes would be insensitive to the addition of salt and would not flocculate because of a change of the ionic strength.

Although our study has given some important and detailed results, the comparison with theory is still tentative for two reasons: the sample are few (because of the intrinsic difficulty of preparation) but the theories are also crude compared to what has been developed for neutral chains. In particular, it is not clear that "classical" electrostatics can be used at  $5M$  in NaCl. Therefore, we need to extend our investigations by varying in a more systematic way the length of the chains and the grafting density. We know from this study that this is feasible. However, we have already emphasized that these polyelectrolyte brushes are a fascinating system with potentially important applications in the physical and biological sciences.

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