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## Structure of grafted polyelectrolyte layer

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**Abstract.** — The equilibrium structure of a monolayer formed by long polyelectrolyte chains grafted at one end onto an impermeable planar surface is analyzed. In contrast to the case of uncharged grafted polymer layer the unit density profile in a swollen state is not of the parabolic, but of the exponential type. The decrease in the solvent strength below the  $\theta$ -point leads to the jump-wise collapse transition accompanied by the drastic change in the shape of the density profile. The increase in the ionic strength of the solution causes gradual decrease in the layer dimensions and change of the density profile which tends to the parabolic shape.

### Introduction.

The grafted polymer monolayers (« polymer brushes ») immersed in a solvent were actively investigated both theoretically and experimentally during the last decade. The interest to these systems was initiated by practical applications (colloid stabilization and flocculation, friction weakening, selective membrane modification, etc).

At the same time the grafted polymer layers are very interesting in the theoretical aspect. In the pioneering papers by Alexander [1] and de Gennes [2] the scaling analysis of the equilibrium layer structure was performed. It was shown that under the conditions of strong overlapping the chains in a layer are stretched in the direction normal to the grafting surface due to the interchain volume interaction, so that their dimensions in this direction scales proportionally to  $N$ . This analysis used the blob concept so that every chain in a layer was presented as a sequence of blobs completely stretched in a normal direction and retaining the Gaussian dimensions in the lateral one.

Although this picture in which all the chains in the layer are assumed to be stretched equally and uniformly gives the correct dependences of the average chain stretching on the main parameters of the layer (grafting density, solvent strength) the actual layer structure appeared to be quite different from that described above. As it was shown in a number of works by authors [3-6] and independently by Milner *et al.* [7-9] the grafted polymer layer is inhomogeneous as a whole : the chains are stretched unequally and ununiformly, their ends are distributed throughout the layer thickness and the density profile in a layer is not of step-wise character as it follows from the blob picture but has a parabolic shape (under the conditions of good solvent). These results were obtained on the basis of the self-consistent

field (SCF)-approach and so-called Newtonian approximation proposed by Semenov for the entropy of strongly stretched chains [10].

In the authors works [5, 6, 11] the collapse of a grafted layer caused by the decrease in a solvent strength and accompanying structural rearrangements of a layer were analyzed. It was shown that strong chain stretching in the layer makes the system effectively one-dimensional and the collapse transition loses its phase character. So the layer dimensions, free ends distribution and the density profile vary smoothly with the decrease in the solvent strength.

All this refers to the layers formed by uncharged polymer chains. However, the polyelectrolyte effects were almost not investigated up to recently. Not long ago several papers concerning the layers of grafted weakly charged polyelectrolytes appeared. Two groups of papers were based on the Flory-type approximation and devoted to the analysis of power asymptotics for the mean layer characteristics. Pincus [12] considered the polyelectrolyte brush neglecting volume interaction and obtained the dependences of the layer thickness and elasticity on the charge density and ionic strength of the solution. In the authors previous papers [13, 14], the dependence of the dimensions of polyelectrolyte/polyampholyte grafted layer on the solvent strength, charge density and ionic strength of the solution were analyzed. It was shown, that the osmotic pressure of counterions contributes an effective long-range interaction in this quasi-one-dimensional system, so that the collapse of the these layers caused by the decrease in the solvent strength may occur as the first order phase transition, i.e. with a jump in a layer dimensions.

On the other hand, the problem of the monomer density profile in the grafted polyelectrolyte layer was considered in references [15, 16] on the basis of SCF-approach and full Poisson-Boltzmann equation for the system of grafted charged chains. However, this approach made it possible to obtain only numerical solutions for the density profiles at finite (non-zero) ionic strength of the solution.

Therefore the aim of the present paper is to develop the SCF analytical theory describing of the structure (density profile, free chain ends distribution) of swollen polyelectrolyte brush and its rearrangement accompanying the layer collapse caused by the decrease in the solvent strength or by the increase in the ionic strength of the solution. We shall also generalize the layer structure analysis to the scaling region.

MODEL. — Let us consider a layer formed by long ( $N \gg 1$ ) polyelectrolyte chains grafted at one end onto an impermeable planar surface with a density  $1/\sigma$  ensuring the overlapping of polymer coils and immersed in a dielectric solvent. A chain part of length equal to chain thickness  $a$  is chosen as a unit. For simplicity let the backbone of the polyelectrolyte chain be flexible, i.e. its Kuhn segment length is  $A \cong a$ . The non-electrostatic volume interactions between the monomer units will be described by the second,  $v$ , and the third,  $w$ , virial coefficients. The former depends on temperature (solvent strength) near the  $\theta$ -point as  $v \cong v_0 \tau$ , where  $\tau = (T - \theta)/T$ , and we will consider the changes in layer characteristics accompanying the variations of  $\tau$ , whereas the latter is approximately independent of temperature (solvent strength),  $w \cong \text{const.}(\tau)$ . Let every  $m$ -th unit of each chain carries an elementary charging group, so that the total number of charges per chain is  $N/m \gg 1$ . We will restrict our consideration by weakly charged polyelectrolytes, for which

$$m^{1/2} \gg u = e^2/(\varepsilon a T) \quad (1)$$

where  $\varepsilon$  is the dielectric constant of the solvent. In this case the intrachain Coulomb interactions do not lead to the changes of chain stiffness [17].

We will first consider the situation when no salt is added into the solution. The condition of the total electroneutrality of the system results in the presence of  $N/m$  mobile counterions

(which we assume to be monovalent) per chain in the solution. These counterions are retained by infinite planar layer of grafted polyions near it just as near an infinite charged flat surface. We shall assume the condition  $\kappa H \gg 1$ , where  $\kappa^{-1}$  is the Debye screening length in a layer and  $H$  is the layer thickness, to be fulfilled, so that almost all counterions are located in a layer.

Moreover, this condition allows us to use the local electroneutrality approximation, i.e. we shall suggest that the density profile of counterions coincides with that of charges immobilized on the grafted chains. It is justifiable because the spatial dimensions of the regions with uncompensated volume charge are  $\sim \kappa^{-1}$ , i.e. much less than the layer thickness. (This problem is discussed in details in [18]).

Note that the condition  $\kappa H \gg 1$  is equivalent to that of  $H \gg \sigma m/N$  which is always fulfilled for sufficiently long chains.

### 1. Salt-free solution.

FREE ENERGY. — The equilibrium characteristics of the grafted polyelectrolyte layer may be obtained by the minimization of its free energy functional, which may be presented under the conditions of strong chain stretching in the form

$$\Delta F/T = 3/(2 a^2) \int_0^H g(x') dx' \int_0^{x'} E(x, x') dx + (\sigma/a^3) \int_0^H f[\varphi(x)] dx \quad (2)$$

analogous to that used previously in [3-6]. Here  $E(x, x') = dn/dx$  is the function of local chain stretching at the height  $x$  under the condition that chain free end is at the height  $x'$ ;  $g(x)$  is the normalized distribution function of free chain ends and  $H$  is the upper boundary of the layer (the width of a slit in which the layer is confined). The first term describes the conformational (elastic) contribution to the free energy. The second term is the functional of the unit density  $\varphi(x)$  only and includes the contributions of different origin:

$$f[\varphi(x)] = v\varphi^2(x) + w\varphi^3(x) - (4\pi^{1/2}/3)(ulm)^{3/2} \varphi^{3/2}(x) + (\varphi(x)/m) \ln(\varphi(x)/m). \quad (3)$$

The first and the second terms in equation (3) describe as usually the non-electrostatic interunit volume interactions in the layer. The third term describes the correlation (electrostatic) attraction between immobilized on the chains charges and mobile counterions; it is written in the Debye-Huckel approximation, i.e. as for weakly nonideal plasma [19]. Finally, the last term in equation (16) corresponds to the translational entropy of mobile counterions in the layer.

The density (volume fraction) of monomer units may be expressed by the functions  $E(x, x')$  and  $g(x)$  as usually:

$$\varphi(x) = (a^3/\sigma) \int_x^H g(x')/E(x, x') dx'. \quad (4)$$

RESULTS. — The standard procedure of the minimization of the functional (2) with respect to two unknown functions  $E(x, x')$  and  $g(x)$  at fixed  $H$  taking into account the relationships (3), (4) and normalization conditions

$$\int_0^{x'} dx/E(x, x') = N \quad (5)$$

$$\int_0^H \varphi(x) dx = Na^3/\sigma \quad (6)$$

(see [3-6] for details) gives us the universal expression for  $E(x, x')$ ,

$$E(x, x') = (\pi/2 N)(x'^2 - x^2)^{1/2} \quad (7)$$

which is independent from the type of function  $f[\varphi(x)]$  and retain its form in the polyelectrolyte layer and an equation for the density profile  $\varphi(x)$ :

$$\delta f[\varphi(x)]/\delta \varphi(x) = \lambda - 3 \pi^2 x^2 / (8 N^2 a^2) \quad (8)$$

where  $\lambda$  is an indefinite Lagrangian multiplier, the value of which should be obtained from the condition (6).

The further minimization of the free energy with respect to  $H$  gives the equilibrium characteristics of the free (uncompressed) layer.

Unfortunately, the exact analytical solution of equations (3), (8) can not be obtained in contrast to the case of uncharged grafted polymer layer. However, we can simplify the problem using the comparative estimations of different contributions into the free energy of the *free* grafted polyelectrolyte layer made by us in [13]. These estimations should be valid if the layer is free or slightly ( $H \leq$  the characteristic layer thickness) compressed.

First of all it was shown, that if the chains in a layer carry the charges of only one sign (« pure » polyelectrolyte) the correlation term does not contribute sufficiently at any  $\tau$ .

Depending on the relation between the contributions of the repulsive volume interchain interactions and counterions osmotic pressure (or that is the same between the surface grafting and linear charge densities) two regimes of layer swelling and collapse can be distinguished.

1. The « quasineutral » regime takes place at  $w^{1/2}(a^2/\sigma) m \gg 1$  i.e. the linear charge density on the chains is low and the number of counterions in the layer is comparatively small. In this regime the volume interchain interactions predominates over the osmotic pressure of counterions and polyelectrolyte effects are unessential at any  $\tau$ . At high temperatures (above the  $\theta$ -point) the layer is swollen due to binary repulsive interactions and is characterized by well-known [3-9] parabolic density profile (Fig. 1, curve 1). The decrease in the solvent strength (in  $\tau$ ) leads to the continuous decrease in the layer dimensions and the transition into

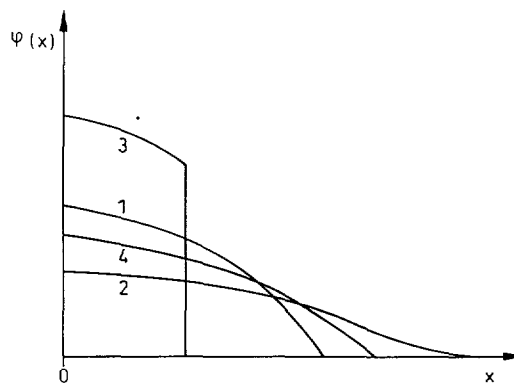


Fig. 1. — Schematic representation of profiles of monomer units in uncharged grafted layer immersed in a good (1) or poor (3) solvent and in a polyelectrolyte layer without added salt,  $\phi_s = 0$ , (2) and with added salt,  $\phi_s = 0$  (4).

the collapsed (globular) state occurs smoothly (Fig. 2, curve 1) in the range of  $\Delta\tau \cong \tau^* \cong w^{3/4}(a^2/\sigma)^{1/2}$  near the  $\theta$ -point. Note, that in the  $\theta$ -region the layer remains swollen due to ternary repulsive interactions. This decrease in the layer dimensions is accompanied by the continuous change of the density profile. Below the  $\theta$ -point the density profile acquires a jump ( $\Delta\varphi \cong |\tau|/w$ ) at the layer upper boundary and tends to the step-wise function with the decrease in  $\tau$  (Fig. 1, curve 3). Figure 3, curves 1, 3 illustrates the change in chain ends distribution accompanying the collapse of the layer (see [6, 7] for details).

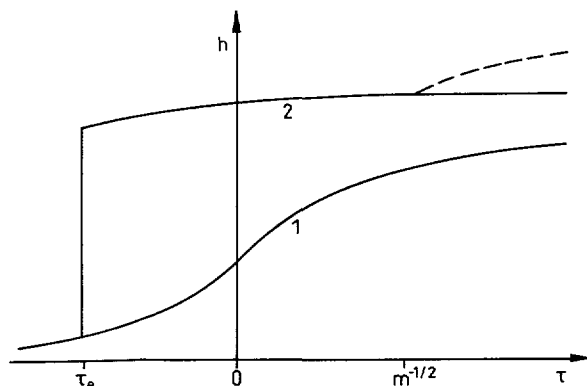


Fig. 2. — The dependences of layer thickness,  $h$ , (arbitrary units) on  $\tau = (T - \theta)/T$  for the cases of uncharged (1) and polyelectrolyte (2) grafted chains.

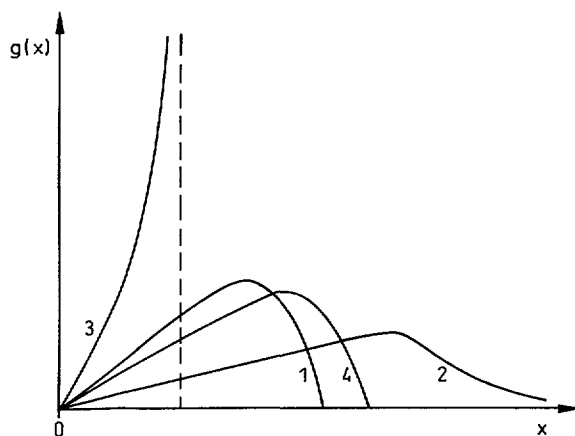


Fig. 3. — Distribution functions,  $g(x)$ , of free chain ends under the same conditions as in figure 1.

2. The « polyelectrolyte » regime takes place at  $w^{1/2}(a^2/\sigma) m \ll 1$ . In this regime the layer is strongly swollen by the osmotic pressure of counterions not only above, but also below the  $\theta$ -point. In this swollen state the contribution of volume interactions is unessential and the layer thickness is almost independent (with the accuracy of scaling corrections, see below) of

the solvent strength. However, below the  $\theta$ -point, at  $\tau \cong \tau_e \cong -m^{-1/2}w^{1/2}$  a jump-wise decrease in the layer dimensions occurs : the layer passes into the collapsed (globular) state described above (Fig. 2, curve 2).

In order to obtain the density profile in a swollen polyelectrolyte layer ( $\tau \geq \tau_e$ ) confined in a slit of width  $H$  we can retain only the last term in equation (3) which is responsible for the counterions entropy. Using equation (8) we have :

$$\varphi(x) = \varphi_0(H) \exp(-x^2/h^2) \quad (9)$$

where

$$h = (8/(3\pi^2))^{1/2} Nam^{-1/2} \quad (10)$$

The near-surface density  $\varphi_0$  should be determined by equation (6) which gives :

$$\varphi_0(H) = 2\pi^{-1/2} Na^3/(\sigma h \operatorname{erf}(H/h)) \quad (11)$$

where

$$\operatorname{erf}(\xi) = (2/\pi^{1/2}) \int_0^\xi \exp(-t^2) dt$$

is the error-function.

The distribution function of free chain ends  $g(x)$  is obtained by the inversion of integral equation (4) with the use of equations (7), (9),

$$g(x) = \frac{2x}{h \operatorname{erf}(H/h) \pi^{1/2}} [\exp(-H^2/h^2)/(H^2 - x^2)^{1/2} + (\pi^{1/2}h) \exp(-x^2/h^2) \operatorname{erf}((H^2 - x^2)^{1/2}/h)] \quad (12)$$

Finally, the free energy of the compressed polyelectrolyte layer and the elastic force acting on the upper plane are

$$\Delta F/T = (N/m) \ln [(3\pi/m)^{1/2} (a^2/\sigma)/\operatorname{erf}(H/h)] \quad (13)$$

$$G/T = \partial \Delta F/\partial(H\sigma T) = [N/(h\sigma m)] (2\pi^{-1/2}) \exp(-H^2/h^2)/\operatorname{erf}(H/h) \cong \bar{\varphi}/m \quad (14)$$

(The last expression for the elastic force is valid at relatively strong compression,  $H \ll h$ , and is equal to the osmotic pressure of counterions ; the same asymptotics was obtained by Pincus [12]).

As it follows from equation (13) the free energy  $\Delta F$  and the elastic force monotonically decrease and the latter tends to zero with  $H$ . On the other hand, the unit density in a layer exponentially decreases with  $x$ , equation (9), with the characteristic scale  $h$  given by equation (10). This means that  $h$  is the only characteristic scale in the free layer. Note, that with the accuracy of the numerical coefficient it coincides with that obtained in [12, 13] by much more simple procedure.

The density profile and free ends distribution function in the free layer may be obtained by substituting  $H = \infty$  in equations (10), (11), (12) :

$$\varphi(x) = \varphi_0 \exp(-x^2/h^2) \quad (15)$$

$$\varphi_0 = 2\pi^{-1/2} Na^3/(\sigma h) \quad (16)$$

$$g(x) = 2(x/h^2) \exp(-x^2/h^2) \quad (17)$$

Note that formally the maximal  $x$  and  $H$  value as the highest position of grafted chain end should be equal to  $Na$ . However, the condition (1) of weak charging of grafted chains provides  $Na/h \gg 1$ , so that a very small fraction of grafted chains reaches the height of  $\cong Na$  and the integration up to  $\infty$  in equations (11), (12) in the case of the free layer is valid.

Curves 2 in the figures 1 and 3 illustrate the density profile and free ends distribution in the swollen polyelectrolyte layer. In contrast to corresponding distributions in the swollen uncharged grafted polymer layer these functions dose not become equal to zero at any finite  $x$  value, but decrease exponentially that provides their normalization.

The decrease in the solvent strength does not lead to sufficient changes in layer dimensions and structure till  $\tau \geq \tau_e$ . However, at  $\tau \cong \tau_e$  the jump-wise collapse of the polyelectrolyte layer occurs and it is accompanied by an abrupt jump-wise changes in the shape of density profile and free ends distribution (the transition from curves 2 to curves 3 in Figs. 1, 3). This is in pronounced contrast to the gradual change of these distributions accompanying the collapse of uncharged grafted polymer layer. With the further decrease in the solvent strength the unit density in the layer increases and tends gradually to the step-function.

SCALING REGIME. — According to equations (10), (15)-(17) the dimensions and structure of swollen polyelectrolyte layer does not depend on the solvent strength,  $\tau$ , at  $\tau \geq \tau_e$ . This independence results from the neglecting of volume interactions on the background of counterions osmotic pressure and Gaussian character of chain stretching proposed above in equation (2). However, it is easy to see that at  $\tau \gg m^{-1/2}$  not inter-, but intra-chain interactions should be taken into account and the chain elasticity should be described not by Gaussian, but by Pincus [20] law :

$$\Delta F_{el}(x') \cong (x'/N)^{3/5} a \tau^{1/5} \quad (18)$$

According to equation (18) the chain elasticity decreases with increase in  $\tau$  that leads to an increase in chain stretching (Fig. 2). Combining expression (18) with the counterions osmotic pressure (from Eq. (3)) and neglecting the chain ends distribution we obtain for the characteristic layer thickness in this regime :

$$h(\tau) \cong Nam^{-2/5} \tau^{1/5} \quad (19)$$

(with the accuracy of numerical coefficient).

Although the direct calculation of the swollen layer structural characteristics taking into account the scaling expression (18) for chain elasticity can not be performed, a reliable description may be obtained using the following simple ideas.

As the layer structure is still determined by the competition between chains elasticity and counterions osmotic pressure, the density profile should have the form of asymptotically decreasing (exponential) function of the ratio  $(x/h(\tau))^\gamma$ . This density profile should provide a special form of self-consistent potential of osmotic pressure that in its turn should provide (combining with the elastic term) chain stretching fluctuations on the scale of  $h(\tau)$ . Under the condition of Gaussian stretching we had  $\gamma = 2$  and the self-consistent potential was of the parabolic shape (see also [21]). Hence, in the scaling region we should set  $\gamma = 5/2$ .

Thus, the density profile in the grafted polyelectrolyte layer at  $\tau \gg m^{-1/2}$  is given by :

$$\varphi(x) = \varphi_0(\tau) \exp[-(x/h(\tau))^{5/2}] \quad (20)$$

where

$$\varphi_0(\tau) = (5/2) Na^3 [\Gamma(2/5) h(\tau) \sigma] \quad (21)$$

is the near-surface concentration and  $\Gamma(\xi)$  in an ordinary gamma-function.



The equations (20), (21) obtained above with the aid of some semi-quantitative arguments can be justified by a rigorous consideration which takes into account non-uniform and non-Gaussian, equation (19), character of chain stretching in the grafted polyelectrolyte layer. This analysis makes it possible to obtain the corresponding chain ends normalized distribution which has the following form :

$$g(x) = (5/2) h(\tau)^{-5/2} x^{3/2} \exp[-(x/h(\tau))^{5/2}]. \quad (22)$$

Note that at  $x \ll h(\tau)$  equation (22) gives  $g(x) \approx x^{3/2}$  in contrast to the linear character of analogous distribution at small  $x$  in the case of Gaussian chain elasticity, equation (17).

## 2. Salt-added solution.

FREE ENERGY. — The addition of low molecular weight salt into the solution (an increase in the solvent strength) leads to an increase in the osmotic pressure in the bulk of solution thus preventing the swelling of the grafted polyelectrolyte layer. Obviously it does not affect the conformations of chains in the « quasineutral » layer swollen by volume interactions.

In order to consider the dependence of the dimensions and structure of the grafted polyelectrolyte layer on the concentration of added salt we suppose that simple 1 : 1 electrolyte is added so that its dimensionless concentration in the bulk of solution is equal to  $\phi_s$ . As the grafted layer contains its own counterions which are inhomogeneously distributed through the layer the concentration of salt  $\varphi_s$  in a layer should differ from  $\phi_s$  and also depend on  $x$ , so that  $\varphi_s(x) \leq \phi_s$ . The last term in equation (3) describing the translational entropy of all mobile ions in the layer and only significant in this regime may be presented as

$$f[\varphi(x), \varphi_s(x)] = (\varphi(x)/m + \varphi_s(x)) \ln (\varphi(x)/m + \varphi_s(x)) + \varphi_s(x) \ln \varphi_s(x). \quad (23)$$

The first term in equation (23) describes the translational entropy of all counterions (including salt ions) and the second term describes the entropy of co-ions of salt.

The minimization of the free energy functional with respect to functions  $E(x, x')$  and  $g(x)$  leads to the equation

$$\delta f[\varphi(x), \varphi_s(x)]/\delta \varphi(x) = \lambda - 3 \pi^2 x^2 / (8 N^2 a^2) \quad (24)$$

analogous to equation (8), where  $\lambda$  should be determined by the normalization condition (6). As we have now one more independent unknown function  $\varphi_s(x)$  we need one more equation which can be obtained from the condition of constancy of chemical potential of salt in the solution :

$$\delta f[\varphi(x), \varphi_s(x)]/\delta \varphi_s(x) = \mu_s^{\text{bulk}}(\phi_s) \quad (25)$$

where

$$\mu_s^{\text{bulk}}(\phi_s) = \partial [2 \phi_s \ln \phi_s] / \partial \phi_s \quad (26)$$

is the chemical potential of salt in the bulk of the solution.

Combining equations (23)-(26) we receive two equations for two unknown density profiles  $\varphi(x)$  and  $\varphi_s(x)$  :

$$\varphi(x)/m + \varphi_s(x) = C(H) \exp(-x^2/h^2) \quad (27)$$

$$\varphi_s(x)[\varphi(x)/m + \varphi_s(x)] = \phi_s^2 \quad (28)$$

where  $C(H)$  should be determined by the normalization condition (6) and the value of  $h$  is still given by equation (10). The value of  $H = h_s$  for the free (uncompressed) layer should

be determined by the condition of equality of osmotic pressure on the outer boundary of the layer to the osmotic pressure in the bulk of solution. However, the same result may be obtained from the condition of continuity of the profiles  $\varphi(x)$  and  $\varphi_s(x)$  at this boundary :

$$\varphi(h_s) = 0, \quad \varphi_s(h_s) = \phi_s. \quad (29)$$

(Note, that as it follows from equation (27) at any  $\phi_s \neq 0$  the density profile  $\varphi(x)$  should become equal to zero at some finite  $x = h_s$ ).

Hence, the concentration profiles of monomer units and salt in a free polyelectrolyte layer are given by

$$\varphi(x) = 2 m \phi_s \operatorname{sh} \left\{ (h_s^2 - x^2)/h^2 \right\} \quad (30)$$

$$\varphi_s(x) = \phi_s \exp[(x^2 - h_s^2)/h^2]. \quad (31)$$

Using normalization condition (6) and equation (30) the equation for the layer height,  $h_s$ , may be obtained :

$$iD(-ih_s/h) - D(h_s/h) = (Na^3/\sigma)(m\phi_s h)^{-1} \quad (32)$$

where

$$D(\xi) = \exp(-\xi^2) \int_0^\xi \exp(t^2) dt$$

is the Dawson integral and  $i = \sqrt{-1}$ .

The distribution of free chain ends in a layer has the form :

$$g(x) = (8/\pi)(2m/3)^{1/2} (\sigma\phi_s/a^2) \{iD[-i(h_s^2 - x^2)^{1/2}/h] + D[(h_s^2 - x^2)^{1/2}/h]\}. \quad (33)$$

As it follows from the equation (32) the height of the polyelectrolyte layer  $h_s$  monotonically decreases with salt concentration  $\phi_s$  and tends to infinity as  $h_s \equiv h(\ln(1/\phi_s))^{1/2}$  at  $\phi_s \rightarrow 0$ .

If the layer is sufficiently strongly compressed by the osmotic pressure of added salt, i.e.  $h_s \ll h$ , the equations (30)-(32) may be expanded by the powers of  $(h_s/h)$  that gives power asymptotic dependence for the layer thickness

$$h_s \cong 2^{1/3} Na(a^2/\sigma)^{1/3} m^{-2/3} \phi_s^{-1/3} \quad (34)$$

which coincides with the accuracy of numerical coefficient with that obtained in [12, 14] and asymptotic profiles

$$\varphi(x) \cong (3/2) \bar{\varphi} (1 - x^2/h_s^2) \quad (35)$$

$$g(x) \cong (3x/h_s^2)(1 - x^2/h_s^2)^{1/2} \quad (36)$$

$$\varphi_s(x) \cong \phi_s [1 + (x^2 - h_s^2)/h^2] \quad (37)$$

where the mean unit density in the layer

$$\bar{\varphi} = (Na^2/\sigma h_s) \cong (a^2/\sigma)^{2/3} m^{2/3} \phi_s^{1/3} \quad (38)$$

These asymptotic expressions are valid at  $h_s \ll h$ , or  $\phi_s \gg \sigma^{-1} m^{-1/2}$ . This condition can be also written as  $\phi_s \gg Na^3/(m\sigma h)$  i.e. the salt concentration in the bulk of solution exceeds the counterions concentration in a free layer greatly.

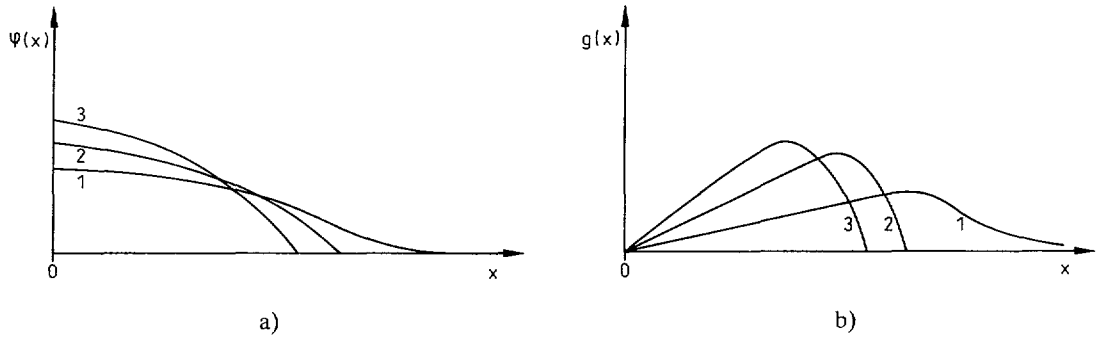


Fig. 4. — Schematic variation of profiles of monomer units (a) and free chain ends (b) with the increase of salt concentration :  $\phi_s = 0$  (1)  $\phi_s = c_1 \geq 0$  (2) and  $\phi_s = c_2 \geq c_1$  (3).

Note, that expressions (34)-(38) may be obtained directly by expanding of free energy, equation (23), in powers of  $\varphi(x)/(m\phi_s)$  at  $\varphi_s \equiv \phi_s$ . If this expansion is restricted by the terms  $\approx \varphi(x)^2$ , the total contribution of the osmotic pressures of counterions and salt ions in the free energy of the layer under the condition of salt dominance may be described by the effective pair interunit interaction with an effective second virial coefficient  $v_{\text{eff}} = (m^2 \phi_s)^{-1}$ . This makes clear the parabolic density profile (35) and the form of  $g(x)$  dependence, equation (36).

Note, that according to equations (32), (34) the thickness of the layer in the presence of salt increases with the grafting density while in the salt-free regime the thickness of swollen polyelectrolyte layer is independent of  $\sigma$ , equation (10).

Thus under the conditions  $h_s \ll h$ , i.e. at salt dominance, the monomer density profile in a layer, equation (35), and free ends distribution, equation (36), acquire the same shape as in the layer swollen by repulsive binary interaction. However, the layer dimension  $h_s$  in this regime is still determined by the linear charge density on the chains and salt concentration. It is independent of  $\tau$  and exceeds greatly the dimensions of the uncharged layer, equation (34). At very high salt concentration (dependent on  $\tau$  and  $\sigma$ ) the layer structure and dimensions tends to that of uncharged layer.

Thus the increase in the salt concentration in the bulk of the solution leads to monotonic and continuous decrease in the dimensions of swollen polyelectrolyte layer and to gradual changes in the layer structure. This is in pronounced contrast to jump-wise collapse of polyelectrolyte layer caused by the decrease in the solvent strength.

The increase in the ionic strength of the solution affects also the character and the point of the transition related to the collapse of the layer caused by the decrease in the solvent strength.

The analysis shows that at comparatively low salt concentrations,  $\phi_s \ll m^{-3/2} w^{1/2}$ , this transition retains its jump-wise character just as in the salt-free solution (Fig. 5, curves 1, 2). An increase in the salt concentration leads to the decrease in the value of this jump and to the shift of the transition point,  $\tau \approx -w^{1/2}(\sigma m^2 \phi_s)^{-1/3}$ , towards the  $\theta$ -point. (Note, that at  $\sigma^{-1} m^{-1/2} \ll \phi_s \ll m^{-3/2} w^{1/2}$  the salt dominance takes place only in the swollen state, but not in the collapsed layer.) Further increase in the salt concentration results in disappearance of the jump in the layer thickness. In the range of  $m^{-3/2} w^{1/2} \ll \phi_s \ll m^{-2} \sigma^{1/2} w^{-3/4}$  the transition from the partially swollen, equation (34), to the collapsed state caused by the decrease in the solvent strength occurs smoothly in the range of  $\tau \approx -v_{\text{eff}} \approx -(m^2 \phi_s)^{-1}$  (Fig. 5, curve 3).

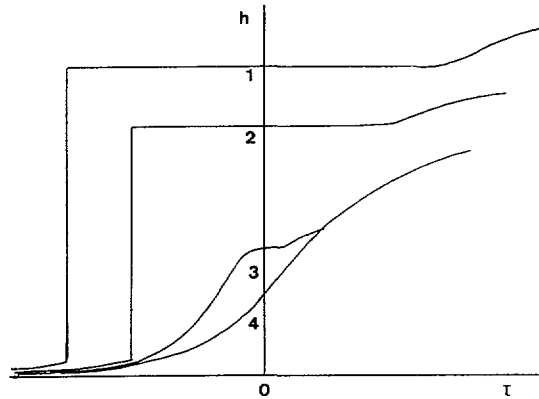


Fig. 5. — Schematic variation of  $\tau$ -dependence of the polyelectrolyte layer thickness with the increase in the salt concentration:  $\phi_s = 0$ ; (1)  $\phi_s \ll m^{-3/2} w^{1/2}$ ; (2)  $m^{-3/2} w^{1/2} \ll \phi_s \ll m^{-2} \sigma^{1/2} w^{-3/4}$ ; (3)  $\phi_s \gg m^{-2} \sigma^{1/2} w^{-3/4}$  (4)

At higher salt concentration,  $\phi_s \gg m^{-2} \sigma^{1/2} w^{-3/4}$  the polyelectrolyte effects are suppressed in the whole range of the solvent strength and the collapse of the layer occurs just as in the quasineutral regime (Fig. 5, curve 4).

SCALING REGIME. — Using the arguments analogous to that used in the part I for the description of the scaling regime of swelling of grafted polyelectrolyte layer we can propose some relations describing the collapse of this layer caused by the increase in the ionic strength of the solution. Hence, monomer and salt concentration profiles in the layer at  $\tau \gg (\sigma m^2 \phi_s)^{-1/3}$  are given by

$$\varphi(x) = 2 m \phi_s \operatorname{sh} [(h_s^{5/2} - x^{5/2})/h(\tau)^{5/2}] \quad (39)$$

$$\varphi_s(x) = m \phi_s \exp [(h_s^{5/2} - x^{5/2})/h(\tau)^{5/2}] \quad (40)$$

where  $h(\tau)$  is the characteristic thickness of the layer at  $\phi_s = 0$ , equation (19).

The power asymptotic dependence of the layer thickness under the condition of salt dominance has the form

$$h_s \cong N a (a^2 / \sigma)^{2/7} m^{-4/7} \phi_s^{-2/7} \tau^{1/7} \quad (41)$$

### Discussion.

Using the combination of the SCF-approach and the local electroneutrality approximation we have obtained analytical expressions for density profiles, free chain ends distributions and characteristic dimensions of the grafted polyelectrolyte layer in the whole range of the solvent strength and the ionic strength of the solution, including salt-free regime. The extension of the SCF-method to the scaling range made it possible to take into account the non-Gaussian elasticity of the stretched chains at high values of  $\tau$ .

It is shown that under the conditions of salt dominance the density profiles in the swollen polyelectrolyte layer are of parabolic type. The characteristic layer thickness in this regime is determined by the grafting density, the linear charge density on the chains and the ionic strength of the solution. The decrease in the salt concentration leads to the increase in the layer thickness and the density profile tends (at  $\phi_s \cong 0$ ) to the Gaussian curve.

The density profiles in the grafted polyelectrolyte layer immersed into the solution of non-zero ionic strength have been obtained previously in references [15, 16] on the basis of SCF-approach combined with numerical solution of Poisson-Boltzmann equation. A very good coincidence of these numerical and our analytical results in the range of the high salt concentration is not surprising, because the local electroneutrality approximation used above should be valid in this range. The calculation for the case of sufficiently low ionic strength has been performed in [16] and the resulting density profiles tend to the Gaussian curves (Fig. 2 in Ref. [16]). This result justifies the validity of our approach at low and zero ionic strength of the solution.

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*Proofs not corrected by the authors*