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Collapse of grafted polyelectrolyte layer

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Abstract. — The theory describing chain conformation in a planar layer of grafted polyelectrolyte (polyampholyte) molecules and the conformational transition related to the collapse of this layer caused by the decrease in solvent strength is developed. Depending on the values of the layer parameters (grafting and charge densities) this transition may occur as a continuous (cooperative) or as a first order phase transition.

The layers of uncharged polymer chains grafted at one end onto impermeable surface and immersed (or not) in a solvent were the objects of intensive theoretical investigations during the last decade [1-12]. The interest to these systems was initiated primarily by many practical applications: the layers of grafted polymer chains used to be the model of superstructures formed by block-copolymers in the strong segregation limit, the grafting (or the adsorption at the anchor end) of the polymer molecules can be used for the sterical stabilization and flocculation of colloidal dispersions, etc.

At the same time the grafted polymer layers appeared to be very interesting in the theoretical aspect. It was shown in a number of papers [1-6] that under the conditions of strong overlapping the chains in the layers are always stretched in the direction normal to the grafting surface, so that their dimension in this direction scales with N as the dimensions of the free chain in the d -dimensional space, where $d = 3 - d_M$ and d_M is the effective dimension of the matrix ($d_M = 2, 1; 0$ and $d = 1; 2; 3$ for the chains grafted onto the planar, cylindrical and spherical surface, respectively). This effective reduction of the grafted chain dimensionality is manifested in the character of the collapse of the layer caused by the decrease of the solvent strength.

As is known [13-14] for an individual chain, this collapse (coil-globe transition) occurs as the second-order phase transition (the first-order phase transition for the stiff chains). In the layers of the chains grafted onto the spherical or cylindrical matrices (an effective dimensionality $d = 3$ and 2 respectively) the transition becomes broader than in an isolated macromolecule, but retains its phase character. In contrast to this, the collapse of the layer of the chains grafted onto a planar surface (effectively one-dimensional chains) occurs as a non-phase conformational transition accompanied by a smooth decrease of the layer height and an exclusion of the solvent from the layer [6, 12]. To prevent any misunderstanding, we should note that the alternative result obtained by Halperin [15] (the possibility of the first-order

phase transition accompanied by the jumpwise change of the dimensions in the planar layer) appeared to be an artifact and was caused by the use of the incorrect expression of the elastic free energy of the compressed chains (see [12] for the discussion).

All the results obtained previously referred to the layers of uncharged grafted polymer chains. We will start the theoretical analysis of the grafted polyelectrolyte layers by the present paper (some results concerning the structure and interaction of these layers were recently obtained by Pincus [16], the corresponding numerical calculations were performed in [17, 18]).

Up to the present time a sufficient progress was achieved in the theoretical investigation of such condensed polymer systems as polyelectrolyte networks. In a series of papers by Khokhlov *et al.* [19, 20] the chain conformations and the conformation transitions in polyelectrolyte networks were investigated. As was shown, the collapse of « dilute » networks caused by the decrease in the solvent strength occurs as the first order phase transition.

The purpose of the present paper is the investigation of the collapse of the layer of polyelectrolyte chains grafted onto a planar surface caused by the decrease in the solvent strength. The dependence of the character of this conformational transition on the main parameters of the system (grafting and charge densities) and the scaling relations for layer dimensions in different regimes will be analyzed.

Model.

Let us consider a layer formed by long ($N \gg 1$) polyelectrolyte (polyampholyte) 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 nonelectrostatic 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 θ -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 τ , whereas the latter is approximately independent of temperature (solvent strength), $w \cong \text{const}(\tau)$. Let every m -th unit of each chain carries positively or negatively charging group, so that the total number of charging groups in the chain is N/m . Let $m' \geq m$ be the mean distance along the chain between uncompensated charges of the same sign, so that the total charge of the macromolecule is $Q = Ne/m'$. We have $Q = 0$, $m' \cong \infty$ in the isoelectric case and $m' \cong m$ for « pure » polyelectrolytes, when the chains carry the groups of one sign. We will restrict our consideration by weakly charged polyelectrolytes, for which

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

where ϵ is the dielectric constant of the solvent. In this case the intrachain Coulomb interactions do not lead to the changes of chain stiffness [21].

We will 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 $S \cong N/m'$ mobile counterions (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 [22]. Under the condition $\kappa H \gg 1$, where $1/\kappa$ is the Debye screening length in a layer and H is the layer thickness, all counterions are located in a layer. In our consideration we will assume this condition to be fulfilled.

Free energy.

For the analysis of the conformations of grafted polyelectrolyte chains in a layer we will use the standard approach based on the minimization of free energy which is presented as a sum of terms of different physical origin.

$$\Delta F = \Delta F_{\text{def}} + \Delta F_{\text{conc}} + \Delta F_{\text{m}} + \Delta F_{\text{corr}} \quad (2)$$

We will restrict ourselves by the simplest approximation in which these terms are expressed as functions of the total layer thickness, H , only. (A precise analysis of a planar layer of uncharged grafted chains shows [11, 12] that this approximation allow to obtain all scaling dependences of layer characteristics on its parameters and to analyze the character of the transition related to the layer collapse). The dependences of the terms in equation (2) on H (through the swelling coefficient with respect to the chain Gaussian dimensions $\alpha = H/N^{1/2}a$ or through the mean unit density in a layer $\varphi = Na^3/(\sigma H)$) have the following forms (per chain) :

— elastic (conformational) term

$$\Delta F_{\text{def}} \cong \begin{cases} \alpha^2 - \ln \alpha^2, & \alpha \geq 1 \\ \alpha^{-2} + \ln \alpha^2, & \alpha \leq 1 \end{cases} \quad (3)$$

— free energy of volume interactions

$$\Delta F_{\text{conc}} \cong Nv\varphi + Nw\varphi^2 \quad (4)$$

— translational entropy of mobile counterions

$$\Delta F_{\text{m}} \cong S \ln (\varphi/m') \quad (5)$$

— electrostatic (correlation) term, related to the correlations of local charge density

$$\Delta F_{\text{corr}} \cong -N(u/m)^{3/2} \varphi^{1/2} \quad (6)$$

Here and below all numerical coefficients are omitted and all energetic values are expressed in kT units.

Note that the correlation (electrostatic) contribution ΔF_{corr} , equation (6), is written in the Debye-Huckel approximation, i.e. as for weakly unideal plasma [23] In the most typical cases $u \cong 1$ and this approximation is valid for the solutions of weakly charged ($m \geq 1$) polyelectrolytes in a wide range of concentrations $\varphi \leq 1$.

Equation for swelling coefficient.

The minimization of the free energy, equations (2)-(6), with respect to α (or φ) leads to the equation for the equilibrium layer thickness. This equation may be presented in the following form :

$$\begin{aligned} \alpha^3 - (S+1)\alpha + G\alpha^{1/2} &= B\tau + C/\alpha, \quad \alpha \geq 1 \\ -\alpha^{-1} - (S-1)\alpha + G\alpha^{1/2} &= B\tau + C/\alpha, \quad \alpha \leq 1 \end{aligned} \quad (7)$$

where

$$B \cong v_0 N^{3/2} a^2 / \sigma \quad (8.1)$$

$$C \cong w N^2 (a^2 / \sigma)^2 \quad (8.2)$$

are the renormalized parameters of pair and ternary nonelectrostatic interactions in a layer, respectively, and

$$G \cong N^{5/4}(u/m)^{3/2} (a^2/\sigma)^{1/2} \quad (9)$$

is the renormalized parameter of electrostatic interactions.

Collapse of the layer.

At $S, G = 0$ equations (7) describe the dependence of the thickness of uncharged grafted layer on τ and give the following scaling asymptotes for it.

$$H \cong \begin{cases} Na(v_0 \tau a^2/\sigma)^{1/3}, & \tau \gg |\tau^*| \\ Na(w^{1/2} a^2/\sigma)^{1/2}, & |\tau| \ll |\tau^*| \\ Na(wa^2/(v_0 |\tau| \sigma)), & \tau \ll \tau^* \end{cases} \quad (10.1)$$

$$(10.2)$$

$$(10.3)$$

in the regions of strong, θ - and poor solvent, respectively (comp [5, 6]). The temperatures

$$\pm \tau^* \cong \mp C^{3/4}/B = \mp (w^{3/4}/v_0)(a^2/\sigma)^{1/2} \quad (11)$$

correspond to the crossover between different regions. The decrease in τ leads to the continuous (without a jump) decrease in the layer thickness, the transition of the layer into a collapsed (globular) state is not of the phase character (see [6, 12] for details).

In the general case of a grafted polyelectrolyte layer, the analysis of equations (7) shows that the character of the dependence of the equilibrium layer thickness H (swelling coefficient α) on the solvent strength, τ , is determined by the relation between the parameters C, S and G and three different regimes of the layer behavior can be distinguished.

1) *The regime of « uncharged » layer* $C \gg S^2, G^{8/5}$ — In this case the polyelectrolyte effects in a layer are weak comparing with strong volume interactions. The thickness of the layer is given by equations (10), (11). The collapse of the layer with decrease in τ occurs smoothly just as the collapse of the layer of grafted uncharged chains (Fig. 1, curve 1). It's easy to see that the condition $C \gg S^2$ means that under the conditions of strong and θ -solvent there is less than one mobile ion (or one uncompensated charge) per one blob [1, 2, 5] of the stretched chain in a layer.

2) *The « polyelectrolyte » regime* $C \ll S^2, G \ll S^{3/4} C^{1/4} (m' \ll m^2)$ — In this case the equilibrium layer dimensions under the conditions of strong and θ -solvent are determined by the competition between the translational entropy of mobile counterions (Eq (5)) and the

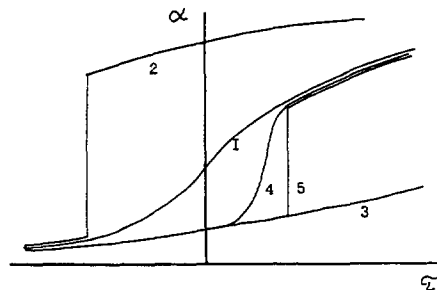


Fig. 1 — Different types of dependence of the swelling coefficient, α , of the grafted polyelectrolyte (polyampholyte) layer on the solvent strength, τ (all comments to the curves are in the text)

elastic free energy of chain stretching (Eq. (3)) and slightly decrease with the decreasing in the solvent strength

$$H \cong Nam'^{-1/2} \quad (12)$$

i.e. the polyelectrolyte effects predominate over the volume interactions. This situation retains in the range of $\tau^{\text{el}} \leq \tau \leq 0$ where

$$\tau^{\text{el}} \cong -S^{1/2} C^{1/2} / B \cong -m'^{-1/2} w^{1/2}. \quad (13)$$

Note that the condition $C \ll S^2$ provides $\tau^{\text{el}} \ll \tau^*$. At the point $\tau = \tau^{\text{el}}$, the attractive pair interactions become strong enough to compete with counterion entropy and the layer thickness suffers a jumpwise decrease up to the value of the thickness of uncharged layer at the same τ (Fig. 1, curve 2)

3) *Isoelectric regime*. $C \ll G^{8/5}$, $G \gg S^{3/4} C^{1/4} (m^2 \ll m')$. — In this case the number of oppositely charged groups in the chains is large and their attraction (correlation term, Eq. (6)) gives a sufficient contribution in the total free energy of the layer. If $m' \gg m^3$, this electrostatic attraction results in the collapsed state of the layer even under the conditions of strong solvent (Fig. 1, curve 3), where the layer dimensions are determined by the competition between electrostatic attraction and pair repulsive volume interactions:

$$H \cong Na(v_0 \tau)^2 (m/u)^3 (a^2/\sigma) \quad (14)$$

In the intermediate case, $m^2 \ll m' \ll m^3$, under the conditions of a strong solvent the layer is in a swollen state, equation (10.1), but the decrease in τ leads to the collapse of the layer into the state described above (Eq (14)) This transition occurs smoothly at $\tau \cong m^{-9/5} (\sigma/\alpha^2)^{2/5}$ if $G \gg S^{5/4}$ or with a jump in layer thickness at $\tau \cong m'/m^3$ if $G \ll S^{5/4}$ (Fig. 1, curves 4, 5, respectively).

The further decrease in the solvent strength, τ , transforms the system into the θ -conditions, where the layer thickness is determined by the competition between repulsive ternary volume interactions and electrostatic attraction

$$H \cong Naw^{2/3} (m/u) (a^2/\sigma). \quad (15)$$

The θ -region occupies the range of $\tau_i^* \ll \tau \ll |\tau_i^*|$, where

$$\tau_i^* \cong -m^{-1} w^{1/3} \quad (16)$$

(Note, that at $C \ll S^2$, $m^2 \ll m'$ we have $|\tau_i^*| \gg |\tau^*|$).

At $\tau \ll \tau_i^*$ the layer passes into the ordinary globular state, equation (10 3)

Discussion.

The jumpwise dependence of the dimensions of the planar layer of grafted polyelectrolyte chains on the solvent strength in contrast to that of the layer of uncharged polymer chains indicates that the collapse of the planar grafted polyelectrolyte layer may occur as the first order phase transition. This result is not surprising, because the translational entropy of mobile counterions, which is responsible for this effect, contributes an affective long-range interaction into the system.

The main relationships of the collapse of grafted polyelectrolyte layer coincide with that of the collapse of polyelectrolyte networks [19, 20]. The main difference is the appearance of the

regime in which strong volume interactions in densely grafted layer dominate over all polyelectrolyte effects

Note that, as was shown above, the layer of strongly charged and moderately densely grafted polyelectrolyte chains remains in a swollen state far below the θ -point. This is why this kind of protecting layers provides a sterical stabilization of colloidal particles below the θ -point in contrast to stabilizing layers of uncharged chains [24]

Note added in proof

Recently Y. Rabin and S. Alexander (*Europhys Lett.* **13** (1990) 49) have shown that if the chains in the layer are stretched by the external force the chain elasticity must be described by the Pincus law ($\Delta F_{el} \cong (H/(N^{3/5} a \tau^{1/5}))^{5/2}$) i.e. differs from that of Gaussian chains. An analogous situation takes place in the « polyelectrolyte » regime when the osmotic pressure of counterions acts as an external stretching force. Analysis shows that if we take this effect into account the factor $m'^{-1/2}$ in equation (12) obtained in the mean field approximation should be replaced by the scaling factor $m'^{-2/5} \tau^{1/5}$ at $\tau \gg m'^{-1/2}$.

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