PHYSICAL REVIEW E, VOLUME 63, 051802

Polyampholyte adsorption on a charged sphere

Andrey V. Dobrynin
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599-3290

(Received 6 November 2000; revised manuscript received 24 January 2001; published 16 April 2001)

A theory of the adsorption of polyampholyte chains on a charged spherical particle is developed. It is shown that the equilibrium polymer density profile near an adsorbing particle may be found by balancing the polarization-induced attraction of polyampholytes to the charged spherical particle with the monomer-monomer repulsion. At intermediate values of the particle charge, the polyampholyte chains touching the surface of the particle form a self-similar flowerlike structure. The structure of an adsorbed polyampholyte in the flowerlike conformation is similar to that of a neutral star polymer.

DOI: 10.1103/PhysRevE.63.051802 PACS number(s): 61.25.Hq, 61.20.Qg

Polyampholytes are charged polymers carrying both positively and negatively charged monomers. In solution these polymers may be anionic, cationic, or neutral (without net electric charge), depending on the pH. Interest in this type of polymeric system is stimulated by their central role in a diverse number of fields ranging from materials science and colloids to the physics of disordered systems and biophysics. The advances in our understanding of these complicated polymeric systems have led to applications in colloid stabilization, wetting, adhesion, and lubrication. In fact, the stabilizing properties of polyampholytes were recognized more than 150 years ago by Faraday. He used gelatin—a polypeptide copolymer (protein) consisting of both basic and acidic amino acid groups—to stabilize gold colloidal particles [1]. At the beginning of the 20th century, this property of gelatin was successfully used by the photographic industry to stabilize silver bromide sols [2,3].

One of the most interesting features of polyampholytes is their polarizability in external electric fields. The electric field pulls oppositely charged monomers in opposite directions, polarizing the chain. However, the redistribution of the charged monomers inside the polymer coil is opposed by the chain elasticity. As a result of these conflicting forces the polyampholyte chain is stretched into a ''tug of war'' configuration [4]. It has recently been established that the polarization of polyampholyte chains is responsible for adsorption of these polymers on charged surfaces, resulting in formation of multiple protective polymer layers. Even neutral polyampholytes with equal numbers of positively and negatively charged monomers are able to adsorb on a charged surface due to a polarization-induced attractive interaction [5–9]. However, theoretical studies of polyampholyte adsorption have been limited to the cases of single chain adsorption [5–7,9] or multichain adsorption on a planar surface [8]. In this paper I study the adsorption of polyampholytes from a salt-free solution on a charged spherical particle, which mimics the formation of the protective polymeric layer near charged colloids.

Consider symmetric polyampholyte chains of degree of polymerization N with equal fractions of positively $f_+ = f/2$ and negatively $f_- = f/2$ charged monomers in a θ solvent with dielectric constant ε. In order for a polyampholyte chain of size R_{ch} to be soluble the fluctuation-induced attractive interactions between charged monomers should be less than the thermal energy kT, where T is the absolute temperature and k is the Boltzmann constant. This attraction is of the order of the thermal energy kT per Debye volume r_D^3, where $r_D \approx (l_B N f / R_{ch}^3)^{-1/2}$ ($l_B = e^2/\varepsilon kT$ is the Bjerrum length). If there are many Debye volumes per chain ($r_D \ll R_{ch}$), the attraction is strong and a polyampholyte with equal numbers of Nf_+ positively charged and Nf_- negatively charged monomers forms a compact globule [10,11] and precipitates from solution. But if the Debye radius is larger than the chain size ($r_D > R_{ch}$), the attraction is weak and the chain remains almost unperturbed. The condition $r_D > R_0$ for a Gaussian chain of radius $R_0 \approx a N^{1/2}$ can be written in terms of the fraction of charged groups f,

$$f < f_{weak} \approx a / l_B \sqrt{N}, \tag{1}$$

where a is the bond length.

Weakly charged polyampholyte chains ($f < f_{weak}$) placed near a charged spherical particle of radius R and charge eQ are polarized by the nonuniform electric field created by the particle and forced into elongated configurations. The polarization energy of a polyampholyte chain with the center of mass located at the distance r from the center of the particle and having excess of eq positive and negative charges in two halves of a chain separated along the direction of the radius vector r by distance $L(r)$ (see Fig. 1) is

$$\frac{W_{pol}^{ch}(r)}{kT} \approx -\frac{l_B Q q}{r^2} L(r) \quad \text{for} \quad L(r) \leqslant r. \tag{2}$$

If the positions of the charged monomers along the polymer chains are uncorrelated, the typical excess charge eq in two parts of a chain is of the order of $e\sqrt{fN}$. The balance of the polarization energy of the chain (2) with its elastic energy $kTL(r)^2/a^2N$ gives the average value of the distance $L(r)$ as a function of the distance from the particle,

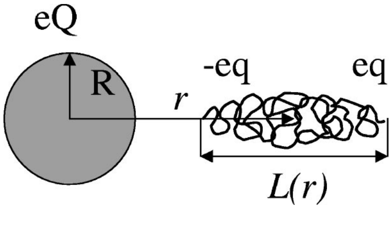

FIG. 1. Schematic sketch of a polyampholyte chain near a charged spherical particle.

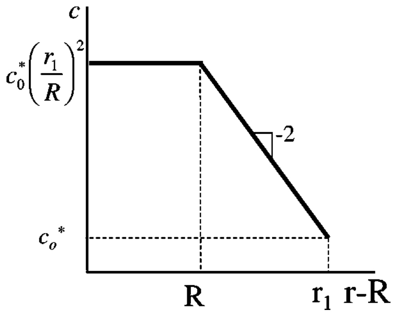

FIG. 2. Polymer density profile in the adsorbed layers for $Q < Q_2$. Logarithmic scales.

$$L(r) \approx \frac{a^2 l_B Q q N}{r^2} \approx \frac{l_B Q R_0^2 \sqrt{fN}}{r^2} \approx R_0 \left(\frac{r_1}{r}\right)^2. \tag{3}$$

The deformation of the chain from its Gaussian shape begins at distances r smaller than the crossover distance $r_1 \approx (l_B Q R_0 \sqrt{fN})^{1/2}$. At larger distances ($r \gg r_1$) the chain keeps its Gaussian shape. Substituting the expression for $L(r)$ given by Eq. (3) back into the expression (2) one obtains the polarization energy of a polyampholyte chain,

$$\frac{W_{pol}^{ch}(r)}{kT} \approx -\frac{(l_B Q R_0 \sqrt{fN})^2}{r^4} \approx -\left(\frac{r_1}{r}\right)^4. \tag{4}$$

Above the overlap concentration in the adsorbed layer, the polarization-induced attractive interaction (4) between the polymer chains and the charged sphere is stabilized by the repulsive interactions between monomers. In a θ solvent for the polymer backbone these repulsive interactions are due to three-body contacts. Thus, the equilibrium density profile $c(r)$ near the charged spherical particle can be obtained by balancing the polarization-induced attraction Eq. (4) with the three-body repulsion $kTNa^6c^2(r)$,

$$c(r) \approx c_0^* \left(\frac{r_1}{r}\right)^2 \approx c_0^* \frac{l_B Q R_0 \sqrt{fN}}{r^2} \quad \text{for} \quad r < r_1, \tag{5}$$

where $c_0^* \approx a^{-3} N^{-1/2}$ is the overlap concentration. At length scales $r < r_1$ the polymer chains form a semidilute polymer solution with polymer density inversely proportional to the square of the distance r from the center of the charged sphere. This polymer density profile $c(r)$ has stronger distance dependence than that in the case of polyampholyte adsorption on a charged planar surface, where it decays hyperbolically with distance [8]. The crossover from the semidilute to the dilute regime of the adsorbed chains occurs at the distance $r \approx r_1$ where the polarization energy (4) of a polyampholyte chain becomes of the order of the thermal energy kT. Therefore, one can consider r_1 to be the thickness of the adsorbed polymer layer. The polymer density profile near the charged spherical particle is shown in Fig. 2.

Integration of the polymer density profile through the layer thickness r_1 gives the amount of adsorbed polymers,

$$\Gamma \approx a^{-2} (l_B Q \sqrt{fN})^{3/2} R_0^{1/2}. \tag{6}$$

There will be more than one chain in this adsorbed layer for values of the charge Q larger than $a/l_B f^{1/2}$.

As the charge Q on the particle increases the size of the chain $L \approx l_B Q R_0^2 \sqrt{fN}/R^2$ near the surface of the particle $r \approx R$ increases as well. It becomes of the order of the particle size at a value of the charge Q of the order of

$$Q_2 \approx \frac{R^3}{a^2 l_B f^{1/2} N^{3/2}}. \tag{7}$$

At higher values of the charge ($Q > Q_2$) the adsorbed layer near the particle surface can be viewed as a brush of polydisperse loops.

To describe this polydisperse brush I will use the strong stretching approximation [12,13] and assume that all loops with $2g$ monomers and given charge distribution $\{q(t)\}$ are stretched in the same way. This means that all the middle points of these loops are located at the same distance $r_g(g)$ from the center of the particle—the Alexander–de Gennes approximation for the polydisperse brush. The total free energy of a loop includes three terms,

$$F_g = F_{elast}^g + W_{pol}^g + W_{rep}^g. \tag{8}$$

The elastic energy F_{elast}^g of a loop is

$$\frac{F_{elast}^g}{kT} \approx \frac{1}{2a^2} \int_0^g \left(\frac{dr_g(t)}{dt}\right)^2 dt. \tag{9}$$

The electrostatic energy of a loop with $2g$ monomers with charge distribution $\{q(t)\}$ in the hyperbolic electrostatic potential of a charged sphere is

$$W_{pol}^g(\{q(t)\}) \approx kT \int_0^g q(t) \frac{l_B Q}{r_g(t)} dt. \tag{10}$$

The monomers in the loops also interact with each other through short range excluded volume interactions. In the mean-field approximation these interactions can be approximated by the effective external potential $h(r)$ whose dependence on the distance r has to be found self-consistently. The contribution to the loop free energy due to short range interactions W_{rep}^g is

$$W_{rep}^g \approx kT \int_0^g h(r_g(t)) dt. \tag{11}$$

After combining all three terms (elastic, electrostatic, and excluded volume) the total free energy of a loop with given charge distribution $\{q(t)\}$ has the form

$$\frac{F_g}{kT} \approx \frac{1}{2a^2} \int_0^g \left(\frac{dr_g(t)}{dt}\right)^2 dt + \int_0^g q(t) \frac{l_B Q}{r_g(t)} dt + \int_0^g h(r_g(t)) dt. \tag{12}$$

In the strong stretching approximation the trajectory of the polymer chain is determined by the classical path of the functional (12),

$$a^{-2}\frac{d^2 r_g(t)}{dt^2} = -q(t)\frac{l_B Q}{r_g^2(t)} + \frac{dh(r_g(t))}{dr} \tag{13}$$

with the boundary conditions $r_g(0)=R$ and $dr_g(g)/dt=0$, which correspond to zero tension at the middle of the loop with given charge distribution $\{q(t)\}$. I will assume that the charges in a loop are randomly distributed with average value $\langle q(t)\rangle=0$ and δ-functional correlations $\langle q(t)q(t')\rangle = f\delta(t-t')$.

Equation (13) is a second order differential equation with Gaussian random noise $q(t)$. To solve this equation I will represent $r_g(t)$ as the sum of its average value $\langle r_g(t)\rangle$ and the fluctuation with respect to it, $\delta r_g(t)$. In terms of these new variables Eq. (13) can be rewritten as a system of coupled second order differential equations,

$$a^{-2}\frac{d^2\langle r_g(t)\rangle}{dt^2} \approx \langle q(t)\,\delta r_g(t)\rangle \frac{2 l_B Q}{\langle r_g(t)\rangle^3} + \frac{dh(\langle r_g(t)\rangle)}{dr}, \tag{14}$$

$$a^{-2}\frac{d^2\,\delta r_g(t)}{dt^2} \approx -q(t)\frac{l_B Q}{\langle r_g(t)\rangle^2}. \tag{15}$$

The solution of Eq. (15) for given charge distribution $q(t)$ and average trajectory $\langle r_g(t)\rangle$ is

$$\delta r_g(t) = a^2 l_B Q \int_0^t ds \int_s^g \frac{q(k)}{\langle r_g(k)\rangle^2} dk. \tag{16}$$

Multiplying both sides of this equation by $q(t)$ and averaging it with respect to distribution of the random variable $q(t)$, one has the following expression for the correlation function: $\langle q(t)\,\delta r_g(t)\rangle = a^2 l_B Q f t/\langle r_g(k)\rangle^2$. After substitution of the expression for the correlation function $\langle q(t)\,\delta r_g(t)\rangle$ into Eq. (15) the differential equation for the average trajectory $\langle r_g(t)\rangle$ reduces to

$$a^{-2}\frac{d^2\langle r_g(t)\rangle}{dt^2} \approx 2f(a l_B Q)^2 \frac{t}{\langle r_g(t)\rangle^5} + \frac{dh(\langle r_g(t)\rangle)}{dr}. \tag{17}$$

Let us construct a solution of Eq. (17) that is scale invariant and is left unchanged under the transformation $\{t \to bt, \langle r_g(bt)\rangle \to b^p \langle r_g(t)\rangle\}$. All terms of Eq. (17) will stay unchanged after this transformation if the function $h(r) \simeq r^{-2}$ and the exponent $p=1/2$. In equilibrium all three terms in Eq. (17) are of the same order of magnitude, which allows one to choose the effective external field $h(r)$ in the form

$$h(r) \approx C\frac{f^{2/3} a^{2/3} l_B^{4/3} Q^{4/3}}{r^2}, \tag{18}$$

where C is a numerical constant whose value may be found by matching the density profile at the boundary of this inner layer at $r=r_2$ with that in the outer region ($r_2<r<r_1$). In the strong stretching approximation the ‘‘time derivative'' d/dt can be transformed into the space derivative $\langle v_g(r)\rangle d/dr$, where $\langle v_g(r)\rangle$ is the average stretching of the chain at a distance r from the center of the particle. Transforming the time derivative on the right-hand side of Eq. (17) into the space derivative and taking into account the zero tension condition at the middle of the loop at $t=g$, one can write a relation between the number of monomers g in one-half of the loop and its middle point position r_g^{max}:

$$r_g^{max} \approx C^{1/6} f^{1/6} a^{2/3} l_B^{1/3} Q^{1/3} g^{1/2}. \tag{19}$$

Substitution of $g \approx N$ in the last equation gives the size r_2 of the largest loop formed by the whole polyampholyte chain. Thus, the self-similar brush of loops ends at the distance

$$r_2 \approx f^{1/6} a^{2/3} l_B^{1/3} Q^{1/3} N^{1/2}. \tag{20}$$

Since Eq. (17) is invariant with respect to transformation $\{t \to bt, \langle r_g(bt)\rangle \to \sqrt{b}\langle r_g(t)\rangle\}$ the solution of this second order differential equation may be written in the general form

$$\langle r_g(t)\rangle = [f a^4 C (l_B Q)^2]^{1/6} \sqrt{t}\, u\left[\ln\left(\frac{t}{g}\right)\right], \tag{21}$$

where the function $u(x)$ satisfies the second order differential equation

$$u_{xx} = \frac{u}{4} + \frac{2}{C^3}(u^{-5} - u^{-3}) \tag{22}$$

with initial conditions $u_x(0) = -1/2$ and $u(0)=1$. Unfortunately, it is impossible to obtain an analytical solution of Eq. (22) in the whole interval of $x \in [-\infty, 0]$. However, in the interval of x where $u(x) \leqslant 1$ the approximate solution of this equation is $u(x) \approx (1 - x/2 + x^2/8)$, which results in the following expression for the average trajectory $\langle r_g(t)\rangle$:

$$\langle r_g(t)\rangle \approx C^{1/6} f^{1/6} a^{2/3} l_B^{1/3} Q^{1/3} \sqrt{t}\left[1 - \ln\left(\sqrt{\frac{t}{g}}\right) + \frac{1}{2}\ln^2\left(\sqrt{\frac{t}{g}}\right)\right]. \tag{23}$$

For a θ solvent for the polymer backbone the effective potential $h(r)$ is proportional to the probability of three-body contacts $a^6 c(r)^2$. Taking this fact into account the monomer density distribution in the adsorbed layer is

$$c(r)a^3 \approx C^{1/2}\frac{f^{1/3} a^{1/3} l_B^{2/3} Q^{2/3}}{r} \approx c_0^* a^3 \frac{r_1^{4/3}}{R_0^{1/3} r} \quad \text{for} \quad R<r<r_2. \tag{24}$$

However, at length scales $r_2<r<r_1$ the polymer density profile is still given by Eq. (5). The polymer density profile in this regime is sketched in Fig. 3.

These results for the polymer density profile and for the loop size can be understood using the following simple

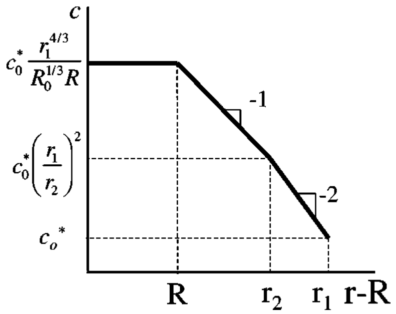

FIG. 3. Polymer density profile in the adsorbed layers for $Q > Q_2$. Logarithmic scales.

Flory-like arguments. The polarization energy of a loop containing g monomers with the center of mass located at distance $r-R \gg R$ from the surface of the particle with excess charges in the two halves of the loop of $q \approx (fg)^{1/2}$ separated by a distance r_g, is given by the expression

$$\frac{W^g_{pol}}{kT} \approx -\frac{q l_B Q}{r_g} \approx -\frac{\sqrt{fg}\, l_B Q}{r_g}. \tag{25}$$

The relation between the loop size r_g and the number of monomers g in it is obtained by balancing the loop polarization energy W^g_{pol} [Eq. (25)] with its elastic energy $F^g_{elas} \approx kTr_g^2/ga^2$,

$$g(r_g) \approx r_g^2 a^{-4/3} l_B^{-2/3} f^{-1/3} Q^{-2/3}. \tag{26}$$

The density of the polarization energy $U_{pol}(r)$ at a distance r from the center of the sphere is equal to the concentration $c(r)/g(r)$ of the loops with g monomers times the polarization energy of a loop $W^g_{pol}(r) \approx -\sqrt{fg(r)}\, l_B Q/r$,

$$\frac{U_{pol}(r)}{kT} \approx -c(r)\sqrt{\frac{f}{g(r)}}\frac{l_B Q}{r} \approx -c(r) f^{2/3}\frac{(l_B Q)^{4/3} a^{2/3}}{r^2}. \tag{27}$$

The balance of this polarization energy density and the three-body repulsion $a^6 c(r)^3$ leads to the equilibrium density profile given by Eq. (24).

The loop distribution function ρ_g in a layer of thickness r_2 can be found from the mass conservation condition

$$\int_1^N \rho_g g\, dg \simeq \int_R^{r_2} c(r) r^2 dr \approx N\left(\frac{l_B^2 Q^2 f}{a^2}\right)^{2/3}. \tag{28}$$

The solution of this equation is a δ function,

$$\rho_g \approx \left(\frac{l_B^2 Q^2 f}{a^2}\right)^{2/3} \delta(g-N) \quad \text{for } 0<g<N. \tag{29}$$

It is interesting to point out that the structure of adsorbed polyampholyte chains at length scale $R<r-R<r_2$ is similar to that of star polymers in a θ solvent [14] with the number of branches $n \approx (l_B^2 Q^2 f/a^2)^{2/3}$ and all end points located at the periphery of the layer of thickness r_2. The polyampholyte chains in this starlike conformation can be viewed as an array of blobs, whose size $\xi(r) \approx n^{-1/2} r$ increases linearly with the distance r from the center of the particle. A schematic sketch of the chains in this inner adsorbed layer with thickness r_2 is shown in Fig. 4.

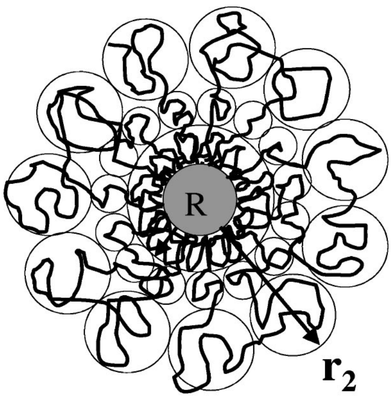

FIG. 4. Schematic sketch of the structure of adsorbed polyampholyte chains on a charged spherical particle on the length scale $R<r<r_2$.

Integrating the polymer density profile between R and r_1 one obtains the amount of polymer adsorbed,

$$\Gamma \approx N(n+n^{9/8}) \approx N\left(\frac{l_B f^{1/2} Q}{a}\right)^{3/2}, \tag{30}$$

which is dominated by the outer region $r_2<r<r_1$. It increases with increasing charge Q of the particle.

I have presented a theory of multichain polyampholyte adsorption on a charged spherical particle. The polymer equilibrium density profile in the adsorbed layer is determined by the balance of the polarization-induced attraction of the chains to the charged particle and the monomer-monomer repulsion. At small values of the charge on the particle $Q<Q_2$, the adsorbed polyampholytes form multilayers of polarized dipoles, with the polymer density in the adsorbed layer decreasing as r^{-2}. The adsorption stops at distances $r \approx r_1$ where the polarization-induced attractive interactions become of the order of the thermal energy kT. At intermediate values of the charge on the particle $Q>Q_2$, polyampholyte chains touching the particle surface form a starlike structure with the number of "branches" increasing with increasing particle charge as $Q^{4/3}$. The polymer density in this self-similar layer is inversely proportional to the distance r from the center of the particle. The outer layers ($r_2 < r < r_1$) of the adsorbed chains are still formed by polarized polyampholyte "dipoles" with the polymer density decaying as r^{-2}.

The financial support of the NSF under Grant No. DMR-9730777 and of the Eastman Kodak Company is gratefully acknowledged. The author is grateful to M. Rubinstein and E. Zhulina for valuable discussions.

[1] P.-G. de Gennes and J. Badoz *Fragile Objects* (Springer-Verlag, New York, 1996).
[2] A. G. Ward and A. Courts, *The Science and Technology of Gelatin* (Academic Press, London, 1977).
[3] R. J. Cox, *Photographic Gelatin* (Academic Press, London, 1972).
[4] H. Schiessel and A. Blumen, Theor. Simul. **6**, 103 (1997).
[5] J.-F. Joanny, J. Phys. II **4**, 128 (1994).
[6] A. V. Dobrynin M. Rubinstein, and J.-F. Joanny, Macromolecules **30**, 4332 (1997).
[7] R. Netz and J.-F. Joanny, Macromolecules **31**, 5123 (1998).
[8] A.V. Dobrynin, S.P. Obukhov, and M. Rubinshtein, Macromolecules **32**, 5689 (1999).
[9] E. B. Zhulina, A. V. Dobrynin, and M. Rubinstein, Eur. Phys. J. B (to be published).
[10] P. G. Higgs and J. F. Joanny, J. Chem. Phys. **89**, 5273 (1988).
[11] A. V. Dobrynin and M. Rubinstein, J. Phys. II **5**, 677 (1995).
[12] A. N. Semenov, Zh. Éksp. Teor. Fiz. **88**, 1242 (1985) [Sov. Phys. JETP **61**, 733 (1985)].
[13] T. M. Birshtein and E. B. Zhulina, Polymer **30**, 170 (1989).
[14] M. Daoud and J. P. Cotton, J. Phys. (France) **43**, 531 (1982).