On the theory of weakly charged polyelectrolytes

A. R. Khokhlov and K. A. Khachaturian
Physics Department, Moscow State University, Moscow 117234, *USSR*
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The problem of the possible regimes of the qualitatively different behaviour of solutions of weakly charged polyelectrolytes in theta- and good solvents are considered. For both cases we constructed the diagram of states with the following variables: polymer concentration in solution and concentration of added low-molecular weight salt. We also describe the behaviour of a polyelectrolyte solution in each of the regimes. To obtain the diagram of states it was necessary to solve the problem of the Debye–Hückel screening by non-point-like objects. This problem is considered in the Appendix.

Keywords Polyelectrolyte; solution; blob; diagram of states; Debye–Hückel screening; persistent length

INTRODUCTION

Great attention has been paid recently to the experimental and theoretical study of polyelectrolyte solutions[1–8]. From the theoretical point of view our understanding of the behaviour of such systems has been advanced considerably since (i) in refs 2 and 5 the concept of the so-called electrostatic persistent length was introduced; and (ii) in refs 1 and 4 the modern scaling theory of polymer solutions has been applied to polyelectrolytes.

In refs 2–8 the main attention was devoted to the solutions of strongly charged polyelectrolytes, where the electrostatic monomer–monomer interactions dominate the usual non-coulombic interactions. The opposite case of weakly charged polyelectrolytes (example: the uncharged chain with rare inclusions of charged monomers), where it is necessary to take into account also the non-electrostatic interactions of monomers, has been studied to a much lesser extent (see refs 1 and 9–10). At the same time, it is clear that in weakly charged polyelectolytes, due to the presence of two qualitatively different types of interaction, many more interesting possibilities can be realized. For example it was shown that the sufficiently poor salt-free solution of weakly charged polyelectrolyte is unstable with respect to the process of the avalanche type condensation of counterions on the macromolecules[10]. This effect is due to the interplay of the electrostatic and non-electrostatic interactions and cannot be observed in the solutions of strongly charged polyelectrolytes.

In this paper we shall consider the solutions of weakly charged polyelectrolytes (for the exact definition of this notion—see the end of the following section. Using modern concepts of polymer theory[11] we shall try to find, for such solutions, all the possible regimes of the qualitatively different behaviour and to obtain characteristic physical quantities in each of these regimes. A somewhat analogous consideration for strongly charged polyelectrolytes was performed by Odijk[4]. As we shall see below, solutions of weakly charged polyelectrolytes have many specific features.

As in ref 10, we shall represent the macromolecule of a weakly charged polyelectrolyte as a flexible filament on which N interacting monomers are strung (the model 'beads on a filament'[12]). We shall assume that the correlation between the adjacent monomers is Gaussian, with a mean-square distance a^2 between them. All the monomers interact by means of the usual non-coulombic forces of the Van der Waals type and, in addition to this, one monomer among σ successive monomers along the chain carries a charge e ($\sigma \gg 1$, since the polyelectrolyte is weakly charged). It is possible to introduce, in the usual way, the θ-temperature with respect to the non-electrostatic forces and to write down the estimation for the second virial coefficient of the non-coulombic interactions of monomers[12]: $B \sim v\tau$, where $\tau = \frac{T-\theta}{\theta}$, $v \sim r_0^3$, T is the temperature and r_0 is the interaction radius of the short-range Van der Waals forces*. We shall consider both the cases of salt-free solution (when the total number of counterions floating in the solution is equal to the number of charged monomers) and of the solution with some added amount of 1–1 low-molecular electrolyte salt.

In our model the state of the polyelectrolyte solution depends on three basic parameters: (i) polymer concentration in the solution c, (ii) concentration of added salt, n, and (iii) the solvent quality with respect to the non-electrostatic interactions, which is characterized by the parameter τ. In the next section we shall begin with the most fundamental case $c = n = \tau = 0$ (isolated macromolecule in salt-free theta solution), for which results have already been obtained[1]. Then, subsequently, we shall consider the conformation of the polyelectrolyte macromolecule in the solution with some added amount of salt ($n \neq 0$, but, as before, $c = \tau = 0$). We shall then discuss the properties of the salt-free polyelectrolyte solution of finite concentration c in the θ-solvent ($n = \tau = 0$; $c \neq 0$). Using the

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* In ref 10 it is shown that in the case of weakly charged polyelectrolytes the results obtained for the model just described can be easily reformulated for any other polymer chain model (in particular for the persistent model).

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results of these two cases we shall then obtain the diagram of states with the variables n–c for the polyelectrolyte solution in the θ-solvent ($\tau=0$). Lastly, the analogous diagram of states for the good solvent region ($\tau>0$) is considered and the behaviour of polyelectrolyte solutions in poor solvents ($\tau<0$) is discussed. The Appendix contains the solution of the problem of the Debye–Hückel screening by non-point-like objects, which will arise in the section dealing with the concentrated salt-free polyelectrolyte solution at the θ-temperature.

It can be seen that in spite of the fact that for weakly charged polyelectrolytes the main interest is in the simultaneous accounting for electrostatic and non-electrostatic interactions, a large part of this paper is devoted to consideration of the theta-solution with respect to the non-coulombic interactions. This is because (i) the diagram of state for the good solvent case appears as a natural generalization of the analogous diagram for the θ-solvent; and (ii) the problem of the diagram of states with the variables n–c, even for the case when the non-electrostatic interactions of monomers are absent, has not yet been considered in the literature.

VERY DILUTE SALT-FREE POLYELECTROLYTE SOLUTION AT THE θ-TEMPERATURE ($c=n=\tau=0$)

The conformation of a weakly charged polyelectrolyte macromolecule for this case has been considered[1,9,10]. In the case of a very dilute solution ($c=0$) it is possible to neglect the influence of counterions on the polyelectrolyte conformation; the charges on the macromolecule interact by means of the non-screened coulomb potential (see ref 1). This interaction leads to the fact that in the sense of the dependence of the mean-square end-to-end distance of the macromolecule, $\langle R^2\rangle$, on N the conformation of the polyion is fully extended: $\langle R^2\rangle \sim N^2$.[1] In order to describe this conformation in ref 1 it was proposed to use the following convenient terminology. The macromolecule is represented as a sequence of blobs (see *Figure 1*); each blob containing g successive charges along the chain, i.e. $g\sigma$ monomers. The spatial size of the blob D is obtained from the condition that the energy of the electrostatic repulsion of two blobs which are adjacent along the chain is of the order T:

$$g^2\frac{e^2}{\varepsilon D}\sim T \qquad (1)$$

(ε being the dielectric constant of the solvent). Then, on the one hand, the polymer chain inside the blob is only slightly perturbed by the coulombic interactions, i.e. we can write

$$D\sim a(g\sigma)^{1/2} \qquad (2)$$

and, on the other hand, the system of blobs forms a fully extended conformation of longitudinal size

$$L\sim\frac{N}{g\sigma}D. \qquad (3)$$

From equations (1)–(3) we obtain:

$$g\sim\frac{\sigma^{1/3}}{u^{2/3}}\,;\quad D\sim\frac{a\sigma^{2/3}}{u^{1/3}}\,;\quad L\sim\frac{Nau^{1/3}}{\sigma^{2/3}}\,, \qquad (4)$$

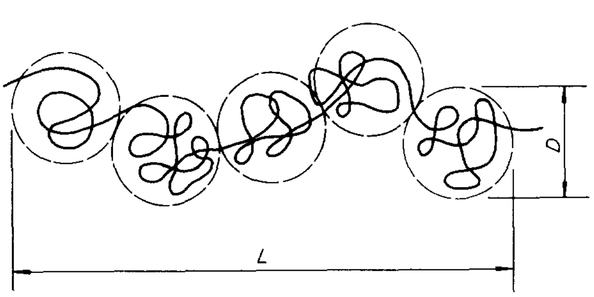

Figure 1 Polyelectrolyte conformation in the very dilute solution: the chain of blobs

where we have used the notation $u\equiv\frac{e^2}{\varepsilon aT}$ for the characteristic dimensionless parameter of the problem. Now it is possible to formulate more exactly the definition of a weakly charged polyelectrolyte: this is a charged macromolecule which assumes the above described conformation of the chain of blobs (*Figure 1*) in the extremely dilute salt-free solution, with the number of charges per blog g much greater than unity: $g\gg1$ (for persistent model it is also necessary that the chain inside a blob contains a large number of persistence lengths[10]).

VERY DILUTE POLYELECTROLYTE SOLUTION WITH ADDED SALT AT THE θ-TEMPERATURE ($c=\tau=0$, $n\neq0$)

Let us now consider the macromolecular conformation in the presence of some added amount of salt to the solution (1–1 electrolyte of concentration n).

In this case coulombic interactions of the charged monomers are screened by the ions of the added salt, the corresponding Debye screening radius r_D being equal to

$$r_D\sim\frac{1}{(uan)^{1/2}}. \qquad (5)$$

Since at $n\neq0$ *the value of* r_D is finite, at large values the macromolecular conformation is no longer as described in the previous section; the chain of blobs is no longer fully extended in the sense of the asymptotic dependence of $\langle R^2\rangle$ on N.

The conformation of a macromolecule of a strongly charged polyelectrolyte in a salt solution with the screening radius r_D was considered in refs 2 and 5. It was shown that in this case the macromolecular properties can be described in terms of the persistent length $\tilde{l}$, which is the sum of the bare persistent length l of the corresponding uncharged macromolecule and of the so-called electrostatic persistent length l_e

$$\tilde{l}=l+l_e=l+\frac{e^2r_D^2}{4\varepsilon TA^2}, \qquad (7)$$

where A is the distance between the charges e on the chain of a strongly charged polyelectrolyte. The appearance of the electrostatic persistent length is due to the extra stiffening of the chain brought about by the electrostatic interactions of monomers, which are close to each other along the chain. However, in the presence of salt this stiffening is not sufficiently large to cause the fully extended conformation, as in the previous section. Equation (7) is valid only if the linear charge density of the polyelectrolyte chain is not sufficient to induce the counterion condensation.

If the polyelectrolyte is weakly charged, then equation (7) cannot be used directly. Nevertheless, the analysis of refs 2 and 3 can be easily generalized for this case, if it is applied to the chain of blobs. In this context equation (7) will still be valid if the value of e is replaced by ge, the charge of one blob, and the values of A and l are replaced by D, the distance between adjacent blobs**. Thus, we obtain:

$$\tilde{l} \sim D + \frac{g^2 e^2 r_D^2}{4\varepsilon T D^2} \sim D + \frac{r_D^2}{D} \sim \frac{r_D^2}{D}. \qquad (8)$$

The last equality follows from the fact that the macromolecular conformation can be represented as a sequence of blobs only at $r_D > D$, and if this is the case the second term in equation (8) is much larger than the first term. At $r_D < D$ extra stiffening of the chain due to electrostatic interactions is nonessential and the notion of electrostatic persistent length cannot be introduced.

Taking into account the above considerations, let us describe the main regimes of the qualitatively different behaviour of an isolated polyelectrolyte chain at $\tau = 0$. At $n = 0$ we have an elongated conformation as described in the previous section. Clearly, in this case

$$\langle R^2 \rangle \sim L^2 \sim N^2 a^2 \frac{u^{2/3}}{\sigma^{4/3}}. \qquad (9)$$

As n increases, the persistent length of the chain of blobs (equation (8)) decreases. However, until $\tilde{l} > L$, the mean-square end-to-end distance is determined by equation (9). The persistent length becomes equal to the contour length of the chain of blobs

$$\tilde{l} = L \quad \text{at} \quad r_D \sim N^{1/2} a. \qquad (10)$$

At $r_D < N^{1/2} a$ $\tilde{l} < L$, the contour length of the chain of blobs contains several persistent lengths, thus the value of $\langle R^2 \rangle$ is given by

$$\langle R^2 \rangle \sim L\tilde{l} \sim \frac{N r_D^2 u^{2/3}}{\sigma^{4/3}}. \qquad (11)$$

As we add extra salt (n increases), equation (11) will hold until the number of persistent lengths per macromolecule increases to such extent that the excluded volume effects become essential. This will happen when the excluded volume parameter in the polyelectrolyte coil, Z [12], becomes the order of unity. Since the chain of blobs can be represented as a persistent chain of width $r_D{}^3$ and of the persistent length $\tilde{l}$, we can write

$$Z \sim \left(\frac{L}{\tilde{l}}\right)^{1/2} \frac{r_D \tilde{l}^2}{\tilde{l}^3} \sim \frac{N^{1/2} a^2}{r_D^2} \frac{\sigma^{2/3}}{u^{1/3}} \qquad (12)$$

(see ref 13). Excluded volume effects become pronounced at $Z > 1$, i.e. at

$$r_D < a N^{1/4} \frac{\sigma^{1/3}}{u^{1/6}}. \qquad (13)$$

If inequality (13) is fulfilled, we have instead of equation (11)

$$\langle R^2 \rangle \sim L\tilde{l} Z^{2/5} \sim N^{6/5} r_D{}^{6/5} u^{8/15} a^{4/5} \sigma^{-16/15}. \qquad (14)$$

Finally, as the concentration of added salt, n, further increases, the Debye radius, r_D, can become of the order of the blob size, D. At $r_D < D$ the notion of a sphere cannot be used and the value of $\langle R^2 \rangle$ can be calculated following the usual methods of the excluded volume theory[12] (in this case the excluded volume is due to the screened coulombic interactions of charged monomers). This gives

$$\langle R^2 \rangle \sim N^{6/5} \frac{u^{2/5}}{\sigma^{4/5}} r_D^{4/4} a^{6/5}. \qquad (15)$$

Equation (15) is valid provided r_D is much larger than the microscopic scale ($\sim a$).

Now let us summarize all the possible regimes of qualitatively different behaviour for a weakly charged polyelectrolyte chain at $c = \tau = 0$:

I $r_D > N^{1/2} a$—elongated chain of blobs (see equation (9)).

II $N^{1/2} a > r_D > N^{1/4} a \frac{\sigma^{1/3}}{u^{1/6}}$—chain of blobs forms the coil without excluded volume (see equation (11)).

III $N^{1/4} a \frac{\sigma}{u^{1/6}} r_D > D = \frac{q \sigma^{2/3}}{u^{1/3}}$—chain of blobs forms the coil with excluded volume (see equation (14)).

IV $r_D < D$ chain of blobs disappears and the macromolecule takes the conformation of a usual coil with excluded volume (see equation (15)).

The four above mentioned regimes are shown at the n-axis in *Figure 2*. The value of r_D is connected with the concentration of added salt according to equation (15).

CONCENTRATED SALT-FREE POLYELECTROLYTE SOLUTION AT THE θ-TEMPERATURE ($n = \tau = 0$, $c \neq 0$)

Suppose now that we have a salt free solution at $\tau = 0$ and that we increase the polymer concentration in the solution, c. As c increases, the number of counterions increases also, since the solution remains globally neutral. These counterions screen the interactions of charged monomers. Thus in this case we have a finite Debye radius r_D as well as the finite persistent length(8)* of the chain of blobs.

Let us consider, first of all, the concentration region where although polyelectrolyte coils overlap strongly, the volume fraction of spheres in the solution is still small: $c \ll \frac{g\sigma}{D^3}$. In this region we can naturally introduce the

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** Weakly charged polyelectrolyte differs from strongly charged polyelectrolyte in the following respect: in the chain of blobs large fluctuations in the transverse direction are possible. For example for transverse dimensions of the polyelectrolyte coil considered in the previous section we have $L_\perp \sim (N/g\sigma)^{1/2} D$. To perform the analysis, which is analogous to refs 2 and 3, it is necessary to take an average, with respect to these fluctuations. After this averaging the chain of spheres becomes similar to the chains considered in refs 2 and 3.

* In ref 8 it was shown that even in the concentrated solution, the degree of flexibility of the chain of blobs can still be determined by equation (8). Naturally the notion of blobs itself can only be applied when they do not overlap, i.e. at $c < g\sigma/D^3$.

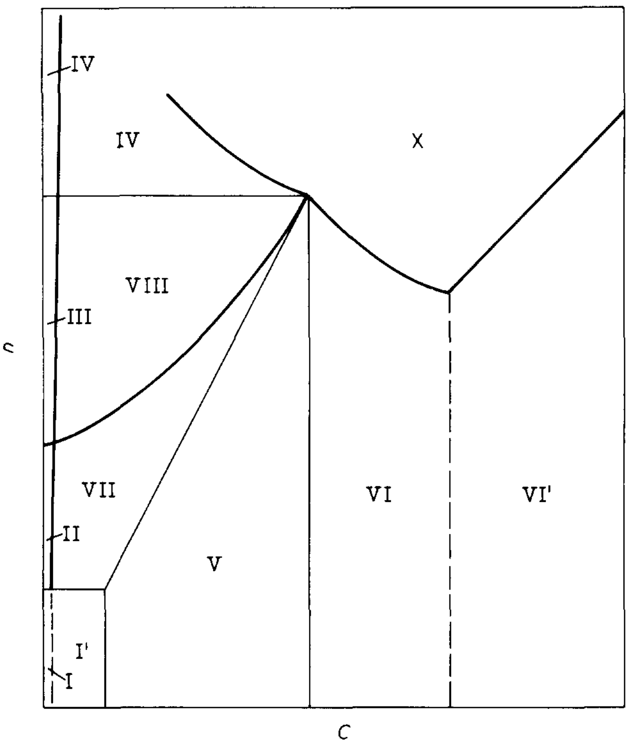

Figure 2 Diagram of states for the solution of weakly charged polyelectrolytes

characteristic distance ξ, the average distance between two neighbouring chains of blobs. Since the volume fraction occupied by the blobs in the solution is $\gamma \sim cD^3/g\sigma$, we have

$$\xi \sim \frac{D}{\gamma^{1/2}} \sim \frac{a\sigma^{1/3}}{u^{1/6}} \frac{1}{(ca^3)^{1/2}}. \tag{16}$$

In refs 4 and 8 it was shown that ξ is the correlation length for the regime under consideration. What is the relation between r_D and ξ? Of course the behaviour of the solution would be more simple if these two lengths are of the same order of magnitude: $\xi \sim r_D$.

However, if we take into account that the average counterion concentration in the salt-free solution is equal to $\frac{c}{\sigma}$ and use for r_D the formula analogous to equation (5), we obtain

$$r_D \sim \left(\frac{\sigma}{uac}\right)^{1/2} \sim \frac{\sigma^{1/6}}{u^{1/3}} \xi \sim g^{1/2} \xi. \tag{17}$$

For weakly charged polyelectrolytes $g \gg 1$, thus we conclude that, in the case equation (17) is valid $r_D \gg \xi$. We note also that for strongly charged polyelectrolytes $g \sim 1$ and thus, as it was shown in refs 4 and 8, $r_D \sim \xi$.

However a more detailed analysis shows that equation (17) is not valid for the case of weakly charged polyelectrolytes. It was deduced using the assumption that the screening is due to the monovalent point-like charges of concentration $\frac{c}{\sigma}$, which are not connected in the chain[14]. At the same time, in the polyelectrolyte solution in addition to the point-like counterions, there are charged monomers, which can also contribute to the screening. The fact that these charges are connected in the chain changes, significantly, the expression for r_D for the case of weakly charged polyelectrolytes.

In the case of non-overlapping blobs under consideration, $c \ll \frac{g\sigma}{D^3}$, the screening is due to the counterions and the chains of blobs. At the scale $\sim r_D$ the chains of blobs can be represented as elongated rods (the persistence length of the chain of blobs is much larger than r_D (see equation (8)). Thus we come to the problem of screening by the rod-like charged objects. This problem is considered in the Appendix, where it is shown that, provided the Debye–Hückel approximation is valid, screening by rods is much more effective than the screening by point-like charges with the same volume charge density. For a solution of rods with the linear charge density ρ and the volume density of charges on the rods η (rods float in the oppositely charged, homogeneously distributed 'background', so that globally the system is neutral) the Debye radius is equal to (see Appendix)

$$r_D \sim \left(\frac{\varepsilon T}{\rho\eta}\right)^{1/3}. \tag{18}$$

Equation (18) has a simple qualitative interpretation. We can recall that according to the Debye–Hückel theory[14] if the screening is due to the point-like charges of concentration c and the valency Z the corresponding Debye radius is

$$r_D \sim \left(\frac{\varepsilon T}{e^2 c Z^2}\right)^{1/2} \sim \left(\frac{\varepsilon T}{\eta e Z}\right)^{1/2}. \tag{19}$$

Let us calculate the effective value of Z for the solution of rods with the Debye radius r_D. If two charges on the rod are separated by a distance smaller than r_D, from the point of view of the screening they can be represented as a single charge of double valency. If the distance between the charges is larger than r_D, they take part in screening independently. Consequently, for the calculation of the Debye radius in the solution of rods we can use equation (19), substituting as the charge eZ of an elementary screening unit the value ρr_D, the charge of the portion of the rod of length r_D. As a result we obtain directly equation (18).

In the application to polyelectrolyte solution equation (18) yields

$$r_D \sim \left(\frac{\sigma^{4/3}}{u^{2/3} c}\right)^{1/3}. \tag{20}$$

Comparing equations (16) and (20) we can see that $r_D \ll \xi$, i.e. the screening due to the other macromolecules is much more effective (i.e. it leads to the smaller Debye radius), than the screening by the point like counterions.

However, equation (20) also does not give the correct expression for the screening radius of the polyelectrolyte solution. The reason for this is that at $r_D \ll \xi$ the condition of validity of the Debye–Hückel approximation is not fulfilled. This approximation is valid only at $r_D \gg \xi$ when, within the screening radius r_D, there are many screening objects, i.e. many other macromolecules.

Taking into account the above considerations it seems more natural to assume that in semidilute solutions of non-overlapping blobs the Debye radius r_D and the correlation length ξ are of the same order of magnitude: $r_D \sim \xi$—the same relation as in the solution of strongly charged polyelectrolytes[4,8]. In actual fact, since the screening is contributed to, not only by the counterions, but also by the neighbouring macromolecules, the value of r_D decreases in comparison with the value $r_D \gg \xi$ defined by equation (17). However the decrease in r_D, due to the neighbouring macromolecules, cannot be very large because, at the scales smaller than ξ, this type of screening is ineffective. Thus r_D cannot become smaller than ξ, the value of $r_D \ll \xi$ defined by equation (20) cannot be reached. From this it follows that the decrease in r_D will stop at the level $r_D \sim \xi$.

With the help of this result we can calculate any conformational characteristics of the semidilute solution of non-overlapping spheres. For example, the persistence length of the chains of blobs is equal to

$$\tilde{l} \sim \frac{r_D^2}{D} \sim \frac{\xi^2}{D} \sim \frac{1}{ca^2}. \tag{21}$$

For the mean-square end-to-end distance of a polyelectrolyte chain $\langle R^2 \rangle \sim L\tilde{l}$ (volume interactions in this regime are always screened, since $\tilde{l} \gg \xi$) we obtain

$$\langle R^2 \rangle \sim L\tilde{l} \sim Na^2 \frac{u^{1/3}}{\sigma^{2/3}} \frac{1}{ca^3}. \tag{22}$$

Equation (22) is valid only at concentrations higher than the concentration c^* at which $L \sim \tilde{l}$. At the concentrations $c < c^*$ the solution is dilute, in this regime macromolecules take the elongated conformation described earlier.

Using equations (4) and (21) we obtain

$$c^* a^3 \sim \frac{1}{N} \frac{\sigma^{2/3}}{u^{1/3}}. \tag{23}$$

The concentration c^* is still much larger than the overlap concentration, $c \sim \frac{N}{L^3}$ of the elongated coils of the very dilute salt-free solution.

Until now we have only considered the case $c \ll \frac{g\sigma}{D^3}$ of a small volume fraction of blobs in the solution. It should be noted that at $c \sim \frac{g\sigma}{D^3}$ $\tilde{l} \sim r_D \sim \xi \sim D$. At $c > \frac{g\sigma}{D^3}$ blobs begin to overlap. In this region the influence of the electrostatic interaction on the macromolecular conformation is negligible and $\langle R^2 \rangle \sim Na^2$.

Let us now calculate the value of the Debye radius in the region $c > \frac{g\sigma}{D^3}$ of overlapping blobs. We shall also assume that $c \ll \frac{1}{a^3}$, i.e. that the polyelectrolyte solution is not too concentrated. In this case we come to the problem, which is in a sense analogous to the problem described above, of the screening by rods: the screened potential is formed by the point-like counterions and by the non-point-like objects; in our case by the charge Gaussian chains of other macromolecules.

The problem of screening by the Gaussian chains is also considered in the Appendix, where it is shown that due to the connectivity of charges in the chain, the degree of screening always increases (i.e. r_D decreases) in comparison with the case of disconnected charges of the same volume density. The expression for r_D obtained in the Appendix can be qualitatively interpreted as follows. Since in the region $c > \frac{g\sigma}{D^3}$ there is no influence of charges in the macromolecular conformation, we can, as in the neutral solution of concentration c in the θ-solvent, introduce the correlation length $\xi \sim \frac{1}{ca^2}$[15]. Clearly, elementary screening units forming the Debye radius r_D are the parts of macromolecules of dimension ξ (at larger scales the correlation disappears and the charges connected in the chain can no longer be represented as one elementary screening object). This means that in this case, equation (19) for r_D is still valid, with the valency $Z \sim \frac{\xi^2}{a^2\sigma} \sim \frac{1}{c^2a^6\sigma}$ being the charge of part of the macromolecule of dimension ξ. Thus we obtain (see also Appendix):

$$r_D \sim \left(\frac{\varepsilon T}{\eta e Z}\right)^{1/2} \sim \left(\frac{\varepsilon T}{\eta \frac{e\xi^2}{a^2\sigma}}\right)^{1/2} \sim \frac{\sigma(ca^3)^{1/2}a}{u^{1/2}}. \tag{24}$$

The concentration dependence of the Debye radius in this regime is unusual: $r_D \sim c^{1/2}$. The increase of r_D with concentration is connected with the rapid decrease of ξ as a function of c (and, consequently, with the decrease of the valency of elementary screening objects). The Debye radius will increase with concentration according to equation (24) until $Z > 1$. At concentrations larger than $ca^3 \sim \frac{1}{\sigma^{1/2}}$, when the part of macromolecule of dimension ξ contains on the average less than one charge ($Z < 1$) we must use for r_D the usual formula:

$$r_D \sim \left(\frac{\varepsilon T}{\eta e}\right)^{1/2} \sim \left(\frac{\sigma}{uac}\right)^{1/2}. \tag{25}$$

In conclusion, we list the possible regimes for weakly charged polyelectrolyte solutions at $n = \tau = 0$:

I $c < d^* \sim \frac{1}{Na^3} \frac{\sigma^{2/2}}{u^{1/3}}$—elongated chain of blobs.

V $c^* < c < \frac{g\sigma}{D^3}$ — semidilute solution of the chains of blobs with finite persistent length: $r_D \sim \xi$ (see equations (16), (21), (22)).

VI $\frac{g\sigma}{D^3} < c \leqslant \frac{1}{a^3}$ — solution of Gaussian chains; $\langle R^2 \rangle \sim Na^2$. At $c < \frac{1}{a^3\sigma^{1/2}}$ the value of r_D is given by equation (24); at $c > \frac{1}{a^3\sigma^{1/2}}$ — by equation (25).

The above mentioned regimes are shown in *Figure 2* (c-axis).

DIAGRAM OF STATES FOR THE SOLUTION OF WEAKLY CHARGED POLYELECTROLYTES AT THE θ-TEMPERATURE

Now we have all the necessary information to obtain the diagram of states for the solution of weakly charged polyelectrolytes at $\tau = 0$ (i.e. in the absence of the nonelectrostatic interactions) with the variables: concentration of the added salt n and polymer concentration in solution c. This diagram of states is shown in *Figure 2*. It was constructed having in mind the well-known diagram of states for a neutral polymer solution with variables τ–c obtained in ref 15. The boundaries of the regimes of qualitatively different behaviour have the same meaning as that in ref 15: they are the lines of smooth crossover, but not of the abrupt phase transition.

Regimes I–VI were described in detail in the previous two sections. Regimes I–IV correspond to the solution of non-overlapping macromolecules at various concentrations of added salt. In regimes I, V, VI the influence of the added salt on the macromolecular conformation is negligible (see previous section). The boundary of the regions I and I′ corresponds to $c \sim N/L^3$, the overlap concentration for the spheres of radius L (L in the length of the elongated conformation of regime I). Region VI differs from region VI′ in the expression for the Debye radius (see equations (24) and (25)).

Boundaries of the regions I–IV, on the one hand, and the regions I′, VII–IX, on the other hand, correspond to the overlap concentration of macromolecules, i.e. to the transition from the dilute to the semidilute solution:

$$c_{\mathrm{I-I'}}a^3 \sim \frac{\sigma^2}{N^2 u} \ ; \quad c_{\mathrm{II-VII}}a^3 \sim \frac{\sigma^2 u^{-5/2}(na^3)^{3/2}}{N^{1/2}}$$

$$c_{\mathrm{III-VIII}}a^3 \sim \sigma^{24/5}(na^3)^{9/10}u^{-3/10}N^{-4/5} \ ; \tag{26}$$

$$c_{\mathrm{IV-IX}}a^3 \sim \sigma^{6/5}(na^3)^{3/5}N^{4/5}$$

Thus regions VII–IX are the regions of semidilute solutions corresponding to the dilute regimes II–IV. In region VII we have overlapping chains of blobs without volume interactions; in region VIII, due to the volume effects, there is some swelling of the overlapping chains of blobs; in region IX the screening is so pronounced that the notion of blobs cannot be introduced ($r_D < D$). Thus the electrostatic interactions lead to the usual excluded volume effect. If, in this latter region the concentration c is further increased we come to the region X where, due to the high concentration, volume effects are completely screened. In this region we have simply the solution of Gaussian chains with $\langle R^2 \rangle \sim Na^2$. The expressions for $\langle R^2 \rangle$ in regions VII–IX are as follows

$$\langle R^2 \rangle_{\mathrm{VII}} \sim \frac{Nu^{-1/3}}{na\sigma^{4/3}}; \ \langle R^2 \rangle_{\mathrm{VIII}} \sim (au)^{2/5}n^{-3/5}N^{6/5}\sigma^{-16/5}; \tag{27}$$

$$\langle R^2 \rangle_{\mathrm{IX}} \sim \left(\frac{a^2N^3}{n\sigma^2}\right)^{2/5}$$

The boundaries of the regions VII–X correspond to:

$$(ca^3)_{\mathrm{VII-VIII}} \sim (na^3)\sigma^{32/9}u^{29/18} \ ; \quad n_{\mathrm{VIII-IX}}a^3 \sim \frac{1}{\sigma^{4/3}u^{1/3}} \ ; \tag{28}$$

$$(na^3)_{\mathrm{IX-X}} \sim \frac{1}{(ca^3)u^{4/3}\sigma^{3/17}}.$$

Finally, the difference between domains VII and V; X and VI is in that in the regions VII and X the screening is determined by the ions of the added salt, while in the regions V and VI it is due to the counterions of macromolecules themselves. The boundaries of the regions V–VII and VI–X can be determined from a comparison of the expressions for r_D in these regions: at the boundaries these expressions must give the same values. We therefore obtain:

$$c_{\mathrm{V-VII}}a^3 \sim na^3\frac{\sigma^{4/3}}{u^{2/3}}; \ c_{\mathrm{VI-X}}a^3 \sim \frac{1}{\sigma na^3} \ ; \ c_{\mathrm{VI-X}}a^3 \sim na^3. \tag{29}$$

It should also be noted that the obtained diagram of states, as well as the majority of the formulae above, can also be applied after slight reformulation for strongly charged polyelectrolytes. In this case we shall have on the diagram of states only the regimes I–III, V and VII–VIII.

DIAGRAM OF STATES FOR THE SOLUTION OF WEAKLY CHARGED POLYELECTROLYTES IN THE PRESENCE OF NON-ELECTROSTATIC INTERACTIONS

Firstly let us consider the properties of the solution of weakly charged polyelectrolytes at temperatures higher than the θ-temperature ($\tau > 0$) when the non-electrostatic volume interactions of monomers are repulsive, their second virial coefficient being of order $B \sim v\tau$ (see earlier). For simplicity we shall restrict ourselves to the case of a flexible polymer chain ($v \sim a^3$)[13] and of a very good (athermal) solvent $\tau \cong 1$[11], then $B \sim a^3$. In this case the general form of the diagram of states of *Figure 2* remains practically unchanged (with one exception—see below). However the boundaries of different regimes and the behaviour of characteristic quantities (such as $\langle R^2 \rangle$) in these regimes will, of course, change significantly. The reason is that on the one hand, instead of equation (2) we should now use the relation:

$$D \sim a(g\sigma)^{3/5} \tag{30}$$

and, on the other hand, in some regimes it is necessary to take into account the swelling of macromolecules due to the usual non-electrostatic interactions. Below we list the expressions for the boundaries of different regimes of the diagram of states in the case under consideration, as well as the expressions for $\langle R^2 \rangle$ in each of the regimes.

$$(ca^3)_{\mathrm{I-I'}} \sim \frac{\sigma^{12/7}}{u^{6/7}}N^{-2}; \quad (ca^3)_{\mathrm{I'-V}} \sim \frac{\sigma^{2/7}}{u^{1/7}}N^{-1}; \quad (ca^3)_{\mathrm{V-VI}} \sim \frac{u^{4/7}}{\sigma^{8/7}};$$

$$(ca^3)_{\mathrm{VI-VI'}} \sim \sigma^{-4/5}, \ (na^3)_{\mathrm{I-II}} \sim \frac{1}{Nu^{6/7}\sigma^{2/7}}; \ (na^3)_{\mathrm{II-III}} \sim$$

$$\frac{1}{u^{1/2}N^{1/2}\sigma^{8/7}}; \ (na^3)_{\mathrm{III-IV}} \sim \frac{1}{u^{1/7}\sigma^{12/7}}; \ (ca^3)_{\mathrm{II-VII}} \sim$$

$$(na^3)^{3/2}\sigma^{15/7}u^{3/7}N^{-1/2}; \ (ca^3)_{\mathrm{III-VIII}} \sim \frac{(na^3)^{9/10}\sigma^{54/35}}{N^{4/5}u^{27/35}};$$

$$(ca^3)_{\mathrm{IV-IX}} \sim N^{-4/5}; \ (ca^3)_{\mathrm{VII-VIII}} \sim u^{41/42}\sigma^{199/42}(na^3)^{9/2};$$

$$(na^3)_{\mathrm{V-VII}} \sim \frac{ca^3}{u^{5/7}\sigma^{4/7}};$$
$$(ca^3)_{\mathrm{VI-X}} \sim (na^3\sigma)^{-4};\ (ca^3)_{\mathrm{VI'-X}} \sim (na^3)_{\mathrm{VI'-X}};$$
$$\langle R^2\rangle_{\mathrm{I}} \sim \langle R^2\rangle_{\mathrm{I'}} \sim N^2a^2\sigma^{-8/7}u^{4/7};$$
$$\langle R_{\mathrm{II}}\rangle \sim \langle R^2_{\mathrm{VII}}\rangle \sim \frac{a^2}{(na^3)}N\sigma^{-10/7}u^{-2/7};$$
$$\langle R^2\rangle_{\mathrm{III}} \sim N^{6/5}a^2(na^3)^{-3/5}\sigma^{36/35}u^{18/35};\ \langle R^2_{\mathrm{IV}}\rangle \sim N^{6/5}a^2;$$
$$\langle R^2\rangle_{\mathrm{V}} \sim a^2(ca^3)^{-1}N\sigma^{-6/7}u^{10/7};\ \langle R^2_{\mathrm{VI}}\rangle \sim (ca^3)^{-1/4}a^2N;$$
$$\langle R^2\rangle_{\mathrm{VI'}} \sim Na^2;\ \langle R^2\rangle_{\mathrm{VIII}} \sim a^2u^{6/5}\sigma^{10/7}(na^3)^{7/20}(ca^3)^{-3/10};$$
$$\langle R^2\rangle_{\mathrm{IX}} \sim (ca^3)^{-1/4}a^2N. \tag{31}$$

Equations (31) were obtained in a straightforward manner, combining the considerations of the previous sections of this paper with the results of the conventional theory of polymer solutions with excluded volume. The only comment worthy of making here is that in this case there is no distinction between the regimes IX and X because in both these regimes the swelling is due to the strong excluded volume effect, caused by usual interactions, which prevail over electrostatic interactions.

In conclusion let us make some comments concerning the structure of the polyelectrolyte solution at $\tau < 0$, i.e. in the region, where the binary nonelectrostatic interactions of the monomers are mainly attractive. In this case if we are inside the regions I–III, V or VII–VIII of the diagram of states, where the conformation of the macromolecule of a weakly charged polyelectrolyte can be described in terms of blobs, counterions must undergo the avalanche-type condensation on the chains of blobs[10]. In a sufficiently concentrated solution this may lead to the precipitation of the solution.

If we have a weakly charged polyelectrolyte gel instead of a weakly charged polyelectrolyte solution, the avalanche-type counterion condensation must lead to the abrupt contraction of the gel. We think that it is this fact that is responsible for the so-called collapse of polyacrylamide gels, which was observed in a series of recent experiments[16–20]. This problem will be considered in a separate publication.

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APPENDIX: DEBYE–HÜCKEL SCREENING BY NON-POINT-LIKE OBJECTS

In this appendix we shall consider the problem of calculation of the Debye radius, r_D, in the case of screening by non-point-like objects (instead of point-like ions as in the usual form of the Debye–Hückel theory). We shall have in mind, first of all, the problems of screening by rigid rods and by Gaussian coils, which are important for the consideration in this paper. Rods are rigid objects, whereas Gaussian coils can change their form easily, i.e. they are 'soft'.

Below we shall present a somewhat simplified derivation for rigid objects; then, taking as an example the problem of screening by Gaussian coils, we shall obtain a more general formula for r_D in the solution of non-point-like objects.

Let us assume that we have a solution of charged 'rigid' particles of arbitrary shape floating in the homogeneously distributed oppositely charged 'background', so that the whole system is electroneutral. Let us put a trial point-like charge e at the origin and let us see how the coulombic potential from this charge will be screened by the particles of the solution. The position of each particle can be assigned by the coordinate of its centre of mass $\boldsymbol{r}$ and by the unit vector of its orientation $\boldsymbol{\tau}$. If the particle is placed in some self-consistent potential field $\phi_{eff}(\boldsymbol{r})$, its energy in this field can be written as

$$\phi(\boldsymbol{r},\boldsymbol{\tau}) = \int \phi_{eff}(\boldsymbol{r}')\rho(\boldsymbol{r}'-\boldsymbol{r},\boldsymbol{\tau})\mathrm{d}^3\boldsymbol{r}', \tag{A1}$$

where $\rho(\boldsymbol{r}'-\boldsymbol{r},\boldsymbol{\tau})$ is the charge density on the particle with the orientation $\boldsymbol{\tau}$ at the point separated from its centre of mass by the vector $\boldsymbol{r}'-\boldsymbol{r}$. Naturally, if the end of the vector $\boldsymbol{r}-\boldsymbol{r}'$ is not within the particle then $\rho(\boldsymbol{r}'-\boldsymbol{r},\boldsymbol{\tau})=0$.

The Poisson equation for the self-consistent screened potential φ_{eff} can be written in this case in the usual form

$$\Delta\phi_{eff} = -4\pi\frac{e}{\varepsilon}\delta(\boldsymbol{r}) - \frac{4\pi}{\varepsilon}(\mu(\boldsymbol{r}), \tag{A2}$$

where $\mu(r)$ is the average volume charge density at a distance r from the trial charge. It is easy to understand that

$$\mu(\boldsymbol{r}) = C_0\iint(e^{-\frac{\phi(\boldsymbol{r}',\boldsymbol{\tau})}{T}} - 1)\rho(\boldsymbol{r}-\boldsymbol{r}',\boldsymbol{\tau})\frac{\mathrm{d}\Omega_\tau}{4\pi}\mathrm{d}^3\boldsymbol{r}', \tag{A3}$$

where C_0 is the average concentration of screening objects and $\mathrm{d}\Omega_\tau$ is the element of the spatial angle. Equation (A3) is due to the fact that, as soon as we are considering the non-point-like particles, the charge at the point $\boldsymbol{r}$ may originate from the particle, whose centre of mass is situated at $\boldsymbol{r}' \neq \boldsymbol{r}$.

In the Debye–Hückel approximation we can linearize the integrand of equation (A3). We obtain:

$$\Delta\phi_{eff}=-4\pi\frac{e}{\varepsilon}\delta(\mathbf{r})+\frac{4\pi C_0}{\varepsilon T}\iint\Phi(\mathbf{r}',\tau)\rho(\mathbf{r}-\mathbf{r}',\tau)\frac{d\Omega_\tau}{4\pi}d^3\mathbf{r}'. \tag{A4}$$

Performing Fourier transformation of equation (A4) we arrive at

$$k^2\phi_{eff}(\mathbf{k},\tau)=4\pi\frac{e}{\varepsilon}-\frac{4\pi C_0}{\varepsilon T}\int\Phi(\mathbf{k},\tau)\rho(\mathbf{k},\tau)\frac{d\Omega_\tau}{4\pi}. \tag{A5}$$

In terms of Fourier-transforms, equation (A1) can be written as

$$\Phi(\mathbf{k},\tau)=\phi_{eff}(\mathbf{k})\rho(-\mathbf{k},\tau)=\phi_{eff}(\mathbf{k})\rho^*(\mathbf{k},\tau), \tag{A6}$$

where the asterisk denotes a complex-conjugated value. From equations (A5) and (A6) we finally obtain:

$$\varphi_{eff}(k)=\frac{4\pi e/\varepsilon}{k^2+\dfrac{4\pi C_0}{\varepsilon T}\displaystyle\int|\rho(k,\tau)|^2\frac{d\Omega_\tau}{4\pi}}. \tag{A7}$$

Equation (A7) gives the solution of the problem of screening by rigid non-point-like objects. In the particular case of point-like objects of valency Z $\rho(\mathbf{r},\tau)=Ze\delta(\mathbf{r})$ we return to the usual Debye–Hückel formula. Clearly, the funcion $\rho(\mathbf{k},\tau)$ generally depends on $\mathbf{k}$, so that the screened potential differs from $\frac{1}{r}e^{-r/r_D}$. However if we denote the minimal scale, at which the screening of the coulombic potential of the trial charge becomes essential, as the Debye radius*, we can, in turn, write down the following equation for r_D

$$r_D\sim\left(\frac{4\pi C_0}{\varepsilon T}\int|\rho(\mathbf{k},\tau)|^2\frac{d\Omega_\tau}{4\pi}\right)^{-1/2}\Bigg|_{|\mathbf{k}|=\frac{1}{r_D}}. \tag{A8}$$

When the screening objects are long thin rods (length l, linear charge density ρ), we have

$$\varphi_{eff}(k)=\frac{4\pi e/\varepsilon}{k^2+\dfrac{2\pi^2 C_0}{\varepsilon Tk}\rho^2 l}. \tag{A9}$$

To determine r_D, we must equate two terms in the denominator of equation (A9) and replace k with $\frac{1}{r_D}$. Taking into account that $C_0\rho l=\eta$ (η is the average volume charge density on the rods in the solution) we arrive at equation (18) in the main text.

Clearly, equations (A9) and (A8) are valid only in the framework of the Debye–Hückel approximation, i.e. only if it is possible to perform the linearization in equation (A3). As usual, this procedure is valid if in the volume r_D^3 there are many screening objects. If this is the case, the fact that we are considering the screening of the potential of the point-like trial charge and not of the object, which would be analogous to the screening objects, is also nonessential.

Another assumption used in the above derivation is the following: rods were considered as moving independently in the potential φ_{eff}, i.e. their correlations were not taken into account. We shall see below what are the limits of validity of this assumption.

Now, instead of the solution of rigid objects, let us consider the solution of charged flexible Gaussian macromolecules, spatial distance between two adjacent along the chain charges being equal to b. Let us look once more at how the coulombic potential from the point-like charged particle put at the origin will be screened in such a solution. It is well-known[11] that if some potential field $U(\mathbf{r})(|U|\ll T)$ is acting on the monomers, the change of monomer concentration at point $\mathbf{r},\delta c(\mathbf{r})$, can be written in the form

$$\delta c(\mathbf{r})=-\frac{1}{Ta^3}\int S(\mathbf{r}-\mathbf{r}')U(\mathbf{r}')d^3\mathbf{r}', \tag{A10}$$

where $S(\mathbf{r}-\mathbf{r}')$ is the so-called response function of the concentrated polymer solution. Using equation (A10), the Poisson equation for this case takes the form

$$\Delta\phi_{eff}=-4\pi\frac{e}{\varepsilon}\delta(\mathbf{r})+\frac{4\pi e^2}{\varepsilon Tb^3}\int S(\mathbf{r}-\mathbf{r}')\phi_{eff}(\mathbf{r}')d^3\mathbf{r}'. \tag{A11}$$

Rewriting equation (A11) in terms of the Fourier transforms, we obtain

$$\phi_{eff}(\mathbf{k})=\frac{4\pi e/\varepsilon}{k^2+\dfrac{4\pi e^2}{\varepsilon Tb^3}S(\mathbf{k})}, \tag{A12}$$

where $S(\mathbf{k})$ is the Fourier-image of the response function. It is well known[8,11] that if we have a concentrated polymer solution with the correlation length ξ, the function $S(\mathbf{k})$ can be expressed approximately through the response function of an isolated chain $S_0(\mathbf{k})$ as follows

$$S(\mathbf{k})=S_0(\mathbf{k})\frac{k^2\xi^2}{1+k^2\xi^2}. \tag{A13}$$

At the same time, for $S_0(\mathbf{k})$ we have[11]:

$$S_0(\mathbf{k})=\frac{cb^3}{k^2b^2}. \tag{A14}$$

Substituting equations (A13) and (A14) in equation (A12) and equating two terms in the denominator of equation (A12), we obtain

$$r_D\sim\left(\frac{\varepsilon Tb^2}{e^2c\xi^2}\right)^{1/2}. \tag{A15}$$

Equation (A15), when rewritten in the notation of the 4th section in this paper, gives equation (24) used in the main text.

Equation (A12) gives the most general expression for

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* It is in this sense that the notion of the Debye radius is used in the main text.

the screened potential in the solutions of non-point-like objects. Equation (A7) obtained for rigid objects under the assumption of the absence of correlations, follows from equation (A12) if $S(\boldsymbol{k})$ is replaced by $S_0(\boldsymbol{k})$, the Fourier-transform of the response function for isolated object, since

$$S_0(\boldsymbol{k}) \sim \frac{1}{e^2}\int |\rho(\boldsymbol{k},\tau)|^2 \frac{d\Omega_\tau}{4\pi}. \qquad \text{(A16)}$$

From equation (A13) it can be seen that the substitution $S(\boldsymbol{k}) \rightarrow S_0(\boldsymbol{k})$ is valid only at $|\boldsymbol{k}| > \frac{1}{\xi}$. In the application to the problem of calculation of the Debye radius this procedure can be justified only if $\xi \gtrsim r_D$.

Thus, the derivation of the first part of this Appendix (equations (A1)–(A9)) and equation (18) of the main text are valid if (i) the Deybe–Hückel approximation can be applied and (ii) $r_D \lesssim \xi$. These two requirements are often contradictory (see, for example, 4th section of this paper). Requirement (ii) can easily be relaxed, if we use the more general equation (A12) instead of equation (A7). However, we do not need such a modification in the context in which we use equation (18) in the main text.

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