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On the collapse of weakly charged polyelectrolytes

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Abstract. The behaviour of weakly charged polyelectrolytes in a poor salt-free solution is considered, using the notion of blobs. It is shown that in a very dilute solution, where different polyions do not overlap, a transition of the coil–globule type takes place, upon making poorer the thermodynamic quality of the solvent. This transition occurs in each blob separately. In the region of higher concentrations (the polyions overlap strongly, but the volume fraction occupied by the blobs in the solution is small) an additional effect is predicted: avalanche-type counter-ion condensation. This effect is due to the fact that the polyelectrolyte conformation varies self-consistently, together with the variation of the number of condensed counter ions.

1. Introduction

Considerable attention has been paid recently to the statistical physics of polyelectrolyte solutions (Oosawa 1971, de Gennes *et al* 1976, Bailey 1977, de Gennes 1977, Pfeuty *et al* 1977, Skolnick and Fixman 1977, Odijk and Houwaart 1978, Odijk and Mandel 1978, Pfeuty 1978). However, most of the authors considered the case of strongly charged macromolecules, where the electrostatic monomer–monomer interactions dominate the usual interactions (of the Van-der-Vaals type). In this paper we shall consider the contrary case of weakly charged polyelectrolytes, where the usual interactions play an essential role. This case is realised, for example, in the copolymer with rare inclusions of charged monomers, whereas all the other monomers are neutral and interact by means of Van-der-Vaals forces.

The aim of this paper is the consideration of the intramolecular collapse in the macromolecule of a weakly charged polyelectrolyte, which occurs in the dilute solution, upon making poorer the thermodynamic quality of the solvent with respect to the usual non-Coulomb interactions.

The corresponding theory for the uncharged macromolecule has now been basically constructed (see the reviews by Lifshitz *et al* 1978, 1979). However, experimental study of the intramolecular collapse is strongly impeded by the fact that it is necessary to deal with extremely dilute solutions in order to avoid their precipitation (nevertheless, some recent successes in this field can be mentioned—see the papers by Słagowski *et al* (1976) and by Nierlich *et al* (1978)). The precipitation can also be prevented if each macromolecule carries some electric charge. From this point of view the study of the intramolecular collapse of weakly charged polyelectrolytes seems very interesting.

In this paper we shall basically use the polymer chain model ‘interacting beads on the flexible filament’ (see, for example, Lifshitz *et al* 1978). In this model the polymer chain is represented as a flexible immaterial filament, on which N interacting ‘beads’

(monomers) are strung. The correlation between monomers which are nearest neighbours along the chain is Gaussian, with a mean-square distance a^2 between them. All the monomers interact by means of short-range forces of the Van-der-Vaals type. It is possible to introduce, in the usual way, the θ temperature with respect to these forces, and to write down the estimates for the second and the third virial coefficients, B and C , of the monomer–monomer non-Coulomb interactions near this temperature (Lifshitz *et al* 1978): $B \sim -v\tau$, $C \sim v^2$, where $\tau \equiv (\theta - T)/\theta$, $v \sim r_0^3$, T is the temperature and r_0 is the interaction radius of the short-range Van-der-Vaals forces. Also, each monomer which is the first of σ ($\sigma \gg 1$) successive monomers along the chain carries a charge e , and the corresponding oppositely charged counter ion is floating in the solution. We shall consider only salt-free polyelectrolyte solutions, and thus the total number of counter ions is equal to the total number of charges on the macromolecules.

Our first aim (§§ 2 and 3) will be the consideration of the intramolecular collapse of the macromolecule of a weakly charged polyelectrolyte in an extremely dilute solution, in which different macromolecules do not overlap. It was shown by de Gennes *et al* (1976) that in this case it is possible to neglect the influence of counter ions on the polyelectrolyte conformation—the Coulomb interactions of charges on a given macromolecule are not screened.

However, the polyelectrolyte always takes a strongly elongated conformation in the salt-free dilute solution (see below), and thus the macromolecules can be considered as non-overlapping only at very low concentrations, which are practically inaccessible for experimental study. Fortunately, in § 4 it will be shown that intramolecular collapse takes place in weakly charged polyelectrolytes at higher concentrations as well, and that in this case it is closely connected with the fundamental concept of counter-ion condensation (which is described, for example, by Oosawa (1971)).

It was shown by Khokhlov (1978a,b) that, as soon as the results for the model of ‘beads’ are known, there exists a simple method for obtaining the corresponding results for the more realistic persistent model. The Appendix contains the list of the results of this paper in terms of the persistent model.

2. The macromolecule of a weakly charged polyelectrolyte at the θ temperature

Let us consider first the macromolecule of a weakly charged polyelectrolyte in an extremely dilute solution of non-overlapping chains, in which according to de Gennes *et al* (1976) the counter-ion screening can be neglected. In this section we shall recall the results obtained earlier (de Gennes *et al* 1976, Pfeuty 1978) for the polyelectrolyte conformation in the absence of non-Coulomb volume interactions. In our model this case corresponds to the θ temperature with respect to these interactions.

It was found that, under the influence of the unscreened Coulomb repulsion between the monomers, the macromolecule assumes a strongly elongated non-spherical conformation (the mean square end-to-end distance $\langle R^2 \rangle \sim N^2$). Actually, if this is not the case, i.e. if $\langle R^2 \rangle \sim N^{2x}$ with $x < 1$, then the energy of the Coulomb interactions within the coil $\sim (N/\sigma)^2 e^2 / \epsilon \langle R^2 \rangle^{1/2}$ (ϵ is the dielectric constant of the solvent) is proportional to N^{2-x} , i.e. varies more rapidly than N . As a result, at $N \gg 1$ this energy will dominate all the other contributions to the free energy, and thus the coil will elongate until $\langle R^2 \rangle$ becomes proportional to N^2 . It should be noted that this result remains valid in the presence of the usual Van-der-Vaals monomer–monomer interactions.

Thus, in the sense of the dependence of $\langle R^2 \rangle$ on N , the conformation of the polyion in the very dilute solution is fully extended. In order to describe this conformation, de Gennes *et al* (1976) proposed to use the following convenient terminology. The polymer chain is represented as a sequence of blobs; each blob contains 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 neighbours along the chain is of order T :

$$g^2(e^2/\epsilon D) \sim T. \quad (1)$$

In this case it is possible to say that, on the one hand, the polymer chain inside the blob is only slightly perturbed by the Coulomb interactions, i.e.

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

and, on the other hand, the system of blobs forms an elongated conformation, whose longitudinal size is

$$L \sim (N/\sigma g)D \quad (3)$$

($N/\sigma g$ is the number of blobs in the macromolecule).

The values of g , D and L can be determined from equations (1)–(3):

$$g \sim \sigma^{1/3}/u^{2/3}, \quad (4)$$

$$D \sim a(\sigma^{2/3})/u^{1/3}, \quad (5)$$

$$L \sim Na(u^{1/3})/\sigma^{2/3}. \quad (6)$$

In the formulae (4)–(6) the notation $u \equiv e^2/\epsilon aT$ is used.

We recall that the above consideration is valid in our model only at the θ temperature with respect to the non-Coulomb interactions. Pfeuty (1978) has generalised this consideration to the good solvent region $T > \theta$, where the interaction between the neutral monomers of the weakly charged polyelectrolyte has a repulsive character. Our aim in the next section will be the determination of the polyelectrolyte conformation in the poor solvent region $T < \theta$, where the neutral monomers attract each other.

3. The collapse of the macromolecule of a weakly charged polyelectrolyte

It is clear that sufficiently strong attraction of monomers will lead to the formation of the collapsed globular state of the macromolecule (Lifshitz *et al* 1978, 1979). At the same time, however, the general statement formulated in the beginning of § 2, that the polyelectrolyte assumes a strongly elongated conformation and that $\langle R^2 \rangle \sim N^2$, remains valid. Thus in this case it is also possible to introduce the notion of a blob: the chain inside the blob assumes a globular conformation which is unperturbed by the Coulomb interactions, while the system of blobs forms an extended conformation analogous to the one considered in the previous section.

The formation of such a conformation in the uncharged globule would require, obviously, a free energy $\sim \Delta F_s$ per blob, where ΔF_s is the surface free energy of the globular blob. Thus, in the case of a globular polyelectrolyte, instead of equation (1) we have

$$g^2(e^2/\epsilon D) \sim \Delta F_s. \quad (7)$$

Equation (2) is replaced by

$$D \sim (g\sigma/n)^{1/3}, \quad (8)$$

where n is the average monomer concentration inside the globular blob.

The values of n and ΔF_s for the globular state are well known (Lifshitz *et al* 1978, 1979). As will be clear from the final results, the main interest for us will be in the case $\tau = (\theta - T)/T \ll 1$ of small relative temperature deviation from the θ point with respect to the non-Coulomb interactions. In this case the average monomer concentration inside the globule is small, and all the globule properties can be expressed in terms of the second and third virial coefficients of the monomer-monomer interaction, $B \sim -v\tau$, $C \sim v^2$ (Lifshitz *et al* 1978, 1979):

$$n \sim -B/C \sim \tau/v, \quad (9)$$

$$\Delta F_s \sim (g\sigma)^{2/3} (TB^{4/3}/C^{5/6})a \sim T(g\sigma)^{2/3} \tau^{4/3} (a^3/v)^{1/3}. \quad (10)$$

In the formula (10) we have taken into account the fact that the number of monomers in a blob is $g\sigma$.

From equations (3) and (7)–(10) we obtain for the globular polyelectrolyte macromolecule

$$g \sim \sigma\tau/u, \quad (11)$$

$$D \sim v^{1/3} \sigma^{2/3} / u^{1/3}, \quad (12)$$

$$L \sim Nv^{1/3} u^{2/3} / \sigma^{4/3} \tau. \quad (13)$$

Let us consider now the coil-globule transition in a polyelectrolyte macromolecule. It is clear from above that in the process of this transition each of $N/\sigma g$ blobs collapses approximately as the chain of $g\sigma$ monomers unperturbed by the Coulomb interactions. The characteristics of the coil-globule transition for the uncharged chains have been studied in detail (see the reviews by Lifshitz *et al* 1978, 1979). Taking into account the results quoted in these reviews we obtain, for example, that in our case the transition takes place somewhat below the θ point; the corresponding relative temperature deviation

$$\tau_c \equiv (\theta - T_c)/\theta \sim (a^3/v)^{1/2} (g\sigma)^{-1/2}, \quad (14)$$

where g can be determined from formula (11). Finally we obtain

$$\tau_c \sim (a^3/v)^{1/3} u^{1/3} / \sigma^{2/3}. \quad (15)$$

Analogously, it is easy to obtain the width of the transition,

$$\Delta T \sim \theta (v/a^3)^{2/3} u^{1/3} / \sigma^{2/3}, \quad (16)$$

the change of the blob size at the transition,

$$D_c/D_g|_{\tau=\tau_c} \sim (a^3/v)^{1/3}, \quad (17)$$

the change of the asymmetry parameter L/D at the transition,

$$(L/D)_g/(L/D)_c|_{\tau=\tau_c} \sim (v/a^3)^{1/3}, \quad (18)$$

etc. (in the formulae (17) and (18) the subscripts g and c indicate that the corresponding characteristic is taken in the globular or in the coil state).

It can be seen from formulae (15)–(18) that the coil–globule transition in the macromolecule of a weakly charged polyelectrolyte ($\sigma \gg 1$) occurs in the narrow temperature interval slightly below the θ point, and that the less is the ratio v/a^3 , the sharper is this transition.

4. The effect of the avalanche-type counter-ion condensation

As has been already noted in the Introduction, the case of completely non-overlapping polyelectrolyte macromolecules (when the average monomer concentration in the solution $c \ll N/L^3$), which was considered in the previous sections, is practically inaccessible for experimental study. From the point of view of experiment, the concentration region $g\sigma/D^3 \gg c \gg N/L^3$ is much more important. In this region, on the one hand, the macromolecules overlap strongly and, on the other hand, the solution remains dilute in the sense that the volume fraction occupied by the blobs in the solution is much less than unity (figure 1(a)). In this section we shall show that at these concentrations the collapse of the polyelectrolyte macromolecule is closely connected with the effect of the avalanche-type counter-ion condensation.

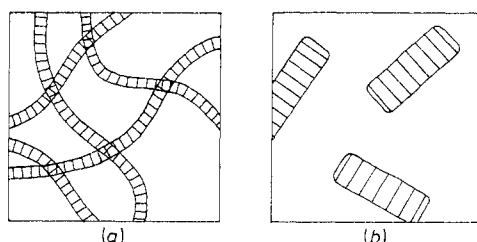


Figure 1. The structure of the polyelectrolyte solution: (a) before the avalanche-type counter-ion condensation; (b) after the avalanche-type counter-ion condensation. The shaded areas are the regions occupied by the blobs in the solution. The spatial size D of a blob is equal to the width of these regions.

In the concentration region under consideration, the total polyion conformation changes significantly in comparison with the case studied in previous sections, because of the overlapping of the macromolecules (de Gennes *et al* 1976). At the same time, the conformation of the blobs remains practically unaffected. Thus the coil–globule transition takes place in this concentration region as well, since, as was shown in § 3, this transition occurs in each blob separately. The formulae (11)–(12) and (14)–(17) connected with the local characteristics of the macromolecule (on the level of the blobs) remain valid in this case, whereas formulae (13) and (18) must be modified.

However, it should be recalled that the results of the previous sections were obtained under the assumption that the counter ions have no influence on the macromolecular conformation and, in particular, on the conformation of blobs. For the weakly charged polyelectrolyte this assumption is valid for $c \ll N/L^3$ (de Gennes *et al* 1976); however, in the concentration range $g\sigma/D^3 \gg c \gg N/L^3$ under consideration this may not be the case.

In order to study the influence of counter ions on the polyelectrolyte conformation we shall use the so-called two-phase approximation, which was described in detail by

Oosawa (1971); this approximation is known to give a rather simple and qualitatively correct picture. Let us divide the polyelectrolyte solution into two regions: region I, occupied by the blobs (the shaded region in figure 1(a)) and region II, free of polyions. Since we are considering the case $c \gg g\sigma/D^3$, the volume of region II is much more than the volume of region I, and thus if the counter ions in the solution were distributed uniformly, the fraction of them in region I would be negligible and they would have practically no influence on the blob conformation. In fact, due to the Coulomb attraction of counter ions to the oppositely charged blobs, there exists a potential difference $\delta\psi$ between regions I and II and, as a result, the concentration of counter ions inside the blobs is increased. In the two-phase approximation the potentials inside regions I and II are considered to be constant; in this case the counter ion concentrations C_I and C_{II} in regions I and II are constants as well and are connected by the Boltzmann formula

$$C_I = C_{II} \exp(e\delta\psi/T). \tag{19}$$

Let us introduce the following notation: β is the fraction of counter ions in region II, φ is the volume fraction of region I in the solution, $\varphi \ll 1$. Then equation (19) can be rewritten in the form (Oosawa 1971)

$$\ln \frac{1-\beta}{\beta} = \ln \frac{\varphi}{1-\varphi} + \frac{e\delta\psi}{T}. \tag{20}$$

It is easy to realise that the situation under study in this section ($g\sigma/D^3 \gg c \gg N/L^3$) corresponds in terms of Oosawa (1971) to the case of the cylindrical polyions (with the difference that the cylinders are composed of blobs), and thus the value of $\delta\psi$ is (see Oosawa 1971, p 18)

$$\delta\psi \cong 2(e/\epsilon)\rho \ln(R/D) \cong (e/\epsilon)\rho \ln(1/\varphi), \tag{21}$$

where ρ is the linear charge density of the chain of blobs and R is the average distance from an arbitrary point in region II to the nearest point of region I. By definition, the linear charge density is equal to $\rho = (N/\sigma')/L'$, where the primes denote the effective values of σ and L calculated with regard for the fact that some counter ions are situated in region I, and so only the fraction β of charges on the polyion remains uncompensated. It is obvious that

$$\sigma' = \sigma/\beta. \tag{22}$$

Using formulae (6) and (13), we obtain

$$L' \sim \begin{cases} Nau^{1/3}/(\sigma')^{2/3} = \beta^{2/3} Nau^{1/3}/\sigma^{2/3} & \text{at } T = \theta \\ Nv^{1/3}u^{2/3}/(\sigma')^{4/3}\tau = \beta^{4/3}Nv^{1/3}u^{2/3}/\sigma^{4/3}\tau & \text{at } T < T_c. \end{cases} \tag{23}$$

Thus

$$\frac{e\delta\psi}{T} \sim \begin{cases} \beta^{1/3}(u^{2/3}/\sigma^{1/3}) \ln(1/\varphi) & \text{at } T = \theta \\ \beta^{-1/3}u^{1/3}\sigma^{1/3}\tau(a^3/v)^{1/3} \ln(1/\varphi) & \text{at } T < T_c. \end{cases} \tag{24}$$

Substituting the expressions (24) in equation (20), and using the fact that in the concentration region under consideration $\varphi \ll 1$, we obtain

$$\ln[(1-\beta)/\beta] = (1-\beta^{1/3}Q_1) \ln \varphi \quad \text{at } T = \theta, \tag{25}$$

$$\ln[(1-\beta)/\beta] = (1-Q_2/\beta^{1/3}) \ln \varphi \quad \text{at } T < T_c, \tag{26}$$

where $Q_1 \sim u^{2/3}/\sigma^{1/3}$, $Q_2 \sim u^{1/3}\sigma^{1/3}\tau(a^3/v)^{1/3}$. It should be noted that equations (25) and (26) were obtained taking into account the fact that the variation of β induces changes in the conformation of the cylindrical polyions. This is the reason why these equations differ from the corresponding equation in Oosawa (1971), where the conformation of the polyion was considered to be fixed.

Analysing equations (25) and (26) analogously to the analysis of the corresponding equation by Oosawa (1971, p 19), it is possible to draw the following conclusions.

At $T = \theta$ the influence of counter ions on the macromolecular conformation is not essential. Actually, $Q_1 \ll 1$ at $\sigma \gg 1$, and thus, as can be seen from equation (25), $1 - \beta \ll 1$ (since $\varphi \ll 1$) i.e. the fraction of counter ions in region I is small.

After the transition of the macromolecule in the globular state (at $T < T_c$) the situation changes drastically. First of all, it can be seen from the definition of Q_2 that at $\tau = \tau_r$, where

$$\tau_r \equiv \frac{\theta - T_r}{\theta} \sim \left(\frac{v}{a^3}\right)^{1/3} \frac{1}{u^{1/3}\sigma^{1/3}}, \quad (27)$$

the value of Q_2 becomes equal to unity. But in the region $Q_2 \geq 1$ (and, consequently, in the region $\tau \geq \tau_r$) equation (26) has no solutions even at $\varphi \ll 1$. This fact can be explained as follows. In the globular state the value of $\rho = (N/\sigma')/L'$ is proportional to $\beta^{-1/3}$ (see formulae (22) and (23)). It means that the decrease of β , i.e. the increase of the counter-ion fraction in region I, leads, nevertheless, to the increase of the linear charge density in this region and, consequently, induces an additional increase in the number of counter ions in region I etc. The avalanche-type process sets in; this process can be called the avalanche-type counter-ion condensation. This process stops only after the moment when the uncompensated charge on the macromolecule becomes so small that the inequality $c \gg N/L^3$ (and, consequently, equations (21) and (26)) become invalid (it is easy to understand that in the case $\varphi \ll 1$ such a moment will actually take place).

As a result of the avalanche-type counter-ion condensation the conformation of polyelectrolyte macromolecules changes significantly: instead of the solution of partially entangled long chains of globular blobs of relatively small size (figure 1(a)), we have the solution of non-overlapping globules with the much smaller asymmetry parameter (figure 1(b)). It should be noted that the precipitation of this solution is possible but, due to the presence of the residual charges on the globules, the region of concentrations at which the precipitation does not take place is in any case much larger than for the uncharged macromolecules.

Thus the fact that equation (26) has no solutions at $Q_2 \geq 1$ means that at these values of Q_2 the avalanche-type counter-ion condensation occurs. It can be seen from formula (27) that if $\sigma \gg 1$ then $Q_2(\tau_r) = 1$ at $\tau_c \ll \tau_r \ll 1$, i.e. the additional lowering of the temperature below the temperature T_c of the coil-globule transition is necessary in order to reach the point T_r . Consequently the region $\tau_c < \tau < \tau_r$ exists in which, on the one hand, the macromolecules are in the globular state and, on the other hand, the avalanche-type counter-ion condensation does not occur.

It should be noted, however, that in this region the solution is metastable: if as a result of the fluctuations the linear charge density in some part of the macromolecule reaches the value corresponding to $Q_2 = 1$, then avalanche-type counter-ion condensation on this macromolecule takes place.

Thus the polyelectrolyte solution is stable with respect to the avalanche-type counter-ion condensation only at $T > T_c$. Below the temperature T_c of the coil-globule

transition the metastable region $T_r < T < T_c$ exists. At $T < T_r$ the solution shown in figure 1(a) is absolutely unstable, and as a result of the avalanche-type counter-ion condensation it comes to the state shown in figure 1(b).

Unfortunately, systematic experiments dealing with weakly charged polyelectrolytes in poor salt-free solutions are unknown to the author. Such experiments would allow us to check the theoretical predictions of this paper.

Appendix: The results for the persistent model

In the persistent model (see, for example, Lifshitz *et al* 1979) the polymer chain is represented as an elastic self-interacting filament of width d and persistent length l . So, instead of the parameters ν and a , in this model the chain structure is characterised by the parameters d and l . It was shown by Khokhlov (1978a,b) that the persistent chain consisting of N 'monomers' (we call the part of the chain whose length along the chain $\sim d$ the 'monomer'), from the point of view of the macroscopic properties, is equivalent to the effective chain of 'beads' with parameters

$$N' \sim Nd/l, \quad a' \sim l, \quad B' \sim -dl^2\tau, \quad C' \sim d^3l^3, \quad (\text{A1})$$

where $\tau = (\theta - T)/T$ is the relative temperature deviation from the θ point. Using the formulae (A1) it is possible to rewrite the results of this paper in terms of the persistent model.

Let us assume that the chains of the polyelectrolyte macromolecules are persistent chains with parameters N , d , l . Let $\sigma \gg 1$ be the number of monomers between two charges which are subsequent along the chain, and let $u \equiv e^2/\epsilon dT$, $p \equiv l/d$. The results listed below are valid only if $g\sigma \gg p$, i.e. if the chain inside a blob contains a large number of persistent lengths (otherwise the polyelectrolyte cannot be considered as a weakly charged one).

A.1.1. Characteristics of the macromolecule of a weakly charged polyelectrolyte in the extremely dilute solution (compare with §§ 2 and 3).

(a) at the θ temperature:

$$g \sim \frac{\sigma^{1/3} p^{1/3}}{u^{2/3}}, \quad D \sim d \frac{\sigma^{2/3} p^{2/3}}{u^{1/3}}, \quad L \sim Nd \frac{u^{1/3} p^{1/3}}{\sigma^{2/3}};$$

(b) for the globular state ($T < T_c$):

$$g \sim \frac{p^{1/2} \sigma \tau}{u}, \quad D \sim d \frac{p^{1/6} \sigma^{2/3}}{u^{1/3}}, \quad L \sim Nd \frac{u^{2/3}}{\tau p^{1/3} \sigma^{4/3}};$$

(c) the characteristics of the coil-globule transition:

$$\tau_c \sim \frac{p^{1/3} u^{1/3}}{\sigma^{2/3}}, \quad \Delta T \sim \theta \frac{u^{1/3}}{\sigma^{2/3} p^{7/6}}, \quad \left. \frac{D_c}{D_g} \right|_{\tau=\tau_c} \sim p^{1/2}, \quad \left(\frac{L}{D} \right)_g / \left(\frac{L}{D} \right)_c \Big|_{\tau=\tau_c} \sim p^{-1/2}.$$

The greater the value of p , i.e. the stiffer the persistent chain, the sharper the coil-globule transition will be.

A1.2.

The equations connecting β and φ have in this case the form (25)–(26) with $Q_1 \sim u^{2/3}/\sigma^{1/3}p^{1/3}$ and $Q_2 \sim \tau(u\sigma p)^{1/3}$. Hence instead of formula (27) we obtain $\tau_r \sim (u\sigma p)^{-1/3}$. In other respects the consideration of § 4 remains unchanged.

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