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Collapse of Polyelectrolyte Macromolecules Revisited

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ABSTRACT: The simplest theory of the collapse transition of single polyelectrolyte chains in dilute solutions is reconsidered. A novel feature of the new treatment is that the counterions can either remain within the coil or float in the outer solution. It is shown that the latter possibility is realized in many cases; thus, for these situations, the electrostatic repulsion between the uncompensated charges plays an important role in the chain behavior. These uncompensated charges lead to a significant difference between the collapse behavior of single chains and macroscopic gels where electrostatic repulsion is normally negligible and the swelling is mainly due to the osmotic pressure of counterions kept inside the gel sample. In addition the intermediate case of microgel particles of different molecular masses is considered, and the role of counterion redistribution between polymer and solution is investigated.

I. Introduction

The phenomenon of the coil−globule transition plays an important role in many processes in polymer systems. A consistent theoretical description of this transition has been developed in the papers of Lifshitz et al.[1−3] It now appears that the coil-globule transition forms the basis of many phenomena in polymer physics.[1−4]

One example of such phenomena is the collapse of polymer gels. Just after its experimental discovery in 1978 in ref 5, it was realized that the collapse is a manifestation of the coil−globule transition for the chains constituting the gel: each chain undergoes this transition, and as a result the gel sample collapses as a whole.[4−6]

While it is rather difficult to observe experimentally the coil−globule transition in a single polymer chain because of interchain aggregation below the Θ-point, polymer gels represent a very convenient system to investigate this transition on a macroscopic level. The influence of external conditions on the chain conformation can be easily monitored by the change of the gel volume. This fact and a large variety of applications have stimulated many experimental works devoted to the problem of swelling and collapse of polymer gels in various solvents.[7,8] Simultaneously, the theoretical description developed for the single-chain problem has been successfuly applied to the case of polymer gel collapse[6] and has been further extended to weakly charged polyelectrolyte gels.[8,9] It was shown that the presence of charges on the gel chains plays a crucial role in the character of the gel collapse: for charged gels it occurs as a jumplike first-order phase transition while for neutral gels it is usually continuous.

Recently, the approach developed for polyelectrolyte networks has been applied to describe the compaction of a single DNA chain in poly(ethylene oxide) solutions.[10]

In this connection one question arises: whether there is a direct correspondence between the swelling and collapse behavior of polyelectrolyte gels and single charged macromolecules in dilute solutions and whether one can apply the results obtained for gels to the problem of a single chain?

In theories describing collapse transitions in polyelectrolyte gels the condition of total electroneutrality of gels is usually used, i.e. it is assumed that in salt-free solutions all the mobile counterions of a network remain inside the network sample and their number is therefore equal to the number of charges on the gel chains. It was shown that it is the osmotic pressure exerted by these counterions that causes the high degree of swelling of the gel in good solvents and is also responsible for the discreteness of the transition to the collapsed state when the solvent quality becomes poorer.[8]

However, if we consider a single macromolecule in a dilute solution, we can hardly assume that the chain is electroneutral; this is a microscopic object and some fraction of counterions may move to the outer solution. It appears that this fact influences significantly the conformation of the single polyelectrolyte chain. Whereas one could imagine that it would lead to expansion of the chain due to electrostatic interactions, in fact, as we show below, the size of the chain in the coil state decreases when it loses its counterions. Furthermore, the character of the collapse transition is now different between a single polymer and a gel: for linear polymers the collapse transition becomes smoother and can proceed continuously with the change of the solvent quality in contrast to the jumplike collapse behavior of corresponding polyelectrolyte gels. The difference in the behavior of gels and single macromolecules was also mentioned in ref 11.

In this paper we do not consider the detailed structure of the collapsing chain and the detailed distribution of counterions inside the volume occupied by the macromolecular coil (or globule) as was done in ref 12. We distinguish only two states of counterions: inside or outside the polymer coil (globule). We investigate how the redistribution of counterions between the polymer and the solution influences the chain conformation and the character of the collapse transition, and we describe this effect using the simplest possible theory.

In the next section, we propose a simple model of a weakly charged polyelectrolyte chain in a dilute solution and write down the free energy of the system taking into account the possibility that the chain may lose its counterions. In section 3 we present the results of our calculations. In section 4 we generalize the theory to the case of a dilute solution of microgels composed of

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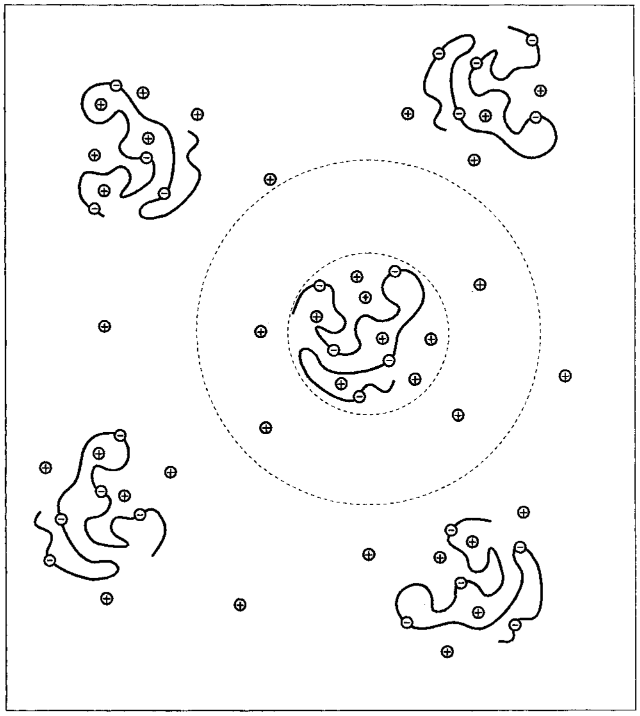

Figure 1. Schematic representation of a dilute polyelectrolyte solution.

different numbers of subchains, and we show that the behavior of the microgels differs significantly from that of macroscopic gels as well as single chains.

II. The Model

Let us consider a dilute solution of weakly charged flexible chains consisting of N monomeric units with a characteristic size a (a schematic picture of the system under consideration is presented in Figure 1). We will deal with weakly charged polyelectrolytes which are formed by copolymers containing neutral monomer units (for instance, acrylamide units) and a small fraction of ionized units (such as sodium methacrylate units) carrying a charge e. Thus, the position of charges along the chains is fixed. The total charge of a chain does not depend on pH and is defined by the number of charged units in the chain. Let N/σ be the total number of charges in each macromolecule; i.e., σ is the number of monomeric units between two nearest charged groups. We consider the case of a salt-free solution; thus, the only mobile ions in the system are the counterions which appear due to dissociation of monomeric units of the chains. The number of counterions per chain is equal to the number of charged groups on the chain, i.e. to N/σ.

We consider a dilute polymer solution; i.e., polymer chains do not overlap, and thus they do not interact with each other. Here we are interested in the properties of an isolated macromolecule surrounded by a solvent. The volume of the solvent per chain, V_{out}, is defined by the total polymer concentration in the system, c : $V_{\text{out}} = N/c$.

The free energy of a single polymer chain can be written as a sum of four terms:

$$F = F_{\text{el}} + F_{\text{int}} + F_0 + F_{\text{el-st}} \qquad (1)$$

The first term in this expression, F_{el}, is the elastic free energy. We write it in the Flory form,[13] modified by Birshtein and Pryamitzyn[14] to take into account the entropy loss due to expansion of the chain in good solvents as well as that due to compression of the chain in poor solvents.

$$F_{\text{el}} = 3kT/2(\alpha^2 + 1/\alpha^2) \qquad (2)$$

where k is the Boltzmann constant, T is the temperature, and α is the swelling coefficient of the chain with respect to the corresponding Gaussian coil, $\alpha = R/R_0$, R is the equilibrium radius of the chain, and R_0 is the radius of the Gaussian coil, $R_0 = N^{1/2}a$.

The next term in eq 1, F_{int}, is the free energy of interaction of the monomer units of the chain. We write it in the form of virial expansion in powers of the concentration of monomer units within the coil, n:

$$F_{\text{int}} = kTNBn + kTNCn^2 \qquad (3)$$

where B and C are the second and the third virial coefficients.

The value of n is connected with the swelling ratio of the chain, α, through

$$n = \frac{n_0}{\alpha^3} \qquad (4)$$

where n_0 is the concentration of monomer units in the Gaussian coil, $n_0 = (3/4\pi)N^{-1/2}a^{-3}$.

We assume that the polymer chains are flexible; then a is the only characteristic length, and the following estimates for the virial coefficients are valid not far from the Θ-point[4]

$$B \sim a^3\tau,\ C \sim a^6$$

where τ is the relative temperature deviation from the Θ-point, $\tau = (T - \Theta)/\Theta$.

It should be mentioned that expression 3 is valid at low polymer concentrations. This is indeed the case in good solvents and near the transition point to the collapsed state in slightly poor solvents. Far from the Θ-point in the extremely poor solvent the density can be rather high, and one needs to use more exact expressions; for instance, this contribution can be written in the framework of the Flory–Huggins approximation.[4] However, the specific form of the expression for the contribution F_{int} does not influence the qualitative conclusions of the present paper. Thus, below we will use the approximate expression 3 for all values of τ.

Finally, the last two terms in expression 1, F_0 and $F_{\text{el-st}}$, account for the main contributions connected with the charges on the chain. The total number of counterions per one chain is equal to the number of charges on the chain, i.e., N/σ. Let us denote the fraction of counterions which are inside the coil as β; their number is equal to $\beta N/\sigma$. Then the number of counterions which are in the region outside the chain is $(1 - \beta)N/\sigma$. In the free energy we have to take into account the contribution from the translational entropy of counterions both inside and outside the chain. Let us denote this contribution as F_0. Besides, movement of counterions from the interior of the polymer to the solution leads to the appearance of noncompensated charge on the chain and hence to an additional energy of Coulombic interactions, $F_{\text{el-st}}$. The simplest way to express this last contribution is in terms of the energy of a spherical condenser with charge $(1 - \beta)Ne/\sigma$. The radius of the inner electrode of this condenser is of the order of the mean size of the polymer coil, R, and the radius of the outer electrode can be estimated as $R_{\mathrm{out}} \sim V_{\mathrm{out}}^{1/3}$. A similar approach has been appllied to other polyelectrolyte systems in ref 15 and 16.

Taking into account all these contributions, we obtain for F_0 and $F_{\mathrm{el-st}}$ the expressions

$$\frac{F_0}{kT} = \frac{N}{\sigma}\beta \ln\left(\frac{n_0\beta}{\sigma\alpha^3}\right) + \frac{N}{\sigma}(1-\beta)\ln\left(\frac{n_0(1-\beta)}{\sigma(1/\gamma^3 - \alpha^3)}\right) \quad (5)$$

$$\frac{F_{\mathrm{el-st}}}{kT} = \left(\frac{N}{\sigma}(1-\beta)\right)^2 uN^{-1/2}\left[\frac{1}{\alpha} - \gamma\right] \quad (6)$$

using the notations $\gamma = R_0/R_{\mathrm{out}}$ and $u = e^2/\alpha\epsilon kT$. The parameter u is on the order of unity under normal conditions (for aqueous solutions, $\epsilon \sim 81$, room temperatures, $T \sim 300\ K$, and $a \sim 1$ nm). The parameter γ characterizes the degree of dilution of the polymer solution, and $\gamma \ll 1$ for very dilute solutions.

The equilibrium value of the swelling ratio of the chain and the fraction of counterions inside the chain can be obtained by minimizing the total free energy expressed by eqs. 1–6 with respect to α and β.

The conditions $\partial F/\partial\alpha = 0$ and $\partial F/\partial\beta = 0$ lead to the following system of two equations:

$$\frac{\beta}{1-\beta}\,\frac{1-\gamma^3\alpha^3}{\gamma^3\alpha^3} = \exp\left(2\frac{N^{1/2}}{\sigma}(1-\beta)u\left[\frac{1}{\alpha} - \gamma\right]\right) \quad (7)$$

$$\alpha^5 - \alpha - BNn_0 - \frac{2CNn_0^{\,2}}{\alpha^3} - \frac{N}{\sigma}\beta\alpha^3 + \frac{N(1-\beta)\alpha^6\gamma^3}{\sigma(1-\alpha^3\gamma^3)} - \frac{N^{3/2}}{3\sigma^2}(1-\beta)^2u\alpha^2 = 0 \quad (8)$$

For the limiting case $\beta = 1$, i.e. for the case when all the counterions are within the coil, the system of eqs 7 and 8 reduces to one equation that defines the equilibrium value of the swelling ratio α:

$$\alpha^5 - \alpha - BNn_0 - 2CNn_0^{\,2}/\alpha^3 - \frac{N}{\sigma}\alpha^3 = 0 \quad (9)$$

Equation 9 coincides with the equation defining the swelling degree of a polyelectrolyte gel.[4]

Equations 7–9 were solved numerically, and the results are presented in the next section.

III. Swelling and Collapse of Single Chains in a Dilute Solution

The analysis of the system in eqs 7 and 8 shows that at low polymer concentrations when $\gamma\alpha < 1$ the parameter β is close to zero. It means that the condition of electroneutrality of the single chain is totally violated: the counterions are not held within the polymer coil; the entropic contribution to the free energy of the mobile counterions dominates over the electrostatic interactions, and practically all the counterions exit the coil.

This leads to a drastic change in the swelling behavior of the chain compared with the case when $\beta = 1$. In Figure 2 we show the dependence of the swelling ratio α on the parameter τ for $\gamma = 0.001$ and two different degrees of ionization of the chain, $\sigma = 100$ and $\sigma = 50$. For comparison we also show in Figure 2 the corresponding behavior of α in the case $\beta = 1$ which is defined by eq 9; these curves describe the swelling of a polyelectrolyte gel.

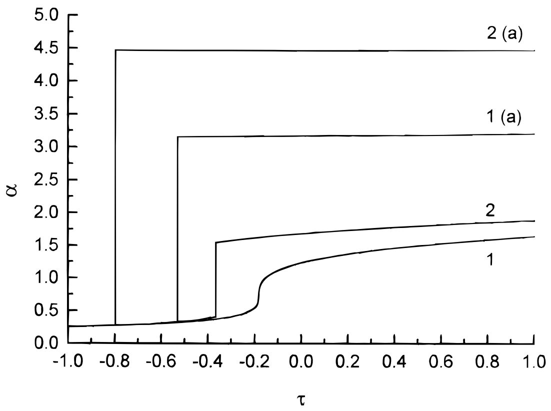

Figure 2. Dependence of the swelling ratio, α in the linear polymer, on the relative temperature deviation from the Θ-point, τ, for the following values of the parameters: $N = 1000$, $u = 1$, $C/a^3 = 1$, $\gamma = 0.001$, and $\sigma = 100$ (curve 1) and $\sigma = 50$ (curve 2). Curves 1a and 2a correspond to the case $\beta = 1$ and $\sigma = 100$ and $\sigma = 50$, respectively.

One can see that removal of the counterions of the chain leads to a significant decrease in its dimension in good solvents. The swelling ratio of the chain is significantly smaller than that for corresponding subchains of a gel for which $\beta = 1$.

This effect can be explained as follows. Since all the counterions leave the chain, the conformation is defined by electrostatic repulsion between charges along the chain. In this case the chain can be represented as a sequence of "blobs".[4,17] Indeed, eq 8 leads to the following estimate for the swelling ratio in good solvents (for $\beta = 0$ and $\alpha \gg 1$ one can neglect in eq 8 all the terms except the first and the last ones):

$$\alpha \sim N^{1/2}u^{1/3}\sigma^{-2/3} \quad (10)$$

Hence for the equilibrium radius of the chain we obtain

$$R \sim Nau^{1/3}\sigma^{-2/3} \quad (11)$$

This result is consistent with the "blob" picture[4,17] and gives an increase of the macromolecular dimensions due to electrostatic repulsion.

On the other hand, for the case of $\beta = 1$ the main reason for the increase of α is the osmotic pressure of counterions rather than the direct Coulomb repulsion. For this case we obtain from eq 9 the following estimate for the swelling ratio and for the equilibrium radius of the chain:

$$\alpha \sim \sqrt{\frac{N}{\sigma}} \quad (12)$$

$$R \sim Na\sigma^{-1/2} \quad (13)$$

One can see that for $\sigma \gg 1$ the swelling ratios for $\beta = 0$ and $\beta = 1$ differ significantly; the osmotic pressure leads to a much higher degree of swelling than electrostatic interactions.

On the other hand, in poor solvents, the value of the swelling ratio of the chain is defined by non-Coulomb interactions of uncharged monomer links described by the virial coefficient B and C, and the swelling degree α does not depend strongly on the value of β. Therefore the amplitude of the collapse transition becomes smaller.

In addition it should be mentioned that the transition point between the swollen and collapsed states of the chain and the character of this transition depends

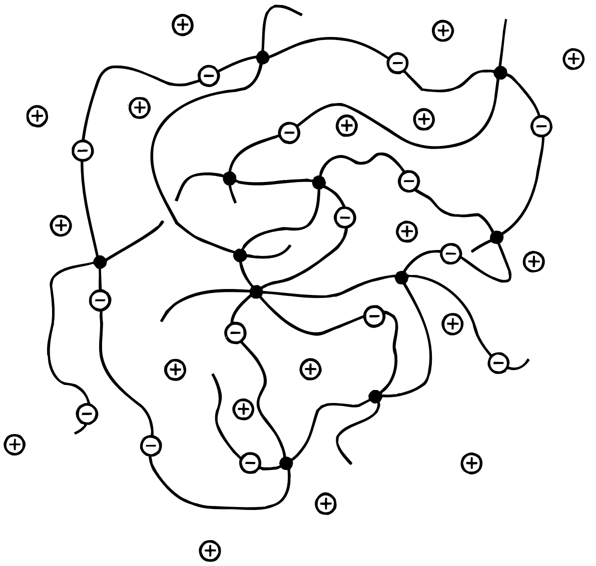

Figure 3. Schematic representation of a microgel particle.

essentially on whether counterions are inside the polymer coil or if they have left for the outer solution region. When $\beta \sim 0$ the transition occurs at higher temperatures than for the case $\beta = 1$, and also the amplitude of the collapse is smaller and in some cases the character of the transition becomes continuous in contrast to a jumplike first-order phase transition for $\beta = 1$ (cf curves 1 and 1a in Figure 2).

It should be noted that curves 1 and 2 in Figure 2 were calculated for an isolated polymer chain. Recently, it has been shown that the results obtained for the collapse of individual chains do not necessarily coincide with the observations of an ensemble of such chains.[18] There should be a significant broadening of the collapse transition for the ensemble average. This theoretical result has been confirmed by the comparison of experimental observations for long DNA chains with fluorescence microscopy and light scattering: while the former method showed the discrete transition,[10,19−21] the latter experiments reveal continuous changes.[22−24] Such behavior was demonstrated for the collapse of long DNA's induced by a neutral polymer (PEG),[10] surfactant,[19,20] multivalent metal cations,[21] and a polyamine.[18] This additional broadening of the collapse transition when it is observed by "ensemble average" methods will further reduce the abruptness of the collapse in Figure 2.

We have considered above a salt-free polymer solution. Addition of some amount of salt leads to the screening of electrostatic interactions. For the case of a polyelectrolyte gel it has been shown (see, for instance, ref 8) that an increase of salt concentration causes a gel deswelling in good solvents and smoothing of the collapse transition. We expect the same tendency for a polyelectrolyte chain, so that at high salt concentrations the difference between the degrees of swelling of the chain and of the corresponding gel should diminish in comparison with that of the salt-free solution (both swelling degrees should correspond to the swelling of a neutral gel in the limiting case). More detailed analysis of the influence of electrostatic screening on the chain behavior will be presented in a separate publication.

IV. Swelling and Collapse Behavior of Microgels

In addition to the collapse of linear chains and macroscopic gels, recently much attention has been paid to the conformational changes of microgel particles.[25,26] Such particles are intermediate between linear chains and macroscopic gels: they normally can be represented as a collection of elastic chains, some of these chains forming a gel framework, while the other chains are pendant (Figure 3). With an increase in the total number of chains, the fraction of pending chains is expected to decrease.

It is therefore tempting to try to develop a theory of the collapse of such microgel particles which would parallel the transition between curves 1 and 2 and curves 1a and 2a in Figure 2. In accordance with Figure 3 we assume that the microscopic gel consists of ν subchains each of N monomeric units.

The free energy of a single microgel is analogous to that of a single chain (see eq 1):

$$F = F_{\mathrm{el}} + F_{\mathrm{int}} + F_0 + F_{\mathrm{el-st}} \tag{14}$$

$$F_{\mathrm{el}} = 3\nu kT/2(\alpha^2 + 1/\alpha^2) \tag{15}$$

$$F_{\mathrm{int}} = kT\nu NBn + kT\nu NCn^2 \tag{16}$$

$$\frac{F_0}{kT} = \frac{N\nu}{\sigma}\beta \ln\left(\frac{n_0\beta}{\sigma\alpha^3}\right) + \frac{N\nu}{\sigma}(1-\beta)\ln\left(\frac{n_0(1-\beta)}{\sigma(1/\gamma^3 - \alpha^3)}\right) \tag{17}$$

$$\frac{F_{\mathrm{el-st}}}{kT} = \left(\frac{N}{\sigma}(1-\beta)\right)^2 \nu^{5/3} u N^{-1/2}\left[\frac{1}{\alpha} - \gamma\right] \tag{18}$$

We use the same notations as in the previous section so that the case $\nu = 1$ corresponds to the situation of a single chain. The swelling ratio of the gel, α, is defined with respect to the reference state in which all the gel subchains are close to Gaussian coils, so that the concentration of the monomeric units within the gel is of the same order as in the ideal chain, n_0, and $\alpha = (n_0/n)^{1/3}$.

The swelling ratio, α, and the fraction of counterions inside the microgel, β, for microgels with different number of subchains, ν, as functions of τ are shown in Figure 4. One can see that if we increase the value of ν the polymer retains inside itself more and more counterions, and the value of β increases and tends to unity, so for rather large particles the condition of electroneutrality holds very well.

The value of β is higher in the globular state and the collapse of the gel is thus accompanied by some kind of "counterion condensation" on the microgel: the fraction of counterions inside the gel increases in a jumplike fashion when the gel shrinks.

It should be mentioned that the swelling ratio of a gel in a good solvent changes non-monotonously with an increase of the number of the subchains (Figure 4). This fact is clearly seen also in Figure 5 where we present the functions $\alpha(\nu)$ and $\beta(\nu)$ for $\tau = 1$, with a constant polymer concentration $\gamma = 0.001$ and three different degrees of ionization. While the value of β increases monotonously with an increase in the number of the gel subchains, the dependence of the swelling ratio, α, on ν has a maximum at some value of ν. This maximum shifts to smaller values of ν with an increase of the ionization degree of the gel chains.

This nonmonotonous behavior of the swelling ratio with change of ν is due to the different distribution of counterions between the interior of the microgel and the outer solution for microgel particles of different molecular masses. In the case of small particles, i.e. particles with small numbers of subchains, the value of β is close

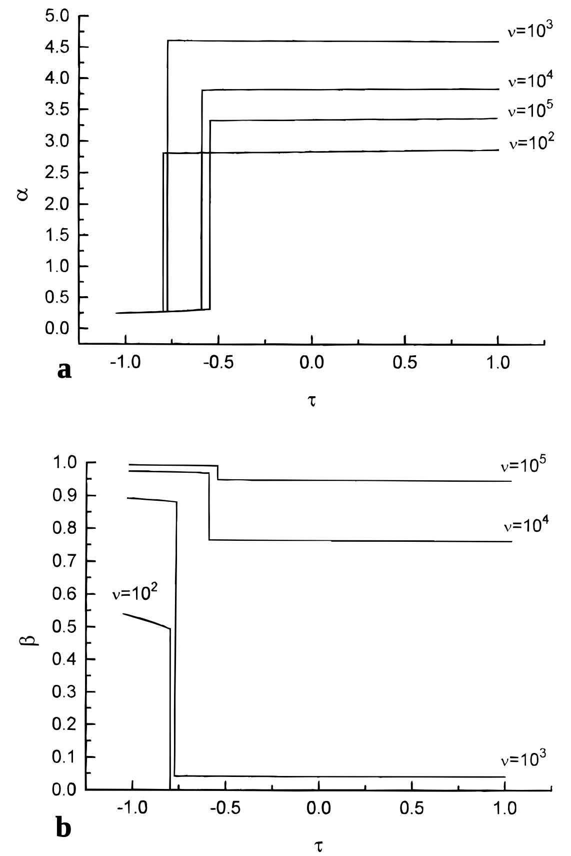

Figure 4. Dependence of the swelling ratio, α in the microgel (a) and the fraction of counterions inside the microgel, β (b), on τ for $N = 100$, $u = 1$, $C/a^3 = 1$, $\sigma = 100$, and $\gamma = 0.001$ and for different number of the microgel subchains, ν.

to zero (Figure 5b). This means that most of counterions leave the gel for the outer solution. Thus, the initial growth of the swelling ratio at small values of ν is connected with an increase in the uncompensated electrostatic repulsion for larger microgel particles. In this case, the swelling ratio of the microgel is defined by the interplay of elastic free energy and the energy of Coulombic repulsion between the charges on the subchains, and we obtain the following estimate for α:

$$\alpha \sim N^{1/2} u^{1/3} \sigma^{-2/3} \nu^{2/9} \tag{19}$$

On the other hand, with increasing ν, more and more counterions are trapped within the gel. Thus the electrostatic repulsion between the gel subchains decreases and the gel volume begins to decrease as well at large values of ν (Figure 5a). It is worth noting that at large ν the value of β is close to unity and we reach the regime of macroscopic gel swelling. In this case, the behavior of the gel is described by the swelling of one subchain, and α is independent of ν and is defined by eq 12.

The swelling ratio, α, and the fraction of counterions inside the gel, β, depend critically on the polymer concentration. The dependencies of α and β on the parameter γ which is proportional to the one-third power of polymer concentration are shown in Figure 6. An increase of polymer concentration leads to an increase in the fraction of counterions inside the gel and hence to the screening of electrostatic interactions. This fact leads to the decrease of the gel dimensions (Figure 6b).

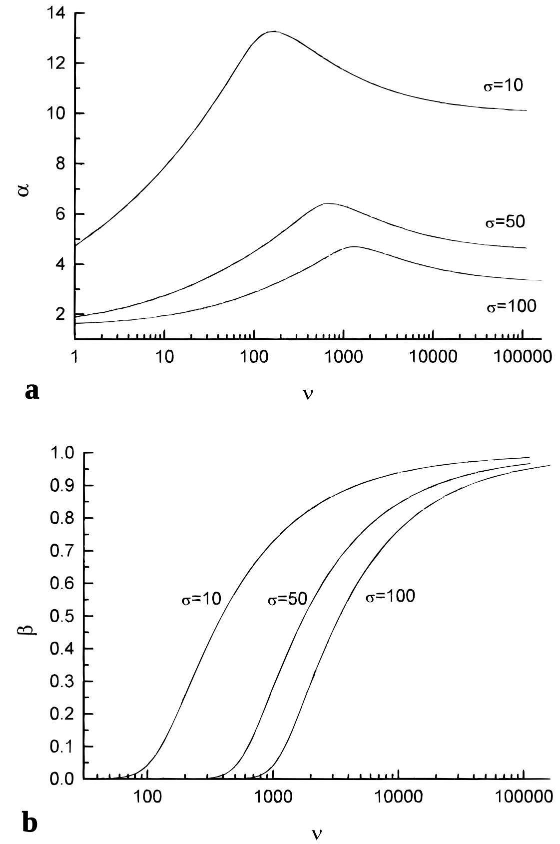

Figure 5. Dependence of the swelling ratio, α (a), and the fraction of counterions inside the microgel, β (b), on the number of the microgel subchains, ν, for $N = 1000$, $u = 1$, $C/a^3 = 1$, $\gamma = 0.001$, and $\tau = 1$ and for different degrees of charging of the gel, $\sigma = 10, 50, 100$.

V. Conclusion

In this paper we tried to propose a unified model to describe and to compare the swelling properties of single polyelectrolyte chains in a dilute solution, microgel particles of various molecular masses and as a limiting case—macroscopic gels. We were paying main attention to one key effect, namely the redistribution of counterions between the interior of a polymer coil and the outer solution. We wanted to concentrate on this main effect in the framework of a simplest model without going into the details of the polymer chain structure. Our estimations show that the introduction of an additional parameter in our model to describe independently the elongation and the width of the chain does not reveal any qualitatively new features of the system under consideration. For instance, an approximation of the chain by a cylinder leads to insignificant changes in the free energy of electrostatic interaction (a new logarithmic factor). Thus, the main qualitative features of the swelling ratio of the chain are unchanged.

In the present article, we have shown that the manner in which the collapse transition occurs will be significantly different for a linear polyelectrolyte and a charged gel, even for the case of similar chain structures. It should also be interesting to examine experimentally the size effect on the collapse transition in polymer gels. Although research on the coil—globule transition has a rather long history, the intrinsic features of the phase-transition in a single polyelectrolyte have been revealed only recently. Thus, further study of the physicochemical properties of charged polymers may be usefully pursued based on the present

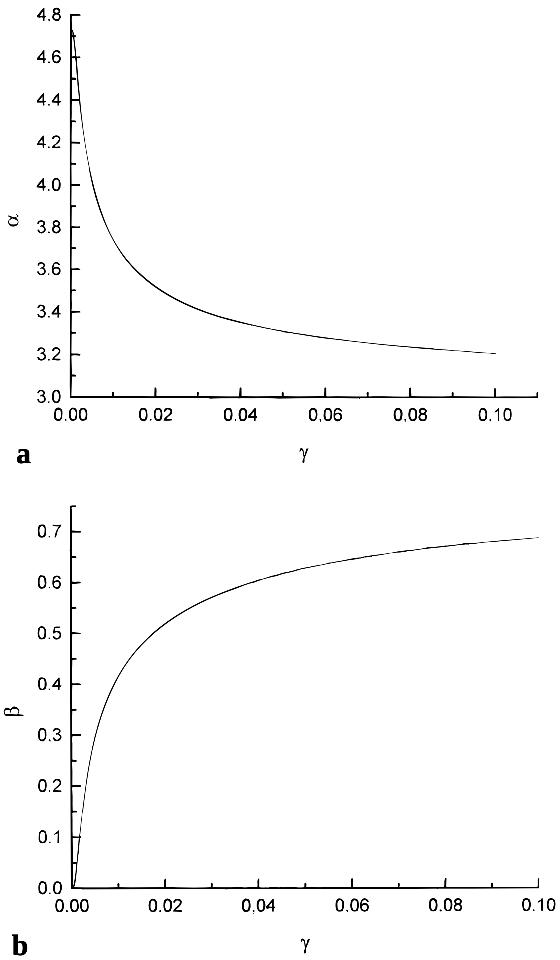

Figure 6. Dependence of the swelling ratio, α (a), and the fraction of counterions inside the microgel, β (b), on the parameter γ, for $N = 1000$, $u = 1$, $C/a^3 = 1$, $\nu = 1000$, $\tau = 1$ and $\sigma = 100$.

theoretical results of the differences and similarities between linear polyelectrolytes and charged gels.

It seems appropriate also to briefly mention two yet unsolved problems in this area.

1. Large differences are expected in the tightly collapsed states of a linear polymer and a gel. As has been found recently, single linear polyelectrolyte chains form a regular packing or a single molecular crystal through the process of nucleation and growth. On the other hand, there should be many defects in the collapsed state of a gel, due to cross-linking. This implies that the most dense packing is possible in a linear polymer chain, whereas a chain network will be compacted in a less dense manner.

In the elongated state, a linear polyelectrolyte can swell much more than $R \sim N^{3/5}$. On the other hand, swelling of the gel is restricted by cross-linking. This means that in the elongated state the swelling factor will be larger in the linear chain than in the gel. For the coil state, this should bring a tendency opposite to that described in the present paper. A more detailed consideration on these effects is necessary for the subsequent theoretical problem.

2. For highly charged polymers the nonlinear effects connected with the Manning counterion condensation become important. From our recent experimental studies on DNA chains, the negative charges along the chain almost disappear with the discrete coil–globule transition.[27] Thus, inclusion of the effect of counterion bridging and/or condensation is necessary for the precise discussion of the collapse transition. Actually, in charged gels, the effect of the enhanced counterion condensation is likely to be important in the recent studies.[28,29]

Study of the interplay of both the loss of counterions to the outer solution and the effect of counterion condensation and the formation of ion pairs are planned.

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