

Counterion-Condensation-Induced Collapse of Highly Charged Polyelectrolytes

H. Schiessel*[†] and P. Pincus^{†‡}

Materials Research Laboratory and Departments of Materials and Physics, University of California, Santa Barbara, California 93106-5130

Received May 26, 1998; Revised Manuscript Received August 18, 1998

ABSTRACT: Dilute or semidilute solutions of polyelectrolytes show below a critical temperature the phenomenon of counterion condensation. This effect leads (a) to a decrease of the effective total charge of the macroion and (b) to a counterion-induced attraction between different parts of the chain. In this paper we provide simple scaling arguments that allow one to calculate the chain size and the effective total charge as a function of temperature, solvent quality etc. Especially we show that effect (a) alone leads to a continuous reduction of the chain size with decreasing temperature. Due to a feedback-type mechanism effect (b) amplifies this collapse process in such a way that it is reminiscent of a first-order phase transition.

I. Introduction

Despite their fundamental importance in biology (DNA, proteins, ...) as well as in technological applications (hydrosolubility, solution thickening, ...) charged polymers, called polyelectrolytes, are still much less understood systems than their neutral counterparts.^{1,2} This is due to the fact that in charged systems one has to deal with the long-ranged Coulombic interaction between the charges. Nevertheless, for the "academic" case of a single polyelectrolyte chain (infinite dilution) its conformational properties can be understood using simple scaling arguments.^{1,3} The stretching of the chain due to the electrostatic repulsion is predicted; with decreasing temperature, this effect is more and more enhanced since the effect of chain entropy becomes less important.

It is important to note that these approaches do not account for the presence of counterions. In any realistic situation one has a finite concentration of chains and—due to the overall electroneutrality of the solution—also a finite number of small counterions. At high temperatures the translational entropy of the counterions dominates and their interaction with the macroions can be neglected. At lower temperatures, however, the counterions are drawn more and more toward the oppositely charged chains leading to counterion condensation.^{1,4} The presence of the condensed counterions affects the single chain properties drastically: With decreasing temperature the macroions begin to collapse, a fact which is observed in computer simulations.^{5–7} Similarly, multichain effects come into play. Thus it was demonstrated theoretically and by computer simulations that two parallel like-charged rods begin to attract.^{8,9} Furthermore, experimentally the precipitation of a highly charged polyelectrolyte solution is observed upon adding multivalent salt.¹⁰ This is also in accordance with a theoretical study by González-Mozuelos and Olvera de la Cruz¹¹ where it is shown that polyelectrolytes are stretched at higher temperatures and collapsed at low temperatures.

It is the purpose of the present work to give a simple scaling approach that allows one to derive the different scaling regimes of the single chain properties of a dilute solution of highly charged polyelectrolytes. In the next section we combine the single chain theories^{1,3,12} and the idea of charge renormalization due to counterion condensation¹³ in a self-consistent manner. This approach is oversimplified in so far as it does not account for an additional counterion-mediated short-range interaction. In section 3 we take this effect into account and find again simple scaling relations which, however, depend on microscopic properties of the system.

II. Effect of the Charge Renormalization

Consider a dilute solution of polyelectrolytes; assume the solvent to be a Θ -solvent for the uncharged backbones. Denote by c the concentration of the chains. The chains are assumed to be ideally flexible in the absence of electrostatic interaction; their degree of polymerization is $N \gg 1$, the size of the monomers is b , and the fraction of charged monomers is f . The total charge of each chain is then $Z = fN$ (in units of the electronic charge e). In the current study we assume that f is of order unity (highly charged polyelectrolytes). Due to electroneutrality, one has fN counterions per chain, each carrying the charge $-e$. Furthermore we focus here on the influence of the long-range electrostatic interaction between charged monomers (and counterions) on the chain conformation; we thus assume in the following the absence of excess ions (added salt) which lead to a screening of the electrostatic interaction between charges.

At sufficiently high temperatures, the interaction between the polyelectrolytes and the counterions is weak so that the counterions are distributed nearly homogeneously in the solution. Thus only a negligibly small fraction of the counterions are near the chains and their influence on chain properties may be neglected. The conformation of the polyelectrolyte is then determined by the competition between the chain entropy and the electrostatic repulsion of the charged monomers. As a result the chain becomes stretched into a globally rodlike shape; on smaller length scales, however, the entropy dominates the behavior and sufficiently small parts are unperturbed by the electrostat-

[†] Materials Research Laboratory.

[‡] Departments of Materials and Physics.

ics. This can be envisaged by the following blob picture:³ The chain consists of a string of electrostatic blobs where each blob has the size ξ_{el} and consists of g_{el} monomers. ξ_{el} and g_{el} can be determined from the following two relationships: (i) The electrostatic energy per blob is on the order of the thermal energy, i.e. $(fg_{el})^2 l_B/\xi_{el} \approx 1$ where l_B denotes the Bjerrum length $l_B = e^2/\epsilon T$ (here T is the temperature in units of the Boltzmann constant and ϵ denotes the dielectric constant of the solvent). (ii) Due to point i the blob is only slightly perturbed by the electrostatic repulsion and thus obeys Gaussian chain statistics, i.e. $\xi_{el} \approx b g_{el}^{1/2}$. From these two relationships one finds for the electrostatic blob size $\xi_{el} \approx b^{4/3}/l_B^{1/3} f^{2/3}$. The length of the polyelectrolyte is then given by $L \approx (N/g_{el})\xi_{el}$ which leads to the well-known result¹

$$L \approx f^{2/3} b^{2/3} l_B^{1/3} N \quad (1)$$

In the high temperature limit, namely for $l_B < l_{HT} = b/(f^2 N^{3/2})$, the chain is unperturbed by the electrostatics and one has $L \approx bN^{1/2}$.

However this picture breaks down for sufficiently large values of the Bjerrum length. There are two different mechanisms that may lead to this breakdown: (i) the finite extensibility of the chain and (ii) counterion condensation. The finite extensibility comes into play when the length of the macroion is of the order bN or equivalently $g_{el} \approx 1$; this is the case when l_B is on the order of b/f^2 . Since the counterion condensation sets in at Bjerrum length of the same order (see below) we will not further discuss this effect in the current study.

The phenomenon of counterion (or Manning) condensation⁴ is due to the fact that with increasing l_B the counterions become more and more drawn toward the macroions, and beyond a critical value l_c some of the counterions are bound to them. This leads then effectively to a renormalized total charge $\tilde{Z} < Z$. A simple estimation of \tilde{Z} can be achieved by comparing the chemical potentials of the free and the bound counterions.^{13,14} The chemical potential μ_f of the free ions is governed by their configurational entropy, i.e. $\mu_f \approx T \ln(\phi)$ where ϕ denotes the volume fraction of the counterions of volume v_c , i.e. $\phi \approx cv_c \tilde{Z}$. Note that $\ln(\phi)$ is slowly varying with \tilde{Z} and c so that we treat this term in following discussion as a constant: $\ln(\phi) = -k$. On the other hand the chemical potential μ_c of the condensed counterions arises from the electrostatic interaction between the counterions and the polyelectrolytes. For the case of a counterion at the surface of a spherical macroion of radius L (with condensed counterions), one finds $\mu_c \approx -T\tilde{Z}l_B/L$; in the case of a cylindrical macroion one has an additional factor on the order of $(1 + \ln(L/\xi_{el}))$ which we neglect in the following. Equating μ_f and μ_c , one finds for the renormalized total charge of the macroion

$$\tilde{Z} \approx k \frac{L}{l_B} \quad (2)$$

a relation which holds as long as $\tilde{Z} < Z$. Consider now the chain for small values of l_B (high temperatures) where one has no counterion condensation. Here eq 2 is not valid since it predicts $\tilde{Z} > Z$. Due to $L \propto l_B^{1/3}$ (cf. eq 1) it is, however, clear that with increasing l_B one will finally reach the critical Bjerrum length l_c for which $\tilde{Z} = Z$. One finds $l_c \approx k^{3/2} b/f^{1/2}$. Then, for $l_B > l_c$ one has condensed counterions.

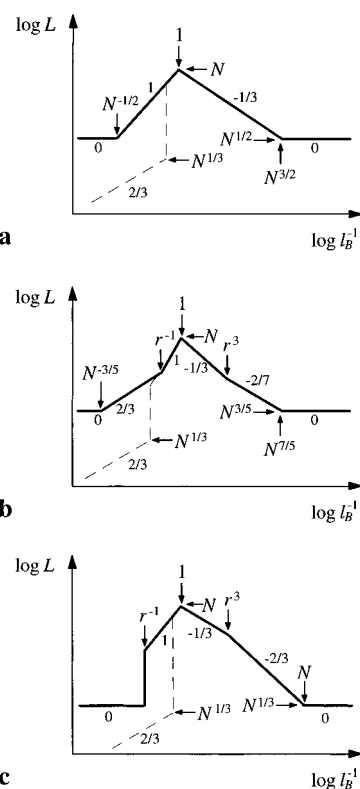


Figure 1. Dependence of the size of a polyelectrolyte chain on the inverse Bjerrum length $l_B^{-1} = \epsilon T l_B^{-1} e^2$ in a Θ -solvent (a), in a good solvent (b), and in a poor solvent (c). The dependence of the crossover lengths on N and $r = b^3/v \gg 1$ is depicted. The solid lines are the predictions when only the chain renormalization is taken into account (cf. section 2); the dashed line accounts for the counterion-induced attraction (see section 3).

This regime can also be treated within the blob picture. Compared to the picture discussed above one has to replace the fraction of charged monomers, $f = Z/N$, by the effective fraction \tilde{f} which is given by $\tilde{f} = \tilde{Z}/N$. Thus the condition is now $(\tilde{f}g_{el})^2 l_B/\xi_{el} \approx 1$. This, together with $\xi_{el} \approx b g_{el}^{1/2}$ leads to the electrostatic blob size $\xi_{el} \approx l_B/k^2$ and to the following size of the total chain:

$$L \approx \frac{k^2 b^2 N}{l_B} \quad (3)$$

From eq 3 follows that with increasing Bjerrum length (decreasing temperature) the size of the chain decreases which follows from the fact that the effective charge of the macroion becomes renormalized. At very low temperatures, namely for $l_B > l_{LT} = k^2 b N^{1/2}$, \tilde{Z} is so small that the chain conformation is again governed by the configurational entropy, $L \approx bN^{1/2}$. In Figure 1a we depict the size L of the macroion as function of the inverse Bjerrum length. Note that the size shows a nonmonotonic dependence on l_B^{-1} .

The case of a good solvent can be treated similarly.¹ Compared to the Θ -case each electrostatic blob is now swollen and obeys $\xi_{el} \approx (v b^2)^{1/5} g_{el}^{3/5}$ where v denotes the excluded volume per monomer. This scaling relation follows from the statistics of a self-avoiding walk where the elementary building blocks are thermal blobs of size ξ_T that consist of g_T monomers so that $\xi_{el} \approx \xi_T (g_{el}/g_T)^{3/5}$. Here ξ_T and g_T are related by $v g_T^2/\xi_T^3 \approx 1$ (the excluded volume interaction equals the thermal energy) and $\xi_T \approx b g_T^{1/2}$ (ideal chain statistics). This leads to $\xi_T \approx b^4/v$.

Now using $(fg_{el})^2 l_B / \xi_{el} \approx 1$ (electrical energy per blob equals thermal energy) and $\xi_{el} \approx (vb^2)^{1/3} g_{el}^{3/5}$ (self-avoiding walk) one finds $\xi_{el} \approx (vb^2)^{2/7} / l_B^{3/7} f^{6/7}$ and

$$L \approx f^{4/7} (vb^2)^{1/7} l_B^{2/7} N \quad (4)$$

This picture is valid as long as the size of the electrostatic blobs is larger than the thermal blob size, i.e. as long as $\xi_{el} > \xi_T$. This leads to the condition $l_B < l_1 \approx f^{-2} (vb^3)^{3/5} b$. For $l_B > l_1$ each blob obeys ideal chain statistics so that eq 1 holds.

At $l_B \approx l_c > l_1$ counterion condensation sets in. For values of l_B beyond the condensation threshold, $l_B > l_c$, the size of the chain is given by eq 3 as long as $\xi_{el} < \xi_T$. This leads to the condition $l_B < l_2 = k^2 b^4 / v$. Then, for $l_B > l_2$ we find by combining $(fg_{el})^2 l_B / \xi_{el} \approx 1$ (electrostatic energy per blob) and $\xi_{el} \approx (vb^2)^{1/5} g_{el}^{3/5}$ (excluded volume statistics) $\xi_{el} \approx l_B / k^2$ (as in the Θ -case) and

$$L \approx \frac{k^{4/3} (vb^2)^{1/3} N}{l_B^{2/3}} \quad (5)$$

We note further that the crossover to the high temperature and low temperature limits takes place at $l_B \approx l_{HT} \approx (vb^2)^{1/5} / f^2 N^{7/5}$ and $l_B \approx l_{LT} \approx k^2 (vb^2)^{1/5} N^{3/5}$, respectively. For $l_B < l_{HT}$ and for $l_B > l_{LT}$ the chain obeys excluded volume statistics; i.e., $L \approx (vb^2)^{1/5} N^{3/5}$. The different scaling regimes can be seen in Figure 1b where we depict L as a function of l_B^{-1} .

Thus we find in both cases (Θ -solvent as well as good solvent) that due to charge renormalization the chain size decreases with increasing $l_B > l_c$. We note, however, that due to the presence of condensed counterions, one has an additional counterion-induced attraction that may lead effectively to poor solvent conditions, as discussed in the next section. As we will see, this effect induces a rapid collapse of the chain, reminiscent of a first-order phase transition. In order to understand this phenomenon we discuss in the following text the case of a polyelectrolyte in a poor solvent and investigate the behavior of the chain as a function of l_B , assuming fixed quality of the solvent.

Consider first an uncharged chain with a negative second virial coefficient $-v$ with $|v| \ll b^3$. Then the polymer may be considered as being a densely packed array of thermal blobs. As in the good solvent case the blob size ξ_T and the number of monomers g_T is related by $|v| g_T^2 / \xi_T^3 \approx 1$ and $\xi_T \approx b g_T^{1/2}$. Thus the thermal blob size is again given by $\xi_T \approx b^4 / |v|$. Due to missing thermal blobs at the surface the globule has a surface tension $\gamma = T \xi_T^2$ and assumes a spherical shape with diameter $L \approx \xi_T (N / g_T)^{1/3}$, i.e.

$$L \approx R \approx \frac{b^2 N^{1/3}}{|v|^{1/3}} \quad (6)$$

Consider now a charged chain at high temperatures (no counterion condensation). Again, as in the good and in the Θ -solvent cases, the chain can be considered as being a sequence of electrostatic blobs. Now, however, each blob is collapsed and its size follows from the competition between the electrostatic repulsion and the surface tension,¹² i.e. $(fg_{el})^2 l_B / \xi_{el} \approx \xi_{el}^2 / \xi_T^2$. This together with $\xi_{el} \approx b^2 g_{el}^{1/3} / |v|^{1/3}$ (cf. eq 6) leads to $\xi_{el} \approx b^{4/3} / l_B^{1/3} f^{2/3}$ and

$$L \approx \frac{f^{4/3} b^{10/3} l_B^{2/3} N}{|v|} \quad (7)$$

Note that the electrostatic blob size ξ_{el} shows the same scaling as in the Θ -case; since each blob comprises more monomers, the size L of the chain is smaller. At very small values of l_B , namely for $l_B < l_{HT} \approx |v| / f^2 b^2 N$, we are in the high temperature limit where $L \approx R$.

This picture also breaks down at sufficiently large values of l_B when the electrostatic blob size becomes smaller than the size of the thermal blobs, i.e. when $\xi_{el} < \xi_T$. In this regime, namely for $l_B > l_1 \approx |v|^{3/5} / b^3 f^2$, each electrostatic blob obeys ideal chain statistics so that for $l_1 < l_B < l_c$ the length of the macroion is given by eq 1. For values of l_B beyond the condensation threshold, $l_B > l_c$, the size of the chain is given by eq 3 as long as $\xi_{el} < \xi_T$. This leads to the condition $l_B < l_2 = k^2 b^4 / |v|$.

In order to describe the behavior for $l_B > l_2$, we may tentatively use again the concept of collapsed electrostatic blobs (with condensed counterions). By equating the electrostatic energy and the surface tension, i.e. $(fg_{el})^2 l_B / \xi_{el} \approx \xi_{el}^2 / \xi_T^2$, we find $\xi_{el} \approx k^2 b^4 / v^2 l_B$ and $L \approx \xi_{el} N / g_{el} \approx |v|^{3/5} l_B^2 N / k^4 b^{10}$. Thus this argument predicts that the size of the chain increases with increasing l_B , a result which is counterintuitive. We show now that indeed another state, namely that of a (nearly) spherical globule with a size given by eq 6 is energetically more favorable. Note first, that both the globular state and the extended state may only exist for sufficiently large values of l_B , namely $l_B > l_g = k^2 b^6 / |v|^{5/3} N^{1/3}$. In the globular case, this follows from the requirement that the electrostatic repulsion is smaller than the surface tension, i.e. $(fN)^2 l_B / R < R^2 / \xi_T^2$, and for the stretched state the same condition follows simply from the requirement $L > R$. Now compare the free energies of both states. In both cases the nonextensive part of the free energy ΔF (in units of T) is given by the sum of the surface tension S / ξ_T^2 (here S denotes the surface of the macroion which is given by R^2 for the globular and $L \xi_{el}$ for the stretched state), the electrostatic energy $Z^2 l_B / L$, and the contribution of the translational entropy of the free counterions $-kZ$. Using eq 2, one finds for the globular state $\Delta F_{glob} / T \approx R^2 / \xi_T^2 - k^2 R / l_B$ and for the stretched state $\Delta F_{str} / T \approx L \xi_{el} / \xi_T^2 - k^2 L / l_B$. Now the globular state is more favorable than the stretched one when $\Delta F_{glob} < \Delta F_{str}$. This leads to the condition $l_B > l_g$, which is exactly the validity condition of both models. This means that a string of electrostatic blobs with charge renormalization does not exist since the collapsed state is more favorable.

We show now that the stretched states with ideal blob statistics in the regimes without counterion condensation $l_g < l_B < l_c$ and with condensed counterions $l_c < l_B < l_2$ are energetically more favorable than the globular state. In order to decide which state represents the global minimum we compare the free energies of the stretched states and of the globular state. The free energy F_Θ of the stretched state without counterion condensation has three contributions: the stretching term, the electrostatic interaction, and the translational entropy of the counterions, i.e. $F_\Theta / T \approx L^2 / b^2 N + f^2 N^2 l_B / L - kfN \approx f^{4/3} N l_B^{2/3} / b^{2/3} - kfN$. On the other hand the free energy F_{glob} of the globular state is governed by the condensation energy, i.e. $F_{glob} / T \approx -v^2 N / b^6$. Note that $F_{blob} / T \ll kfN$ so that the stretched state is favored ($F_\Theta < F_{glob}$) when $f^{4/3} N l_B^{2/3} / b^{2/3} < kfN$. This leads to the condition $l_B < l_c$ which is in fact the condition for validity

of the stretched state (without condensed counterions). The free energy \bar{F}_Θ of the stretched state with Manning condensation is given by $\bar{F}_\Theta/T \approx L^2/b^2N + \bar{Z}^2 l_B/L - k\bar{Z} \approx -k^4 b^2 N/l_B^2$, which is smaller than F_{glob}/T as long as $l_B < l_2 \approx k^2 b^4/v$. Again this means that the stretched state is favored in its whole range of validity.

Summarizing, we find for a polyelectrolyte in a poor solvent the following behavior (cf. Figure 1c). When we start at very small values of l_B , $l_B < l_{\text{HT}}$, the thermal agitation dominates and the chain is in the globular state with $L \approx R$ unperturbed by the electrostatic interaction. Then for $l_{\text{HT}} < l_B < l_1$ the chain size increases with l_B as $L \sim l_B^{2/3}$; cf. eq 7. In the regime $l_1 < l_B < l_c$ the length of the macroion grows as $L \sim l_B^{1/3}$, cf. eq 1. At $l_B \approx l_c$ counterion condensation sets in, and for $l_c < l_B < l_2$, the chain size is given by $L \sim l_B^{-1}$ (cf. eq 3). At $l_B \approx l_2$ the stretched state of the macroion becomes unstable and it collapses into a globular state with $L \approx R$. Due to $\bar{Z} \sim L$ this collapse is accompanied (and indeed induced) by a strong onset of counterion condensation. Whereas the stretched macroion carries the total charge $\bar{Z} = k^{-1}(v/b^3)^{2/3}N$ (at $l_B = l_2$) in the collapsed state one has $\bar{Z} \approx k^{-1}(v/b^3)^{2/3}N^{1/3}$, i.e. nearly all counterions are condensed. Khokhlov¹² already predicted a first-order type collapse of polyelectrolytes in poor solvents and called this effect avalanche-type counterion condensation (cf. also ref 15).

The complete diagram of states of a dilute solution of polyelectrolyte chains in v, l_B^{-1} coordinates is shown in Figure 2. Phases I–III correspond the high temperature limit where the chains are unperturbed by the electrostatics. The boundary between the phases I and II as well as between I and III follows from the condition $\xi_T = bN^{1/2}$. Then at lower temperatures one has stretched chains and free counterions (regimes IV–VI).¹⁶ When the temperature is lowered further, counterion condensation sets in. In a good solvent and around the Θ -case we still have stretched chains (regime VII and VIII) whereas under poor solvent conditions one has a collapsed globule (regime IX). The crossover between regimes VI and IX as well as between VII and IX occurs in a first-order type fashion. Finally, in the low temperature limit the chains in the Θ -solvent and in the good solvent are unperturbed by electrostatics (regime X and XI).

We note that this phase diagram was constructed using two rough approximations: (i) We assumed that we can neglect the discreteness of the charges. In the case of condensed counterions one has, however, dipole–monopole and dipole–dipole interactions; we will address this effect in the next section. (ii) We assumed a cylindrical shape of the stretched state in a poor solvent (regime VI). Dobrynin, Rubinstein, and Obukhov¹⁷ have shown that this shape does not correspond to the global minimum of the free energy. They demonstrated that a necklace shape where one has beads of size ξ_{el} connected by strings of diameter ξ_T are energetically more favorable. We stress that this does not affect the main points of our argument.¹⁸

III. Effect of the Counterion-Induced Attraction

In the last section we discussed the influence of the charge renormalization on the conformation of polyelectrolytes. We showed that in Θ -solvents and in good solvents this effect leads to a moderate shrinking of macroions; in the poor solvent case, however, a rapid first-order-type collapse is predicted. In this section we

will show that this picture is not complete; as we will see the presence of condensed counterions leads to an additional electrostatic short-range interaction (this is also pointed out in refs 10 and 11). This interaction effectively changes the solvent quality so that the solvent becomes poorer. As a result, at sufficiently small temperatures polyelectrolytes in Θ -solvents and even in good solvents are in collapsed conformations, a fact which is observed in computer simulations; cf. refs 6 and 7. As we will show, the transition to the collapsed state may occur in a first-order- or second-order-type fashion.

Let us first estimate how condensed counterions modify the second virial coefficient of a polyelectrolyte. The typical situation is that the condensed ions approach the macroion very closely and form together with oppositely charged monomers dipole-type configurations. Snapshots from molecular-dynamics simulations of charged chains with counterions indeed confirm this picture (cf., for instance, Figure 24b of ref 6). We give now a simple estimate of the second virial coefficient of a chain that carries electrical dipoles. Let us first assume that each monomer represents a dipole (complete counterion condensation). Denote by r_0 the distance between the charge of the condensed counterion and the charge of the corresponding monomer; then the dipole moment is $\mathbf{p} = er_0$. The interaction energy $w(r)$ between two dipoles at a distance r can be calculated by averaging over all the orientations of the dipoles (assuming that the dipoles can rotate freely, i.e., that $w(r) < T$). One finds $w(r)/T \approx -l_B^2 r_0^4/3r^6$.¹⁹ Now usually the non-electric part of the monomer–monomer interaction is of the form $u(r) = u_{\text{core}}(r) + u_{\text{attr}}(r)$ where $u_{\text{core}}(r)$ denotes a hard core potential and $u_{\text{attr}}(r)$ is a weak attractive potential.²⁰ The presence of the condensed counterions which are usually much smaller than the monomer units may only slightly perturb $u_{\text{core}}(r)$ and $u_{\text{attr}}(r)$ so that the interaction potential between monomers with condensed counterions is of the form $u(r) \approx u_{\text{core}}(r) + u_{\text{attr}}(r) + w(r)$. The second virial coefficient can then be estimated from $v' = 4\pi \int dr r^2 (1 - \exp(-u(r)/T))$ which leads to

$$v' \approx 4\pi \int dr r^2 \left[1 - e^{-u_{\text{core}}(r)/T} \left(1 - \frac{u_{\text{attr}}(r)}{T} - \frac{w(r)}{T} \right) \right] \approx v - \frac{16\pi^2}{3v_{\text{core}}} l_B^2 r_0^4 \quad (8)$$

Here v denotes the second virial coefficient between monomers in the absence of counterions (i.e. for $w(r) \equiv 0$). The dipole–dipole interaction leads to a shift of the coefficient toward a somewhat smaller value $v' \approx v - \Delta v$. Note that the shift, Δv , depends on the lower cutoff of the integral which leads to the dependence on v_{core} , the volume of the hard core.

Up to now we estimated the shift of the excluded volume parameter assuming complete counterion condensation. If only a part of the counterions are condensed, say $(fN - \bar{Z})/N = f - \bar{f}$, the shift due to dipole–dipole interactions is smaller, namely $\Delta v \approx -(f - \bar{f})^2 l_B^2 r_0^4/v_{\text{core}}$. Furthermore, one has also to take the much stronger monopole–dipole interaction $w(r) \approx -l_B^2 r_0^2/6r^4$ into account which is on the order of $(r/r_0)^2$ larger than $w(r)$.¹⁹ The contribution $\Delta v'$ of this interaction to the second virial coefficient can be calculated in a similar way. Taking into account the densities of the monopoles, \bar{f} , and of the dipoles, $f - \bar{f}$, one finds $\Delta v' \approx$

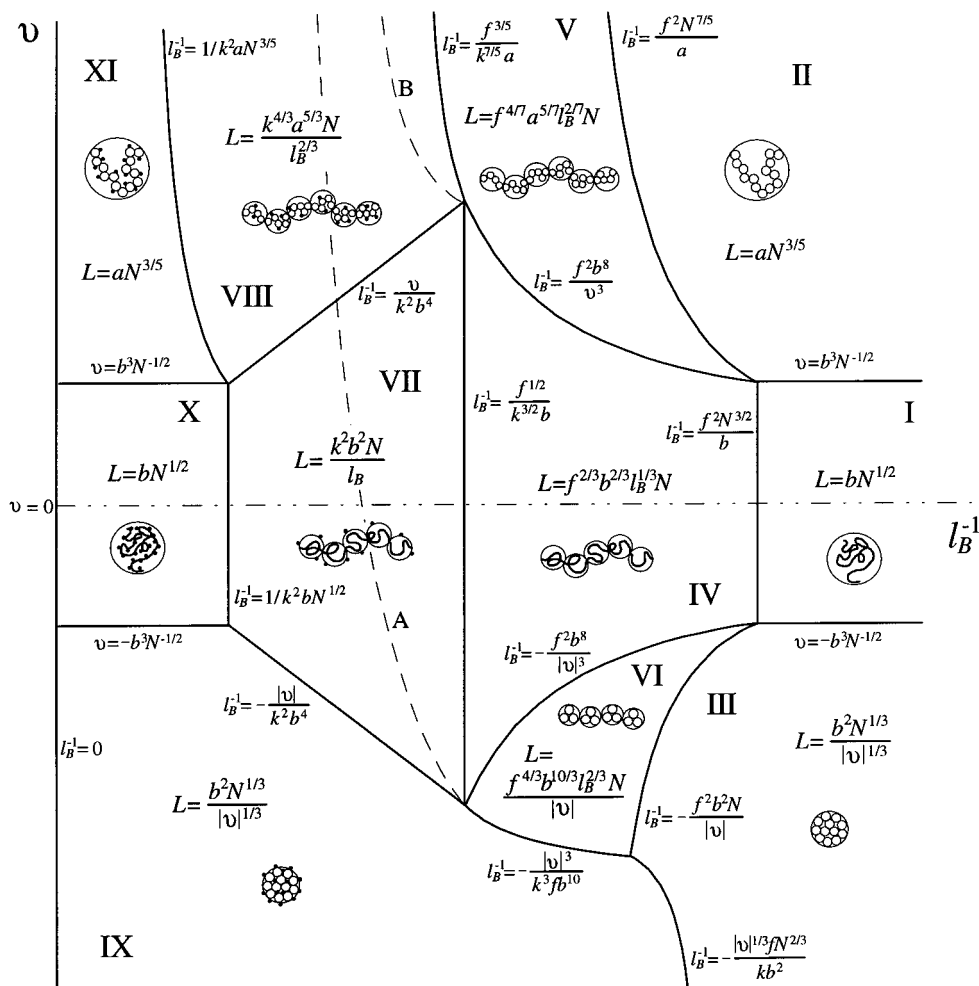


Figure 2. Diagram of states of a dilute solution of polyelectrolytes. For each regime a characteristic conformation of a single chain is depicted together with its length L . Furthermore the equations for the phase boundaries are given. The length a is given by $(\nu b^2)^{1/5}$. Regimes I–VI correspond to states where all counterions are released; in regimes VII–XI condensed counterions are present (schematically depicted as dots). In regimes I, IV, VII, and X one has the statistics of an ideal chain within the electrostatic blob size; regimes II, V, VIII, and XI correspond to swollen blobs whereas in regimes III, VI, and IX the blobs are collapsed. This picture corresponds to the simplified approach of section 2 that only accounts for the charge renormalization. The presence of condensed counterions in regimes VII–XI leads to an additional attractive interaction that modifies the phase diagram at low values of l_B^{-1} (cf. section 3). Regime VII, for instance, is now confined between the dashed lines A and B; i.e., it is bended toward larger values of ν as described in detail in section 3.

$-2\pi\tilde{f}(f - \tilde{f})l_B^2 r_0^2 / 3r_{\text{core}}$ where r_{core} denotes the radius of the hard core. Putting all these contributions together, we find the following second virial coefficient for a chain of monopoles and dipoles (neglecting numerical prefactors):

$$\nu' \approx \nu - (f - \tilde{f})^2 l_B^2 r_0^4 / r_{\text{core}}^3 - \tilde{f}(f - \tilde{f}) l_B^2 r_0^2 / r_{\text{core}} \quad (9)$$

This effect comes only into play in the case when condensed counterions are present; i.e., we have to reconsider the regimes VII–XI of the diagram of states, Figure 2. Consider regime VII where one has a string of electrostatic blobs that obey ideal chain statistics. The change in the solvent quality due to counterion condensation affects the chain conformation when the size of the thermal blobs $\xi_T \approx b^4 / |\nu'|$ becomes of the same order as the electrostatic blob size $\xi_{\text{el}} \approx l_B / k^2$ (see above, eq 3). From $b^4 / |\nu'| = l_B / k^2$ and eq 9, we find that the line in the phase diagram at which this effect comes into play is given by

$$-\nu \approx \frac{b^4 k^2}{l_B} + \frac{fk^3 r_0^2 b^2}{r_{\text{core}}} \left(\frac{2r_0^2}{r_{\text{core}}^2} - 1 \right) + \frac{k^6 b^4 r_0^2}{r_{\text{core}} l_B} \left(1 - \frac{r_0^2}{r_{\text{core}}^2} \right) - \frac{f^2 r_0^4 l_B^2}{r_{\text{core}}^3} \quad (10)$$

This expression shows a strong dependence on the microscopic properties of the system, i.e. on r_0 , r_{core} , and b . Let us now assume that $r_0 \approx r_{\text{core}} \approx b$, i.e., that the minimal distance between the counterions and the charged monomers is of the same order as the monomer size. In this case eq 10 simplifies significantly:

$$-\nu \approx \frac{b^4 k^2}{l_B} + fk^3 b^3 - f^2 b l_B^2 \quad (11)$$

The corresponding line is depicted schematically in the phase diagram, Figure 2, as the dashed line A. The line starts at the point where regimes IV, VI, VII, and IX come together. It crosses the $\nu = 0$ -line (Θ -solvent) when l_B fulfills the condition $l_B^3 - k^3 b^2 l_B / f = k^3 b^3 / f^2$. For sufficiently low concentrations k , so that, e.g., $k >$

10, the terms on the left-hand side dominate, which leads in a first approximation to the condition $l_B < k^{3/2}b/f^{1/2} \approx l_c$. Due to the term on the right-hand side, the Bjerrum length at which the change of the solvent quality comes into play is somewhat above l_c .

In the good solvent case ($v > 0$), line A is still given by eq 11 even when it crosses into regime VIII. This regime becomes strongly modified by the counterion-induced attraction. For large values of $v > k^{1/2}f^{1/2}b^3$ and $l_B^{-1} < f^{3/5}/k^{7/5}(vb^2)^{1/5}$ there remains a small section in the phase diagram where one still has swollen electrostatic blobs with condensed counterions. The functional dependence of the chain size L , eq 5, is now more complicated since L depends on v' which decreases with an increasing fraction of condensed ions; it is given self-consistently by $L \approx k^{4/3}(v'(L)b^2)^{1/3}N/l_B^{2/3}$ where $v'(L)$ follows from eq 9. Note, however, that the electrostatic blob size is still given by $\xi_{el} \approx l_B/k^2$ (see above eq 5). Therefore one can determine the line where the electrostatic blobs start to obey Gaussian statistics by comparing ξ_{el} and ξ_T . This leads to

$$v \approx \frac{b^4 k^2}{l_B} - f k^3 b^3 + f^2 b l_B^2 \quad (12)$$

which is depicted in Figure 2 as line B. In the regime between line A and line B the size of the chain is given by eq 3.

At larger values of l_B , when one is beyond line A (in the regimes VII and VIII), we have effectively a macroion in a poor solvent. As we have shown in the last section such a chain becomes unstable and collapses as soon as counterion condensation sets in. Since the decrease of the chain size is accompanied by an increase of the number of condensed counterions (cf. eq 2), which at the same time leads to a decrease of the solvent quality (cf. eq 9), this collapse is even more enhanced than in the case discussed in the last section. Thus we expect that by crossing line A in the phase diagram the macroion collapses into a globular shape in a first-order fashion.

The size of the collapsed chain in a Θ -solvent can be calculated as follows: Since the majority of the counterions is condensed one has $\tilde{f} \ll f$ and we find from eq 9 (with $v = 0$) $v' \approx -f^2 l_B^2 r_0^4 / v_{core} \approx -f^2 l_B^2 b$. The size of the globule follows then from eq 6 (setting $v = v'$)

$$L \approx \frac{b^{5/3} N^{1/3}}{f^{2/3} l_B^{2/3}} \quad (13)$$

(cf. also the dashed line in Figure 1a). Thus the chain size shows an $N^{1/3}$ -dependence which is characteristic for a collapsed globule. Interestingly eq 13 is also a good approximation for nonvanishing values of $v \ll b^3$; this is the case since $v \ll f^2 l_B^2 b$ for all $l_B > l_c = k^{3/2}b/f^{1/2}$. Therefore even in the case of a good solvent one finds a collapsed state for sufficiently large values of l_B . The consequence is that the chain size in the low temperature limit, eq 13, is significantly smaller than in the high temperature regime where one has excluded volume statistics $L \approx (vb^2)^{1/5} N^{3/5}$ (cf. the dashed line in Figure 1b). This fact is indeed observed in computer simulations.^{6,7} So it was found in ref 7 that $L \propto N^\alpha$ with $\alpha \approx 0.3$ for large values of l_B , $\alpha \approx 1$ for intermediate values, and $\alpha \approx 0.6$ for small ones. The authors observe that α changes its value continuously with changing l_B ; this

observation may be an artifact induced by finite size and crossover effects that may disappear for larger systems.

From our theoretical considerations, it follows that the counterion-induced attraction strongly affects the phase diagram for larger values of l_B . Regimes VII, VIII, and IX are bent toward higher values of v (cf. Figure 2) and are separated by the lines A and B that are given by eqs 11 and 12; furthermore, regimes X and XI vanish.

Note, however, that the A- and B-lines show a strong dependence on the microscopic properties of the chains and counterions. We illustrate this by assuming now another relation between the microscopic length scales, namely $r_0 \ll r_{core} \approx b$ which correspond to the case of counterions that are small compared to the monomers. In this case we find from eq 10 that

$$-v = \frac{b^4 k^2}{l_B} - f k^3 b r_0^2 + \frac{k^6 b^3 r_0^2}{l_B^2} - \frac{f^2 r_0^4 l_B^2}{b^3} \quad (14)$$

Now line A crosses the line $v = 0$ at a much smaller value of l_B^{-1} . One finds the following equation from eq 14 by equating the first and the fourth term on the right-hand side (the other terms are negligible): $l_B^{-1} \approx f^{2/3} r_0^{4/3} / k^{2/3} b^{7/3}$. This is indeed much smaller than $l_c^{-1} \approx f^{1/2} / k^{3/2} b$. Thus for this set of microscopic parameters line A (and similarly line B) are shifted toward much smaller values of l_B^{-1} . It is then even possible that for not too long chains line A crosses the line which separates regimes VII and X. In this case the first-order collapse vanishes at this boundary. The computer simulations in refs 6 and 7 do not show any significance for a discontinuous phase transition; at the present stage, it is not possible to decide whether this follows from the fact that the simulated systems are very small or if the microscopic parameters of the systems are chosen in such a way that the transition is continuous. Our scaling theory allows no definite conclusion and would be consistent with both cases.

IV. Conclusion

In this paper, we discussed the behavior of dilute solutions of highly charged polyelectrolytes. Using a scaling approach, we derived simple scaling relations for the single chain properties. At high temperature the presence of counterions can be neglected and we find the well-known picture of chains stretched out into strings of electrostatic blobs. The blobs obey ideal chain statistics (sufficiently near to the Θ -point) or excluded volume statistics (good solvent), or they are collapsed (poor solvent; here the picture may be more refined by the necklace model that, however, does not affect the main conclusions of this paper). At lower temperatures when the Bjerrum length is of the order of the segment size, counterion condensation sets in. The scaling picture follows now from a self-consistent calculation of the charge renormalization. It turns out that the chains in a Θ -solvent and in a good solvent are still strings of electrostatic blobs; however, the length of the macroions decreases now with decreasing temperature. In the poor solvent case the chain collapses into a globular shape in a first-order-type fashion. In any case, the presence of counterions leads effectively to a decrease of the solvent quality; this follows from short-ranged dipole-monomer and dipole-dipole interactions. Thus a Θ -solvent and even a good solvent becomes

effectively poor at sufficiently low temperatures. Depending on the microscopic properties of the system, the chain collapses in a first-order- or second-order-type fashion into a collapsed state where nearly all counterions are condensed.

Additional Remark: During the writing of this paper, we became aware of a preprint by Brilliantov, Kuznetsov, and Klein²¹ in which a similar idea is considered. Taking counterion condensation into account, the authors calculate the behavior of a polyelectrolyte in a good solvent; the occurrence of a first-order-type phase transition due to counterion condensation is also predicted.

Acknowledgment. We wish to thank M. J. Stevens, C. Williams, and R. G. Winkler for valuable discussions. H.S. acknowledges financial support of the Deutsche Forschungsgemeinschaft (SCHI 418/3-1). Support from NSF Grants No. MRL-DMR-9632716 and No. DMR-9708646 is also acknowledged.

References and Notes

- (1) Barrat, J.-L.; Joanny, J.-L. *Adv. Chem. Phys.* **1996**, *94*, 1.
- (2) Förster, S.; Schmidt, M. *Adv. Polym. Sci.* **1995**, *120*, 51.
- (3) de Gennes, P. G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Paris)* **1976**, *37*, 1461.
- (4) Manning, G. S. *Q. Rev. Biophys.* **1978**, *11*, 179.
- (5) Kremer, K.; Stevens, M. J.; Pincus, P. A. In *Soft Order in Physical Systems*; Rabin, Y., Bruinsma, R., Eds.; Plenum Press: New York, 1994; pp 117–123.
- (6) Stevens, M. J.; Kremer, K. *J. Chem. Phys.* **1995**, *103*, 1670.
- (7) Winkler, R. G.; Gold, M.; Reineker, P. *Phys. Rev. Lett.* **1998**, *80*, 3731.
- (8) Grønbech-Jensen, N.; Mashl, R. J.; Bruinsma, R. F.; Gelbart, W. M. *Phys. Rev. Lett.* **1997**, *78*, 2477.
- (9) Ha, B.-Y.; Liu, A. J. *Phys. Rev. Lett.* **1997**, *79*, 1289.
- (10) Olvera de la Cruz, M.; Belloni, L.; Delsanti, M.; Dalbiez, J. P.; Spalla, O.; Drifford, M. *J. Chem. Phys.* **1995**, *103*, 5781.
- (11) González-Mozuelos, P.; Olvera de la Cruz, M. *J. Chem. Phys.* **1995**, *103*, 3145.
- (12) Khokhlov, A. R. *J. Phys. A* **1980**, *13*, 979.
- (13) Alexander, S.; Chaikin, P. M.; Grant, P.; Morales, G. J.; Pincus, P.; Hone, D. *J. Chem. Phys.* **1984**, *80*, 5776.
- (14) Oosawa, F. *Polyelectrolytes*; Dekker: New-York, 1971.
- (15) Kramarenko, É. Yu.; Khokhlov, A. R.; Yoshikawa, K. *Macromolecules* **1997**, *30*, 3383.
- (16) This part of the phase diagram (regimes I–VI) is also presented in: Borisov, O. V.; Darinskii, A. A.; Zhulina, E. B. *Macromolecules* **1995**, *28*, 7180.
- (17) Dobrynin, A. V.; Rubinstein, M.; Obukhov, S. P. *Macromolecules* **1996**, *29*, 2974.
- (18) A straightforward analysis shows that the boundaries between the phases III and VI as well as between VI and IV are unaffected. In the necklace picture¹⁷ the globule (regime III) becomes unstable at $I_B^{-1} \approx f^2 b^2 N/2|v|$ and splits into two beads connected by a string (dumbbell). Then at $I_B^{-1} \approx f^2 b^2 N/N_{\text{bead}}|v|$ ($N_{\text{bead}} = 3, 4, \dots$) one has a cascade of transitions into necklaces with N_{bead} beads. Finally, at $I_B^{-1} \approx f^2 b^8/|v|^3$ the size of the beads is on the same order as the diameter of the strings so that then Khokhlov's cylindrical model¹² and the necklace state¹⁷ become identical. The same is the case at the phase boundary between VII and IX. Here the necklace and the cylinder are again identical and, as discussed above, unstable due to counterion condensation. The only modification of the phase diagram concerns the boundary between phases VI and IX. Using eq 2 together with the length of the necklace, $L \approx b^2 I_B^{1/2} f N/|v|^{1/2}$ (cf. ref 17) leads to the condition $I_B^{-1} \approx |v|/k^2 b^4$. We note, however, that the scaling picture is questionable at such highly negative values of v : One has $-v \approx k^2 b^4 I_B^{-1} > k^{1/2} f^{1/2} b^3$. The number of monomers per thermal blob is therefore $g_T \approx (\xi_T/b)^2 \approx (b^3/|v|) < 1/kf$ which is of order 1 for highly charged chains, $f \approx 1$.
- (19) Israelachvili, J. *Intermolecular and Surface Forces*; Academic Press: San Diego, CA, 1992.
- (20) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, England, 1986; p 26.
- (21) Brilliantov, N. V.; Kuznetsov, D. V.; Klein, R. *Phys. Rev. Lett.* **1998**, *81*, 1433.

MA980823X