RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 46, NUMBER 6 15 SEPTEMBER 1992

Conformations of a polyelectrolyte chain

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(Received 23 March 1992; revised manuscript received 1 July 1992)

A self-consistent variational theory for obtaining the size of a polyelectrolyte chain, R, for arbitrary values of the experimentally controlable parameters characterizing a dilute polyelectrolyte solution is derived using the Edwards model for the chain. In appropriate limits the theory reproduces the scaling behavior in a good solvent, a Θ solvent, and a poor solvent. In particular, we show that, if the solvent is sufficiently poor, the size of the polyelectrolyte chain changes abruptly from a swollen state ($R \sim bN^{3/5}$, N is the number of monomers, b is the monomer size) to a globule state ($R \sim bN^{1/3}$) or from a rodlike configuration ($R \sim Nb$) to a globule depending on the limiting values of the salt concentration.

PACS number(s): 61.25.−f

There have been numerous theoretical studies of the behavior of isolated polyelectrolyte chains in various solvent conditions [1-6]. Despite this effort a complete theoretical description of the characteristics of a polyelectrolyte chain, at the level comparable to that established for neutral polymer solutions [7], is still lacking. One of the reasons is the presence of many competing length scales arising from the simultaneous presence of repulsive Coulomb interactions and short-range interactions, the sign of which depends on the quality of the solvent. the practical aspects that make this problem important include colloid stabilization by grafted polyelectrolytes [8]. Here we provide a theory at the self-consistent mean-field level for the configurations of an isolated polyelectrolyte chain in dilute solutions focusing largely on the case of poor solvent. By "poor" we mean that the solvent quality is bad for the corresponding neutral chain. Even though the quality of the solvent is "poor" the polyelectrolyte chain may be soluble if the electrostatic interaction between the monomers is sufficiently repulsive.

The principle difficulty in developing a statistical mechanical theory of a polyelectrolyte chain in a solvent is that this system even in a salt-free situation is a ternary system consisting of the solvent (usually water), the polyelectrolyte chains and the associated counter ions. However significant advances have been made using the notion of persistence [2] length (suitable for strongly charged polyelectrolytes where screening due to counter ions is significant) and with the adaptation of the modern scaling theory of polymer solutions [1,3-6]. Recently Raphael and co-workers [5,6] have built on the earlier blob model for a weakly charged polyelectrolyte chain developed by Khokhlov [3] and produced the expected conformations of an isolated polyelectrolyte chains in a poor solvent. For this problem the relevant parameters that affect the conformations of the polyelectrolyte chain are the following: (i) The excluded-volume parameter ω_2 which for temperatures T close to the Θ temperature is proportional to $(T-\Theta)/\Theta$. (ii) The strength of the Coulomb repulsion between monomers $\omega_c = Z^2e^2/4\pi\epsilon kT = Z^2 l$ where Ze is the charge per monomer, l is the Bjerrum length, and ϵ is the dielectric constant of the solvent. (iii) κ^{-1} the Debye screening length which is a measure of the distance beyond which the electrostatic interaction is screened. It should be noted that κ depends on Ze as well as on the concentrations of any added electrolytes. By extending the Khokhlov blob model, Higgs and Raphael [6] argued that the behavior of the polyelectrolyte chain can be extremely complicated and crucially depends on the subtle interplay between ω_2, ω_c, κ, and N the polymerization index. Most notably it has been suggested [5,6] that when ω_2 is constant and sufficiently negative (i.e., the solvent is poor for the neutral chain) and κ is varied there exists a critical value of the salt concentration at which the chain may abruptly make a transition from a rodlike configuration to a globulelike state. The approximate concentration at which this transition occurs is roughly given by $\kappa D \sim 1$ where $D \sim b(uZ^2)^{-1/3}$ is the blob radius, $u = l/b$, and b is the size of a monomer.

In this paper we provide a self-consistent variational theory for both strongly and weakly charged isolated polyelectrolyte chain under all solvent conditions building largely on the recent work of Muthukumar [9]. For the dilute polyelectrolyte (the interaction between the chains is negligible) solutions we derive approximate equations for the size of the chain for arbitrary values of ω_2, ω_c, and κ. The complete numerical analysis of this equation can account for the phase diagram suggested by using scaling arguments and Higgs and Raphael [6]. However, in order to make the physical content of this theory transparent we focus here on the conformational changes in the small-κ (more precisely when $\kappa D < 1$) and the large-κ ($\kappa D \gg 1$) limits. The limit of small κD is obtained in the case of weakly charged chains in the absence of salt whereas large values of κD result upon the addition of salt. Our principle results obtained for negative values of ω_2 (corresponding to poor solvent conditions) are the following:

(1) When κD is small and the temperature of the system is reduced then there exists a critical value of ω_c (or equivalently Z) below which the chain contracts smoothly from a rodlike configuration (the mean-square end-to-end distance, R, scales as $R \sim Nb$) to a globule state where $R \sim N^{1/3}b$. This transition becomes abrupt at a critical value of ω_2 and resembles a first-order transition which

would be steeply discontinuous as $N \rightarrow \infty$.

(2) For large κD (obtained by adding salt) there exists a value of $Z = Z_0$ above which the conformation of the polyelectrolyte is swollen, i.e., $R \sim N^{3/5} b_e$ where b_e is an effective Kuhn length. In this case despite the large and negative value of ω_2 the chain behaves like a neutral chain with an effective positive excluded volume parameter. For $Z < Z_0$ the chain collapses into a globule. This collapse transition can be continuous or abrupt depending on the value of the effective three-body interaction. This prediction is consistent with the scaling theory of Higgs and Raphael [6] who examined this case with Z fixed and varying ω_2 and κ. It should be emphasized that the results stated here are not due to Manning condensation [10] but arise naturally from the competition between short-range attraction achieved in poor solvents and long-range Coulomb repulsion.

(3) In addition to the above two results, which have so far been obtained only using the assumption of scaling, we provide equations for obtaining the shape of the polyelectrolyte chain for arbitrary values of ω_2, Z, and κ. These equations can be used to obtain the entire phase diagram for an isolated polyelectrolyte chain under any solvent conditions. In particular we derive the scaling behavior for the polyelectrolyte conformations in both good solvent and the Θ solvent.

As stated before even in the infinite-dilution limit (whether this can be achieved in the laboratory at all is questionable) the polyelectrolyte solution is a ternary system. If this can be approximated as a binary system consisting of only the counter ions and the polyelectrolyte chain in which the effective interactions are renormalized by the solvent, then the recently developed variational theory can in principle be applied [11]. However, in this paper we treat this system as an isolated polyelectrolyte chain in which the effect of the solvent and the counterions are taken into account in terms of an effective screening length mediating the range of the Coulomb interaction between the charged monomers. With these assumptions we model the uniformly charged flexible polyelectrolyte chain in terms of an effective Edwards Hamiltonian [9]

$$\beta H(r(n)) = \frac{3}{2b^2}\int_0^N \left(\frac{dr}{dn}\right)^2 + \frac{\omega_c b^2}{2}\int_0^N dn \int_0^N dn' \frac{e^{-\kappa|r(n)-r(n')|}}{|r(n)-r(n')|} + \frac{\omega_2 b^3}{2}\int_0^N dn \int_0^N dn' \delta(r(n)-r(n'))$$

$$+ \frac{\omega_3}{3!} b^6 \int_0^N dn \int_0^N dn' \int_0^N dn'' \delta(r(n)-r(n'))\delta(r(n')-r(n'')) , \qquad (1)$$

where $r(n)$ is the position of the monomer n, b is the effective size of a monomer, N is the total number of monomers, ω_2 [$\propto (T-\Theta)/\Theta$ for T close to the Θ temperature when $\omega_c = 0$] is the term due to the excluded-volume interactions, and ω_3 is the coefficient of the three-body term needed for obtaining the size of the chain when ω_2 becomes negative. For wormlike polyelectrolytes we also have to consider curvature terms due to local stiffness [2]. The second term in Eq. (1) is the screened Coulomb interaction between the monomers in the Debye-Huckel approximation with $\omega_c = Z^2 l$. The Debye screening length κ^{-1} for a 1-1 electrolyte is given by $(8\pi n \omega_c)^{-1/2}$ where n is the total density of the counter ions including those from the addition of salt. The model that we consider [see Eq. (1)] in the limit of $\kappa D \rightarrow 0$ and for $Z \ll 1$ corresponds to the case of weakly charged polyelectrolyte chains in which the screening between the monomeric charges is negligible. In this case the effect of the counter ion is not important and the conformations of the chain in a poor solvent are determined by the long-range Coulomb repulsion and the competition between short-range attraction. In this limit our model reduces to that analyzed by Higgs and Raphael [6]. For large values of κD or for $Z \gg 1$ the counter ions do play a significant role and even within the validity of the Debye-Huckel theory one has to worry about the electrostatic persistence length. In fact we show that the variational solution in the large κD limit explicitly reproduces the same expression for the electrostatic persistence length obtained in Ref. [2]. The free energy and size of the polyelectrolyte chain for the theory given by Eq. (1) can be calculated by the standard self-consistent variational treatment of Edwards and Singh [12]. This in fact has recently been extended to polyelectrolyte chains in good solvents [9,13]. If we assume that the reference Hamiltonian is given by the Gaussian theory with an effective step length b_1 then the self-consistent variational equation satisfied for b_1 is given by [14]

$$b_1^{3/2}\left(\frac{1}{b} - \frac{1}{b_1}\right) = \frac{X}{b_1} + \frac{y}{b_1^{5/2}} + \zeta_c , \qquad (2a)$$

where

$$X = \frac{4}{3}\left(\frac{3}{2\pi}\right)^{1/2} \omega_2 N^{1/2} , \qquad (2b)$$

$$\zeta_c = \frac{15}{2}\lambda \left[\frac{\sqrt{\pi} e^a}{a^{5/2}}(a^2 - 4a + 6)\operatorname{erfc}\sqrt{a} - \frac{6\sqrt{\pi}}{a^{5/2}} - \frac{2\sqrt{\pi}}{a^{3/2}} + \frac{12}{a^2} \right] , \qquad (2c)$$

$$\lambda = \frac{2}{45}\left(\frac{6}{\pi}\right)^{1/2} Z^2 u N^{3/2} , \qquad (2d)$$

$$a = \frac{N\kappa^2 b b_1}{6} , \qquad (2e)$$

y is proportional to the value of the three-body interaction term, and erfc(x) is the complement to the error function. The complete analysis of Eq. (2) in terms of the variables X, λ, and κ is complicated and will be presented elsewhere [14]. Here we focus on the limit of small κD (which is appropriate for the recent scaling theories) and large κD.

The limit of large κD is obtained whenever $Z \gg 1$ (strongly charged polyelectrolytes) or upon addition of salt. In these limits the equation for the size of the polyelectrolyte chain simplify considerably and can be written in terms of the swelling ratio $\alpha^2 = R^2/R_0^2 = b_1/b$ where $R_0 = bN^{1/2}$. The result is

$$\alpha^5 - \alpha^3 - \frac{y}{\alpha^3} - g(\kappa)\alpha^2 = X \tag{3a}$$

where

$$g(\kappa) = \lambda \begin{cases} 1, & \kappa \to 0, \\ \dfrac{45}{N(\kappa b)^2 \alpha^2}, & \kappa b a \to \infty . \end{cases} \tag{3b}$$

The above equation with $g(\kappa)=0$ was considered by de Gennes to describe the collapse of a neutral polymer from a swollen configuration to a compact globular state [15]. In particular he noted that if y is less than a critical value ($y < 0.023$) this collapse transition is abrupt.

If the quality of the solvent is good, which corresponds to $X \gg 1$, then it follows from Eq. (3) that [9]

$$R \sim \begin{cases} bN(uZ^2)^{1/3}, & \kappa \to 0, \\ b\left[\omega_2 + \dfrac{Z^2 u}{(\kappa b)^2} C\right]^{1/5} N^{3/5}, & (\kappa b a) \to \infty , \end{cases} \tag{4}$$

where C is a numerical constant.

Similar analysis for the conformations at the Θ point ($X=0$) shows that

$$R \sim \begin{cases} bN(uZ^2)^{1/3}, & \kappa \to 0, \qquad (5a) \\ bN^{3/5}\left[\dfrac{Z^2 u}{(\kappa b)^2}\right]^{1/5}, & (\kappa b a) \to \infty . \qquad (5b) \end{cases}$$

The result for R at the Θ solvent for small κ was first obtained by de Gennes *et al.* using the concept of electrostatic blobs [1]. It should be noted that Eq. (5b) is an asymptotic result valid only when κD is larger than unity, i.e., when the range of the screened Coulomb interaction becomes comparable to D. In this regime the chain dimension is determined by the "effective excluded volume" due to the screened Coulomb interaction between the monomers. This equation is identical to that obtained by Khokhlov and Khachaturian [3] using scaling arguments. The expression $Z^2u/(\kappa b)^2$ in Eq. (5b) can be written as l_e/b where l_e can be identified as the electrostatic contribution to the persistence length valid when κb is very large [2]. It is interesting to note that this result for the electrostatic contribution to the persistent length coincides with that calculated by a different variational method by Odijk [2] for short polyelectrolyte chains. Thus the variational ansatz automatically yields an approximate equation for l_e in the limit of large κD. Notice that Eqs. (3b) and (5b) are only valid when $l_e/b \ll N$. If this condition is not satisfied the conformation of the polyelectrolyte would be rodlike.

We now describe the behavior of the chain in a poor solvent which corresponds to negative values of X. We first consider the case of small κ which means that the screening length is much larger than the typical blob size. In principle this situation is obtained for very small values of Z and this corresponds to the case of weakly charged polyelectrolytes. More precisely we show that in this regime the critical parameter controlling the conformation of the polyelectrolyte chain is the dimensionless variable λ [cf. Eq. (2d)]. In Fig. 1 a plot of $X(\alpha)$ for various values of λ for a fixed $y(=1)$ is shown. From Fig. 1 it is clear that there are two distinct cases to be considered depending on the value of the control parameter λ. If λ is less than a y-dependent critical value $\lambda_c(y)$ ($=2.48$ for $y=1$) the chain collapses smoothly from the rodlike state (for large positive values of X) to the globule phase when $X \ll 0$. This change in X can be obtained by reducing the temperature of the system. On the other hand when $\lambda > \lambda_c(y)$ then we obtain an unstable branch. This implies there is an abrupt transition from the rod configuration to a compact collapsed globule state at a certain critical value of X. At the critical value of X the free energies of the two locally stable branches are equal. We should emphasize that $\lambda_c(y)$ changes drastically as y changes. For example, $\lambda_c(y=0.025)=0.034$. Finally we find that when $y=0.023$, then $\lambda_c \equiv 0$. This is precisely the value of y at which an abrupt collapse from a swollen phase to a globule phase takes place in a neutral chain [16]. We have also examined the behavior of the weakly charged chain in a poor solvent in the presence of salt by numerically solving the variational equations. We find that there is an abrupt transition between a rodlike state to a globule phase at a critical value of κb as long as the solvent is poor enough, i.e., $|X|$ exceeds a λ dependent critical value $|X_c|$. This is in accord with the scaling predictions of Higgs and Raphael [6].

In the opposite limit of almost complete screening of the electrostatic interaction ($\kappa b a \to \infty$) which is obtained by the addition of salt the equation for α is given by

$$\alpha^5 - \alpha^3 - \frac{y}{\alpha^3} = X_{\mathrm{eff}}, \tag{6a}$$

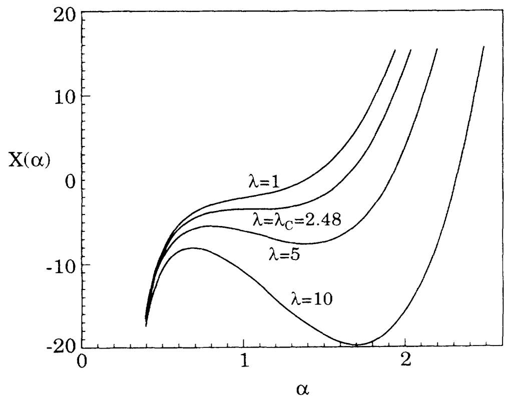

FIG. 1. Size of a weakly charged polyelectrolyte chain in terms of the reduced temperature calculated using Eq. (2a). The curves correspond to different values of the control parameter λ [see Eq. (2d)]. The effective three-body interaction parameter y has been set to unity. The value of y in practice can be changed by altering the number of side groups in the chain (see Ref. [15]).

$$X_{\rm eff}=\left\{-k_1|\omega_2|+k_2\frac{Z^2u}{(\kappa b)^2}\right\}N^{1/2}, \tag{6b}$$

where k_1 and k_2 are numerical constants. The terms in the parenthesis in Eq. (6b) can be identified as an effective excluded-volume term. The analysis of this equation proceeds along the lines suggested by de Gennes [15]. If $X_{\rm eff} > 0$ the chain remains swollen and behaves like a neutral chain in a good solvent. Below a certain effective Θ point (determined by the vanishing of $X_{\rm eff}$) $X_{\rm eff}$ becomes negative and this leads the chain to collapse into a compact globule ($R \sim bN^{1/3}$). As shown by de Gennes this transition to a collapsed state is continuous when $y > 0.023$ [17]. However, when $y < 0.023$ the chain contracts abruptly at a critical value of $X_{\rm eff}$.

In this paper we have provided a unified theoretical description, at the mean-field level, for the behavior of an isolated polyelectrolyte chain in solvents of differing quality. We have obtained an expression for the size of the polymer chain in terms of the parameters of the system, namely the solvent quality, the salt concentration and the effective charge on the polymer. Our theory reproduces the results of the recently announced scaling behavior of weakly charged polyelectrolytes in the limit of small κD as well as large κD. In addition, numerical solution of our equations [14] indicate that the predictions of our theory for the persistence length appear to be consistent with those obtained earlier for restricted models [2]. The major advantage of our theory is that we have a framework for computing the shape, free energies, and other characteristics such as the scattering function [14] for an isolated polyelectrolyte chain for arbitrary values of the salt concentration and effective charge on the monomer. For this the full expression has to be used in appropriate numerical calculations to obtain the complex phase diagrams for the chain in a poor solvent.

This work was supported in part by a grant from the National Science Foundation and the Camille and Henry Dreyfuss Foundation.

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[1] P. G. de Gennes, P. Pincus, R. M. Velasco, and F. Brochard, J. Phys. (Paris) **37**, 1461 (1976).

[2] J. Skolnick and M. Fixman, Macromolecules **10**, 944 (1977); T. Odijk, J. Polym. Phys. Edn. **15**, 477 (1977).

[3] A. R. Khokhlov, J. Phys. A **13**, 979 (1980); A. R. Khokhlov and K. A. Khachaturian, Polymer **23**, 1742 (1982).

[4] P. Pincus and T. A. Witten, Europhys. Lett. **3**, 315 (1987).

[5] E. Raphael and J. F. Joanny, Europhys. Lett. **13**, 623 (1990).

[6] P. Higgs and E. Raphael, J. Phys. I (France) **1**, 1 (1991).

[7] See, for example, Y. Oono, Adv. Chem. Phys. **61**, 301 (1985).

[8] P. Pincus, Macromolecules **24**, 924 (1991).

[9] M. Muthukumar, J. Chem. Phys. **86**, 7230 (1987).

[10] G. Manning, J. Chem. Phys. **51**, 924 (1969).

[11] M. R. Shaw and D. Thirumalai, Phys. Rev. A **44**, R4797 (1991).

[12] S. F. Edwards and P. Singh, J. Chem. Soc. Faraday Trans. 2, **75**, 1001 (1979).

[13] M. Muthukumar, in *Molecular Basis of Polymer Networks*, edited by A. Baumgartner and C. E. Picot (Springer-Verlag, Berlin, 1989).

[14] B.-Y. Ha and D. Thirumalai (unpublished).

[15] P. G. de Gennes, J. Phys. (Paris) Lett. **36**, L55 (1975).

[16] M. Muthukumar, J. Chem. Phys. **81**, 6272 (1984).

[17] The critical value of y reported in Ref. [15] is somewhat in error. The correct value, $y = 0.023$, was first reported in Ref. [16]. Since the theory itself is somewhat qualitative, the precise numerical values are not that important.