Counterion Condensation and Phase Separation in Solutions of Hydrophobic Polyelectrolytes

Andrey V. Dobrynin and Michael Rubinstein*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

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ABSTRACT: We have developed a theory of counterion condensation in solutions of hydrophobic polyelectrolytes. In the framework of Oosawa's two-zone model we demonstrate that solutions of necklaces can be unstable with respect to phase separation. This phase separation is triggered by the concentration-induced counterion condensation. For the range of parameters at which the polyelectrolyte solution is stable, we predict nonmonotonic dependence of the chain size on polymer concentration. This nonmonotonicity in the chain size manifests itself in the dramatic increase in solution viscosity at the crossover to concentrated polyelectrolyte solution. There is also a possibility of two peaks in the scattering function of qualitatively different physical nature observed in different concentration regimes. The scattering intensity at the peak position increases with polymer concentration in low concentration (necklace) regime and decreases with concentration in concentrated polyelectrolyte solutions.

I. Introduction

Numerous theoretical studies in recent years have been devoted to properties of polyelectrolyte solutions.[1−19] Polyelectrolytes are macromolecules carrying ionizable groups,[1−3] which under appropriate conditions dissociate, leaving charges on the chain and counterions in the solution. Common polyelectrolytes include polyacrilic and methacrylic acids and their salts, cellulose derivatives, sulfonated polystyrene, DNA, and other polyacids and polybases.

Most synthetic polymers do not dissolve in water due to strong hydrophobic interactions between hydrocarbon backbone and water molecules. The solubility of these polymers can be significantly improved by introducing charged groups. In aqueous environment these charged groups dissociate by releasing counterions into solution and leaving ionized charged groups on polymer backbone. The shape of a hydrophobic polyelectrolyte molecule is determined by the competition between electrostatic and hydrophobic interactions. The hydrophobic interactions cause polymer chain to collapse into a spherical globule in order to minimize the number of unfavorable monomer−solvent contacts while electrostatic interactions force the polymer chain to extend to minimize the electrostatic repulsion between charged monomers. Optimization of the hydrophobic and electrostatic interactions results in the formation of a necklace globule[11,17,20−25]—a set of small charged globular chain sections connected by long and narrow sections, called strings.

At finite polymer concentrations some counterions are attracted to polyelectrolyte chains and may condense on them.[3,5,26] The counterion condensation is due to a fine interplay between the strong electrostatic attraction of counterions to the polymer chain and the loss of translational entropy by counterions due to their localization in the vicinity of polyelectrolytes. In very dilute polyelectrolyte solutions, the entropic penalty for counterion condensation is very high, and almost all counterion leave polyions and stay in solution. However, as the polymer concentration increases, the entropic penalty for counterion condensation decreases resulting in the gradual increase in the number of condensed counterions. For polyelectrolyte solutions in good or Θ solvents for the polymer backbone the fraction of free counterions decreases logarithmically with increasing polymer concentration.[22]

The new phenomena for hydrophobic polyelectrolytes is the avalanche-like counterion condensation.[5,27] By increasing the polymer concentration or by decreasing the quality of the solvent, one can induce spontaneous condensation of counterions inside the beads of the necklacelike globule. The reduction of the effective charge by condensing counterions increases the mass of the beads initiating further deficit of counterions that starts the avalanche-like counterion condensation process. At finite polymer concentrations, this avalanche-like condensation results in the phase separation of polyelectrolyte solutions into dilute and concentrated phases. In the present paper, we develop a theory of the counterion condensation in solutions of hydrophobic polyelectrolytes and calculate the phase diagram of this polymeric system as a function of solvent quality and polymer concentration.

In the next section, we review the necklace model of hydrophobic polyelectrolytes. In section III, we investigate the stability of hydrophobic polyelectrolytes with respect to the avalanche-like counterion condensation in dilute and semidilute solutions. For the polymer chains above the counterion condensation threshold we calculate the chain properties, taking into account effects of progressive counterion condensation with increasing polymer concentration. Section IV discusses the scattering from solutions of necklaces with condensed counterions. In section V, we address the problem of the condensation-induced phase separation in solutions of hydrophobic polyelectrolytes and calculate the phase diagram of this polymeric system as a function of solvent quality and polymer concentration. Finally, in conclusion we present the comparison of our results with computer simulations and experiments.

II. Necklace Model of a Polyelectrolyte Chain in a Poor Solvent[11,17]

Consider a polymer chain with degree of polymerization N, monomer size b, and fraction of the charged

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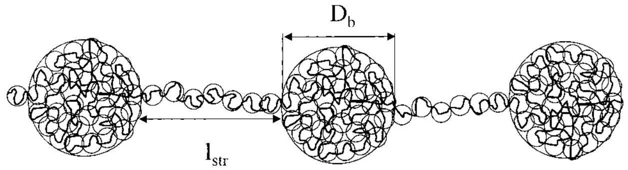

Figure 1. Necklace structure of a polyelectrolyte chain in a poor solvent.

monomers f in a poor solvent with dielectric constant ϵ. An uncharged chain in a poor solvent forms a globule.[5,27,28] The monomer density ρ inside this globule is defined by the balance between the two-body attraction $-\tau b^3\rho N$ and the three-body repulsion $b^6\rho^2 N$. The resulting density inside the globule is

$$\rho \approx \tau/b^3 \tag{1}$$

where the reduced temperature is given by

$$\tau = (\Theta - T)/\Theta \tag{2}$$

and Θ is the theta temperature of the polymer. Note that in eq 1 and throughout the paper, we drop numerical coefficients and keep our discussion at the scaling level. The size R of the globule with the average monomer density ρ is equal to

$$R \approx (N/\rho)^{1/3} \approx N^{1/3} b\tau^{-1/3} \tag{3}$$

The density fluctuations inside the globule are suppressed on the length scales larger than the thermal blob size $\xi_T \approx b/\tau$. On the length scales smaller than ξ_T the polymer statistics is Gaussian.

The electrostatic interactions between charged monomers on a polyelectrolyte chain in a poor solvent can change the shape of the globule without significantly affecting its volume. As in the case of the uncharged polymer, the occupied volume is still controlled by the solvent quality. A charged globule can spontaneously deform if the energy of the electrostatic repulsion between charges $F_{Coul} \approx e^2 f^2 N^2/\epsilon R$ becomes comparable to its surface energy $F_{surf} \approx kTR^2\xi_T^{-2}$. This deformation occurs when the total valency of the charge fN becomes larger than the critical value $(N\tau/u)^{1/2}$. Here the dimensionless interaction parameter

$$u = l_B/b \tag{4}$$

is the ratio of the Bjerrum length l_B—the length scale on which the electrostatic interaction between two elementary charges is on the order of the thermal energy kT—to the bond size b.

For higher charge densities $f > (\tau/uN)^{1/2}$ the polyelectrolyte globule splits into a set of smaller charged globules (beads) connected by narrow strings—the necklace globule (see Figure 1).[11,17] The size of the beads

$$D_b \approx b(uf^2)^{-1/3} \tag{5}$$

is determined by the stability condition

$$e^2 f^2 m_b^{\,2}/\epsilon D_b \approx kTD_b^{\,2}\,\xi_T^{\,-2} \tag{6}$$

where

$$m_b \approx \tau/uf^2 \tag{7}$$

is the number of monomers in a bead ($m_b \approx \rho D_b^3$). The diameter of the strings is on the order of thermal blob size $\xi_T \approx b/\tau$. The length l_{str} of the string connecting two neighboring beads can be estimated by balancing the electrostatic repulsion between two closest beads $kTl_B f^2 m_b^2/l_{str}$ and the surface energy of the string kTl_{str}/ξ_T. The equilibrium distance between neighboring beads is

$$l_{str} \approx b\left(\frac{\tau}{uf^2}\right)^{1/2} \approx bm_b^{\,1/2} \tag{8}$$

The mass of a string between neighboring beads $m_{str} \approx \rho l_{str}\xi_T^2$ is much smaller than the mass of a bead m_b

$$\frac{m_{str}}{m_b} \approx \left(\frac{uf^2}{\tau^3}\right)^{1/2} \ll 1 \tag{9}$$

In this case, the number of beads N_{bead} per chain is approximately equal to $N/m_b \approx uf^2N/\tau$. Since most of the necklace length is due to the strings ($l_{str} \gg D_b$), the length of the necklace can be estimated as the number of beads N_{bead} on the chain times the length of a string l_{str} between neighboring beads

$$L_{nec} \approx N_{bead} l_{str} \approx b\left(\frac{uf^2}{\tau}\right)^{1/2} N \approx b\frac{N}{m_b^{\,1/2}} \tag{10}$$

In this approximation the total free energy of the polyelectrolyte chain in a poor solvent is

$$\frac{F_{ch}}{kT} \approx N\frac{l_B f^2 m_b}{D_b} + \frac{l_B f^2 N^2}{L_{nec}} - N\tau^2 \tag{11}$$

where the first term is the electrostatic and surface energies of the beads, the second one is the electrostatic repulsion between beads which is on the order of the surface energy of the strings, and the last one is the free energy of the polymer backbone in a poor solvent. The electrostatic repulsion between beads (the second term in the rhs of eq 11) is smaller than the electrostatic energy of the beads (the first term) as long as the length of the string l_{str} between two neighboring beads is larger than the bead size D_b and can be neglected.

$$\frac{F_{ch}}{kT} \approx N(uf^2)^{1/3}\tau - N\tau^2 \tag{12}$$

Below we develop a theory of counterion condensation for solutions of hydrophobic polyelectrolytes based on the necklace model[11,17] reviewed above.

III. Counterion Condensation in Solutions of Necklaces

Consider a salt-free solution of hydrophobic polyelectrolytes with monomer concentration c. At this monomer concentration the volume V_{ch} per chain is N/c. To describe the counterion condensation we will use the two-zone Oosawa model.[3] In the framework of this model, the average volume per chain V_{ch} is divided into two zones (see Figure 2). The first zone is occupied by the polymer chain, the volume of which in our case can be estimated as the number of beads on the chain N/m_b times the volume of a bead D_b^3. The second zone is the volume free of the polymer $V_{ch} - D_b^3 N/m_b$. In a salt-free solution the number of counterions in the volume

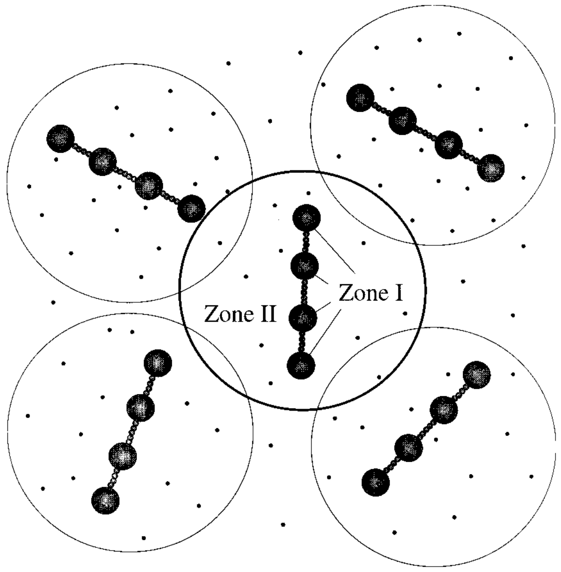

Figure 2. Schematic representation of the two-zone model.

V_{ch} is equal to the net charge on the polymer chain fN. The fraction x of these counterions occupies the second zone with volume $V_{ch} - D_b{}^3N/m_b$ and is considered to be free, while the fraction $1 - x$ is localized (condensed) inside the beads (the first zone). The counterions localized inside the beads reduce the effective charge on each bead to m_bfx, weakening the electrostatic repulsion. The equilibrium size of a bead D_b with condensed counterions is still determined by the stability condition (see eq 6) where the fraction of the charged monomers on the chain f is substituted by fraction of the effectively charged ones fx. Taking this fact into account we can rewrite the expression for the free energy per chain (eq 12) in the following form

$$\frac{F_{ch}}{kT} \approx N(uf^2x^2)^{1/3}\tau - N\tau^2 \qquad (13)$$

The ideal gas contribution to the free energy of the system due to translational entropy of all counterions (both free and localized inside beads) is

$$\frac{F_{tran}}{kT} = f(1-x)N\ln\left(\frac{f(1-x)m_b b^3}{eD_b{}^3}\right) + fxN\ln\left(\frac{fxNb^3}{e(V_{ch} - D_b{}^3N/m_b)}\right) = fN\left((1-x)\ln\frac{(1-x)}{e} + x\ln\frac{x}{e} + x\ln\left(\frac{\tilde{c}}{1-\tilde{c}}\right) + \ln(f\tau)\right) \qquad (14)$$

where $\tilde{c}$ is the ratio of the average monomer density c in solution to the monomer density ρ inside the beads

$$\tilde{c} \approx \frac{c}{\rho} \approx \frac{cb^3}{\tau} \qquad (15)$$

The condensed counterions inside the beads also have an additional "correlation" part of the free energy F_{corr}.[29−32] This part of the free energy can be expressed in terms of the coupling parameter

$$\Gamma = l_B((2-x)f\rho)^{1/3} \qquad (16)$$

which is the ratio of the Coulomb interaction between two elementary charges separated by the typical distance $(f(2 - x)\rho)^{-1/3}$ to the thermal energy kT. The expression for correlation part of the free energy F_{corr} has a simple analytical form in the two limiting cases. In the case of weak electrostatic interactions $\Gamma \ll 1$ the correlation part of the free energy reduces to the Debye−Huckel weak coupling law.[29,30,32]

$$\frac{F_{corr}}{kT} \approx -Nf(2-x)\Gamma^{3/2}, \quad \text{for } \Gamma \ll 1 \qquad (17)$$

In the limit of large values of the coupling parameter $\Gamma \gg 1$, strong electrostatic interactions between charges lead to the formation of a strongly correlated Wigner liquid. The correlation energy of the liquid can be estimated as the cohesive energy per charge Γ times the number of charges $f(2 - x)N$

$$\frac{F_{corr}}{kT} \approx -Nf(2-x)\Gamma, \quad \text{for } \Gamma \gg 1 \qquad (18)$$

These correlation-induced attractive interactions can be neglected as long as their contribution to the free energy is weaker than that of the monomer−monomer interactions. This is true when the parameter $(2 - x)f\Gamma^{3/2}$ is smaller than τ^2 in the weakly interacting case ($\Gamma \ll 1$) and $(2 - x)f\Gamma \ll \tau^2$ in the case of strong coupling ($\Gamma \gg 1$). For these two inequalities to be satisfied, the fraction $(2 - x)f$ of the charged monomers on a chain has to be smaller than τu^{-1} for the Debye−Huckel limiting case or $\tau^{5/4}u^{-3/4}$ in the strongly correlated Wigner liquid. If the opposite inequalities hold, the monomer concentration inside the beads has to be obtained by balancing the correlation energy with the three-body repulsion. This case is similar to the formation of a polyampholyte globule.[33−36] Below we will restrict our consideration to the case with negligible correlation energy.

Combining the free energy of the necklace eq 13 with the translational entropy of the counterions eq 14, we can write the total free energy per chain in the following form

$$\frac{F_{neckl}}{kT} = fN\left((1-x)\ln\frac{(1-x)}{e} + x\ln\frac{x}{e} + x\ln\left(\frac{\tilde{c}}{1-\tilde{c}}\right) + \epsilon_c x^{2/3} + \ln f\tau - \tau^2 f^{-1}\right) \qquad (19)$$

where we have introduced a new parameter ϵ_c—the electrostatic interaction between a bead and a counterion at its surface in units of thermal energy kT.

$$\epsilon_c \approx \frac{l_B f m_b}{D_b} \approx \left(\frac{u}{f}\right)^{1/3}\tau \qquad (20)$$

Minimization of the free energy eq 19 with respect to the fraction of the free counterions x results in the following nonlinear equation

$$\tilde{c}(\epsilon_c, x) = \frac{1-x}{1 + x\left(\exp\left(\frac{2}{3}\frac{\epsilon_c}{x^{1/3}}\right) - 1\right)} \qquad (21)$$

This equation gives the relation between the fraction of free counterions x and the polymer concentration c.

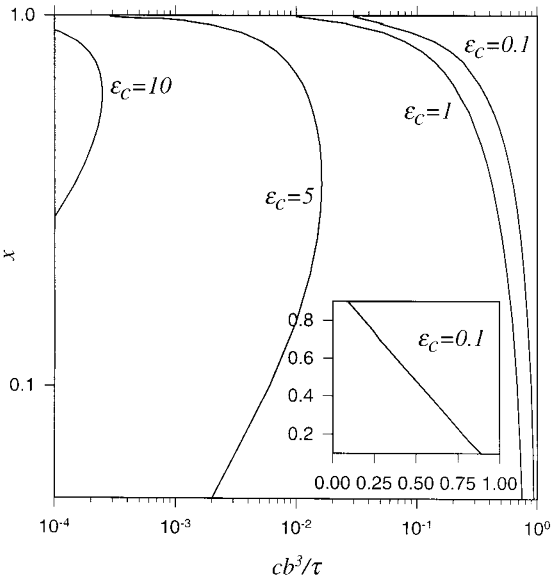

Figure 3. Fraction of free counterions x as a function of reduced polymer concentration $\tilde{c}$ for different values of the parameter ϵ_c.

Figure 3 shows the dependence of the fraction of the free counterions x on the reduced polymer concentration $\tilde{c}(\epsilon_c,x)$ for different values of the counterion energy at the surface of the bead ϵ_c (eq 20). Each curve for the value of the parameter ϵ_c consists of two branches separated by the turning point ($\tilde{c}_{\max},x_{\max}$). The stable solution of the eq 21 corresponds to the upper branch of the curve ($x > x_{\max}$) where $x_{\max}$ is the solution of equation

$$\epsilon_c = \frac{9}{2}\frac{x_{\max}^{1/3}}{(1 - x_{\max})} \tag{22}$$

For higher reduced polymer concentrations $\tilde{c} > \tilde{c}_{\max}$, there is no solution of eq 22 and the free energy of a single chain eq 19 is minimal at $x = 0$ with no free counterions. This result indicates that the solution of hydrophobic polyelectrolytes is unstable with respect to macrophase separation into a concentrated phase and a dilute phase of necklaces with a finite fraction of free counterions. If the parameter $\epsilon_c \gg 1$, counterions are strongly attracted by beads and condense onto them. However, for the small values of the parameter $\epsilon_c \ll 1$, the polyelectrolyte solution of necklaces is stable in the entire concentration interval $\tilde{c} < 1$. This stability condition of the necklace globule with respect to counterion condensation is similar to the one derived in our previous publications.[11,17]

If the polymer solution is stable with respect to phase separation ($\epsilon_c < 1$), we can calculate the properties of hydrophobic polyelectrolytes in dilute and semidilute polyelectrolyte solutions, taking into account the counterion condensation. In this regime the fraction of free counterions decreases almost linearly with increasing polymer concentration (see insert in Figure 3)

$$x \approx 1 - \tilde{c}, \quad \text{for } \epsilon_c < 1 \tag{23}$$

Thus, there will be a concentration-induced cascade of transitions between necklaces with different number of beads. The conditions for these transitions are determined by the stability of beads with condensed counterions $m_b \approx N/k \approx \tau/(uf^2x^2)$ leading to the following expression

$$c_k \approx \frac{\tau}{b^3}\left(1 - \sqrt{\frac{\tau k}{uf^2N}}\right), \quad \text{for } k = 1, 2, 3,... \tag{24}$$

where k is the number of beads on a chain.

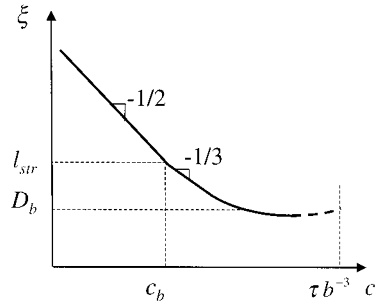

Figure 4. Dependence of the correlation length ξ on reduced polymer concentration $\tilde{c}$ in semidilute solutions. Logarithmic scales.

The crossover from dilute to semidilute solutions occurs at the overlap concentration for which the distance between chains $(c/N)^{-1/3}$ becomes on the order of the chain size $L_{\rm nec}$

$$c^* \approx N/L_{\rm nec}^{\,3} \approx b^{-3}N^{-2}\left(\frac{\tau}{uf^2(1 - \tilde{c}^*)^2}\right)^{3/2} \tag{25}$$

where $\tilde{c}^* \approx c^*b^3/\tau$ is the value of the reduced polymer concentration at the necklace overlap. In semidilute solutions ($c > c^*$), the configurations of the chain on length scales shorter than the correlation length ξ is similar to that in dilute solutions. On length scales longer than the correlation length ξ, the chain is assumed to be a random walk of correlation segments ξ. The correlation length at the overlap concentration $\xi(\tilde{c}^*)$ is equal to the necklace size $L_{\rm nec}$ and in the semidilute regime ($\tilde{c} > \tilde{c}^*$) is independent of the degree of polymerization N[4,8,10,28]

$$\xi \approx b(uf^2\tau)^{-1/4}(1 - \tilde{c})^{-1/2}\tilde{c}^{-1/2} \tag{26}$$

For small values of the reduced polymer concentration $\tilde{c} \ll 1$, the correlation length is inversely proportional to the square root of polymer concentration.[4,8,10] With increasing polymer concentration, the dependence of the correlation length on concentration is weakened by the decrease in the fraction of free counterions (see Figure 4). This string-controlled regime continues as long as the correlation length ξ is larger than the length of the string $l_{\rm str}$ between neighboring beads. These two lengths become of the same order of magnitude ($\xi \approx l_{\rm str}$) at reduced polymer concentration

$$\tilde{c}_b \approx \left(1 + \left(\frac{\tau^3}{uf^2}\right)^{1/2}\right)^{-1} \tag{27}$$

For higher polymer concentrations $\tilde{c} > \tilde{c}_b$, the electrostatic interactions between beads are screened, and we expect one bead per every correlation volume ξ^3.

The correlation volumes ξ^3 are space filling $c \approx g\xi^{-3}$. The number of monomers inside the correlation volume $g \approx m_b$, since we have assumed that most of the polymer mass is in beads (eq 9). Therefore, the correlation length

$$\xi \approx b(uf^2)^{-1/3}(1 - \tilde{c})^{-2/3}\tilde{c}^{-1/3} \tag{28}$$

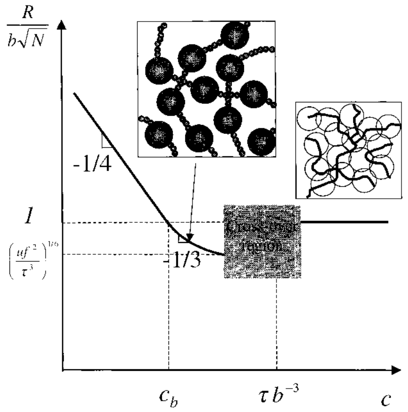

Figure 5. Dependence of the chain size R on reduced polymer concentration $\tilde{c}$ in semidilute solutions. Logarithmic scales.

decreases inversely proportional to the one-third power of polymer concentration for the small values of the reduced concentration $\tilde{c} \ll 1$. In this regime, the system behaves as a dilute solution of beads. For higher values of the reduced polymer concentrations closer to bead overlap ($\tilde{c} \approx 1$), counterion condensation dramatically modifies this dependence, significantly reducing the effective exponent (see Figure 4). Correlation length becomes almost independent of polymer concentration. Equation 28 predicts a minimum at $\tilde{c} \approx {}^1/_3$ and an increase of the correlation length above this value. However our model is unreliable in this regime $\tilde{c} > {}^1/_3$. The scaling model cannot describe the transition from semidilute bead-controlled regime for $\tilde{c} < 1$ to concentrated polyelectrolyte solution without necklaces $\tilde{c} > 1$.

Another interesting feature of the solution of necklaces is the nonmonotonic concentration dependence of the chain size (see Figure 5). In the string-controlled and bead-controlled regimes, the size of polyelectrolyte chains decreases with increasing polymer concentration.

$$R(\tilde{c}) \approx b\sqrt{N} \begin{cases} \left(\dfrac{uf^2}{\tau^3}\right)^{1/8} \left(\dfrac{1-\tilde{c}}{\tilde{c}}\right)^{1/4} & \text{string-controlled, } \tilde{c}^* < \tilde{c} < \tilde{c}_b \\ \left(\dfrac{uf^2}{\tau^3}\right)^{1/6} \left(\dfrac{1-\tilde{c}}{\tilde{c}}\right)^{1/3} & \text{bead-controlled, } \tilde{c}_b < \tilde{c} < 1 \end{cases} \tag{29}$$

At the crossover between the two regimes, the size of the necklace is on the order of the Gaussian size $R(\tilde{c}_b) \approx b\sqrt{N}$, but the conformation of the necklace consisting of beads and strings is significantly different from that of a Gaussian chain. Throughout the bead-controlled regime the size of the necklace decreases below the Gaussian size $b\sqrt{N}$. However above the beads overlap concentration $c > \tau b^{-3}$ the polyelectrolyte chain can be viewed as a polymer chain in a concentrated Θ solution with size $R(c) \approx b\sqrt{N}$ independent of polymer concentration. Thus, there is a sharp crossover between bead-controlled necklace regime for $\tilde{c} < 1$ and concentrated polyelectrolyte solution for $\tilde{c} > 1$ with a jump in polymer size on the order of $(\tau^3/uf^2)^{1/6}$ at polymer concentration $c \approx \tau b^{-3}$ ($\tilde{c} \approx 1$). Our scaling model cannot describe the details of this conformational transition at beads overlap.

To experimentally verify our predictions of nonmonotonic concentration dependence of polymer size and of its sharp increase at $c \approx \tau b^{-3}$, one would need to carry out scattering experiments on mixtures of labeled and unlabeled chains. There is also a direct effect of the sharp size increase on polymer dynamics that should be easily observed with unlabeled chains. The increase of the chain size at the bead overlap concentration $c \approx \tau b^{-3}$ is manifested in the dramatic increase in the solution relaxation time and viscosity and in the decrease in polymer self-diffusion coefficient. Below the crossover threshold ($c < \tau b^{-3}$) the viscosity of the solution is that of a semidilute solution of necklaces (see for details ref 17). The viscosity η of the semidilute polyelectrolyte solution of necklaces in the bead controlled regime is[17]

$$\eta_{\text{nec}}(\tilde{c}) \approx \eta_s \begin{cases} \dfrac{N}{m_b} \\ \dfrac{N^3}{n^4 m_b{}^3} \end{cases} \approx \eta_s \begin{cases} N\dfrac{uf^2}{\tau}(1-\tilde{c})^2, & \text{unentangled} \\ \dfrac{N^3}{n^4}\left(\dfrac{uf^2}{\tau}\right)^3 (1-\tilde{c})^6, & \text{entangled} \end{cases} \tag{30}$$

where η_s is the solvent viscosity and n is a constant of the order 5−10 related to the number of chains overlapping with a given one at the entanglement onset. Viscosity of the concentrated polyelectrolyte solution ($c > \tau b^{-3}$) is that of a solution of uncharged polymers in a Θ-solvent.[37]

$$\eta_\Theta(\tilde{c}) \approx \eta_s \begin{cases} N(cb^3)^2 \\ \dfrac{N_3}{n^4}(cb^3)^{14/3} \end{cases} \approx \eta_s \begin{cases} N\tau^2\tilde{c}^2, & \text{unentangled} \\ \dfrac{N^3}{n^4}\tau^{14/3}\tilde{c}^{14/3}, & \text{entangled} \end{cases} \tag{31}$$

Thus, at the crossover ($c \approx \tau b^{-3}$) between unentangled bead-controlled necklace regime and unentangled concentrated polyelectrolyte solution the increase in the solution viscosity can be estimated as

$$\eta_\Theta(\tilde{c})/\eta_{\text{nec}}(\tilde{c}) \approx \frac{\tau^3}{uf^2}, \quad \text{unentangled/unentangled} \tag{32}$$

For the crossover between the unentangled bead-controlled necklace regime and the entangled concentrated polyelectrolyte solution this increase is

$$\eta_\Theta(\tilde{c})/\eta_{\text{nec}}(\tilde{c}) \approx \frac{N^2}{n^4}\frac{\tau^{17/3}}{uf^2}, \quad \text{unentangled/entangled} \tag{33}$$

and finally at the crossover between entangled bead-controlled necklace regime and entangled concentrated polyelectrolyte solution, it is

$$\eta_\Theta(\tilde{c})/\eta_{\text{nec}}(\tilde{c}) \approx \frac{\tau^{23/3}}{(uf^2)^3}, \quad \text{entangled/entangled} \tag{34}$$

This sharp increase in viscosity at $c \approx \tau b^{-3}$ may have an appearance of a "gelling" transition.

IV. Scattering from Solution of Necklaces

To compare the predictions of our theory with the scattering experiments, we have to calculate the scattering function for solutions of necklacelike molecules. This scattering function can be written as

$$S(q) = (cm_{\mathrm{b}} + C(q))\left(\frac{\sin(qD_{\mathrm{b}}) - qD_{\mathrm{b}}\cos(qD_{\mathrm{b}})}{(qD_{\mathrm{b}})^3}\right)^2 + \frac{c}{m_{\mathrm{b}}}S_{\mathrm{con}}(q) \quad (35)$$

where the first term describes the scattering in the solution of charged spheres with size D_{b}, mass m_{b}, and interbead correlation function $C(q)$. In semidilute polyelectrolyte solutions the interbead correlation $C(q)$ has a peak at $q_{\mathrm{peak}_1}\xi \approx 1$. The second term in the rhs of eq 35 is due to polymer density fluctuations inside the beads. The beads can be considered as concentrated polyelectrolyte solutions with the average density $\rho \approx \tau b^{-3}$ and fraction $(1-x)f$ of the counterions condensed inside beads. In this case, the monomer−monomer correlation function $S_{\mathrm{con}}(q)$ on the length scales $q^{-1} < D_{\mathrm{b}}$ can be approximated by[38,39]

$$S_{\mathrm{con}}(q) = \frac{D_{\mathrm{b}}^{\,3}}{\dfrac{q^2b^2}{12\rho} + \dfrac{4\pi l_{\mathrm{B}}f^2}{q^2+\kappa^2} + \tau b^3} \quad (36)$$

where κ is the inverse Debye screening length due to counterions condensed inside beads

$$\kappa^2 = 4\pi l_{\mathrm{B}}\rho f(1-x) \quad (37)$$

For the wavenumbers $q < D_{\mathrm{b}}^{-1}$ the function $S_{\mathrm{con}}(q)$ is constant $S_{\mathrm{con}}(D_{\mathrm{b}}^{-1})$. The correlation function $S_{\mathrm{con}}(q)$ has a maximum at the value of the wavenumber q equal to q_{peak_2}.

$$q_{\mathrm{peak}_2}^{\;2}b^2 = (48\pi uf^2\rho b^3)^{1/2} - \kappa^2b^2 \approx (uf^2\tau)^{1/2} \quad (38)$$

In the range of the wavenumbers q such that $qD_{\mathrm{b}} \geq 1$ the scattering function eq 36 can be rewritten as

$$S(q) \approx cm_{\mathrm{b}}\frac{\cos^2(qD_{\mathrm{b}})}{(qD_{\mathrm{b}})^4} + \frac{c}{\dfrac{q^2b^2}{12} + \dfrac{4\pi l_{\mathrm{B}}f^2\rho}{q^2+\kappa^2} + \tau^2} \quad (39)$$

The scattering function $S(q)$ in the region of the wavenumbers $q \approx q_{\mathrm{peak}_2}$ is controlled by the interbead scattering because the first term in the rhs of the eq 39 is larger than the second one by the factor $(\tau^3/uf^2)^{1/6}$. Thus, the peak position in the scattering function $S(q)$ is due to interbead scattering and is inversely proportional to the correlation length of the polyelectrolyte solution $\xi(c)$ for polymer concentrations $c < \tau b^{-3}$ (see eqs 26, 28 and Figure 4).

Above the beads overlap concentration $c > \tau b^{-3}$, beads disappear, and the polymer−polymer scattering function reduces to

$$S(q) = \frac{1}{\dfrac{q^2b^2}{12c} + \dfrac{4\pi l_{\mathrm{B}}f^2}{q^2+4\pi l_{\mathrm{B}}cf} - \tau b^3 + cb^6} \quad (40)$$

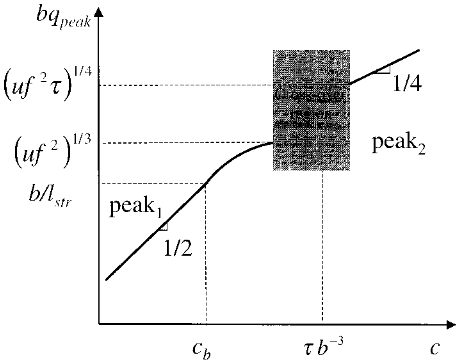

Figure 6. Schematic sketch of the concentration dependence of the peak position in the scattering function. Logarithmic scales.

In this range of polymer concentrations, the peak position of the scattering function $S(q)$ will change with polymer concentration as[38,39]

$$q_{\mathrm{peak}_2} = b^{-1}\sqrt{(48\pi uf^2cb^3)^{1/2} - 4\pi l_{\mathrm{B}}fcb^2} \approx (uf^2cb^3)^{1/4} \quad (41)$$

However, for this peak to be observed, the ratio

$$S(q_{\mathrm{peak}_2})/S(0) \approx (f + (cb^3)^2)/((uf^2cb^3)^{1/2} + (cb^3)^2) \quad (42)$$

has to be much larger than unity. If the opposite condition holds, the peak disappears. It happens when there is less than one charge per correlation volume or $f \ll (cb^3)^2$.

Figure 6 shows the schematic plot of the concentration dependence of the position of both peaks q_{peak_1} and q_{peak_2} in scattering function $S(q)$. In semidilute solution of necklaces at polymer concentrations c for which the correlation length of polyelectrolyte solution $\xi(c)$ is larger than the distance between beads l_{str} the peak position $q_{\mathrm{peak}_1} \approx \xi(c)^{-1}$ shifts toward the region of the higher wavenumbers with increasing polymer concentration c as $c^{1/2}$. As the polymer concentration increases the fraction of the condensed counterions increases as well leading to growth of the beads and to decrease of the effective exponent from $^1/_2$ to a slightly lower value (eq 26). The crossover from string-controlled to bead-controlled necklace solution occurs at concentration c_{b}, when the correlation length of the solution $\xi(c)$ is on the order of the distance between beads l_{str}. In the bead-controlled regime, the peak position is predicted to increase with concentration as $q_{\mathrm{peak}_1} \approx c^{1/3}$. But in this regime, one expects stronger contribution from condensed counterions. Near the bead overlap concentration $c \approx \tau b^{-3}$, our two zone model does not work well. At this concentration there is a crossover between interbead scattering with $q_{\mathrm{peak}_1} \approx b^{-1}(uf^2)^{1/3}$ for $c < \tau b^{-3}$ and scattering from concentrated polyelectrolyte solution without necklace structure for $c > \tau b^{-3}$. In this concentration range, the peak position shifts toward the region of higher q values as $q_{\mathrm{peak}_2} \approx b^{-1}(uf^2cb^3)^{1/4}$. Thus, there is a sharp crossover in the peak position from $q_{\mathrm{peak}_1} \approx b^{-1}(uf^2)^{1/3}$ to $q_{\mathrm{peak}_2} \approx b^{-1}(uf^2\tau)^{1/4}$. The peaks at $q_{\mathrm{peak}_1} \approx \xi(c)^{-1}$ for $c < \tau b^{-3}$ and $q_{\mathrm{peak}_2} \approx b^{-1}(uf^2cb^3)^{1/4}$ for $c > \tau b^{-3}$ have qualitatively different physical origins, and their intensities have different concentration dependences. The necklace peak in the bead-controlled regime grows with concentration due to counterion condensation. The intensity of the peak in the concentrated polyelectrolyte solution for $c > \tau b^{-3}$ decreases with polymer concentration (see eq 40).

V. Phase Separation of Necklaces

Strong electrostatic attraction of counterions to beads for larger values of parameter $\epsilon_c \gg 1$ forces polyelectrolyte solution to phase separate into two phases: the concentrated and the dilute ones. The equilibrium polymer concentrations in these two phases are determined from the balance of the osmotic pressure and the chemical potentials.

The free energy density in the dilute phase is obtained by multiplying the free energy of a necklace with its counterions (eq 19 with substituted $\tilde{c}$ from eq 21) by the density of polyelectrolyte chains c_{dil}/N and adding it to the entropy of mixing of polymer chains

$$\frac{1}{V}\frac{F_{dil}(c_{dil})}{kT} = \frac{c_{dil}}{N}\ln\frac{c_{dil}}{Ne} + c_{dil}f\left(\frac{1}{3}\epsilon_c x^{2/3} + \ln(1-x) + \ln f\tau - f^{-1}\tau^2\right) \quad (43)$$

The free energy of the homogeneous concentrated polyelectrolyte solution with monomer density c_{conc} can be written as follows

$$\frac{1}{V}\frac{F_{conc}(c_{conc})}{kT} \approx \frac{c_{conc}}{N}\ln\frac{c_{conc}}{Ne} + fc_{conc}\ln\frac{fc_{conc}}{e} - \frac{\tau b^3 c_{conc}^{\ 2}}{2} + \frac{b^6 c_{conc}^{\ 3}}{6} \quad (44)$$

where the first and the second terms describe the entropy of mixing of polymer chains and counterions and the last two terms are from the virial expansion of the Flory−Huggins free energy. The balance of the osmotic pressure ($\pi = -F/V + c\partial(F/V)\partial c$) in the two phases leads to the following equation:

$$\frac{c_{dil}}{N} + fxc_{dil} + f(1-x)c_{dil}\exp\left(-\frac{2\epsilon_c}{3x^{1/3}}\right) \approx \frac{c_{conc}}{N} + fc_{conc} - \frac{\tau b^3 c_{conc}^{\ 2}}{2} + \frac{b^6 c_{conc}^{\ 3}}{3} \quad (45)$$

Neglecting the small $1/N$ and f terms we obtain the polymer concentration in the concentrated phase c_{conc} determined by the balance between the second and the third virial terms. This concentration c_{conc} is on the order of the monomer concentration inside the beads:

$$c_{conc} \approx \rho \approx \tau b^{-3}\ (46) \quad (46)$$

The polymer concentrations in the two phases can now be found by equating the chain's chemical potentials. Differentiation of the free energy density in the concentrated phase eq 44 and in the dilute phase eq 43 with respect to polymer concentration c/N gives the chemical potential of the chains in the concentrated phase

$$\frac{\mu_{conc}}{kT} \approx \ln\frac{c_{conc}}{N} + fN\ln fc_{conc} - N\tau^2 \quad (47)$$

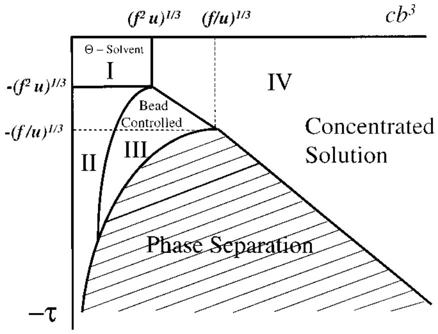

Figure 7. Phase diagram of hydrophobic polyelectrolytes. Logarithmic scales.

and in the dilute phase ($\tilde{c}(c_{dil}) \ll 1$)

$$\frac{\mu_{dil}}{kT} \approx \ln\frac{c_{dil}}{N} + fN\ln\frac{f\tau}{b^3} + fN\left(\frac{\epsilon_c}{3}x^{2/3} + \ln(1-x)\right) - N\tau^2 \quad (48)$$

From the balance of the chemical potentials we can obtain the relation between the fraction of the free counterions x, the strength of the electrostatic potential ϵ_c, and the ratio of polymer concentration in the dilute and the concentrated phases

$$\ln\frac{c_{dil}}{\rho} \approx -fN\left(\frac{\epsilon_c}{3}x^{2/3} + \ln(1-x)\right) \quad (49)$$

Solving this equation together with eq 21 and assuming that $fN \gg \epsilon_c/x$, we can write the relation between the fraction of the free counterions x_{dil} on the coexistence curve and the parameter ϵ_c

$$\epsilon_c(x_{dil}) \approx -\frac{3\ln(1-x_{dil})}{x_{dil}^{\ 2/3}} \quad (50)$$

To find the polymer concentration in the dilute phase, the value of the parameter $\epsilon_c(x_{dil})$ given by eq 50 has to be substituted into the expression for the reduced concentration $\tilde{c}(\epsilon_c,x)$ in eq 21. In the limit of $x_{dil} \rightarrow 1$ and $\epsilon_c \gg 1$ this substitution results in

$$c_{dil} \approx \frac{\tau}{b^3}\exp(-\epsilon_c) \quad (51)$$

The last equation gives the dependence of the polymer concentration in the dilute phase on the effective temperature τ.

The results of this section are summarized in Figure 7, which shows the schematic phase diagram of a salt-free solution of hydrophobic polyelectrolytes. The shaded area corresponds to the two phase region. Above the critical temperature for the values of the parameter $\tau < (f/u)^{1/3}$, a polyelectrolyte solution is stable with respect to phase separation. In regime I of the phase diagram (Figure 7), the thermal blob size $\xi_T \approx b/\tau$ is larger than the electrostatic blob size $D_e \approx D_b \approx b(uf^2)^{-1/3}$. For the range of the effective temperatures $\tau < (uf^2)^{1/3}$ the polymer−solvent interactions are not strong enough to collapse chains, and they adopt the conformations similar to the ones for polyelectrolytes in a Θ-solvent (regime I). In regime II the polymer−solvent interactions start to dominate at small length scales and polyelectrolytes form necklace globules. Depending on polymer concentrations the chains can either be in a dilute regime for polymer concentration below the overlap concentration c^* (see eq 25) or in a semidilute regime for $c > c^*$. In the semidilute regime the correlation length ξ decreases with increasing polymer concentration c (see eq 26). The correlation length ξ becomes on the order of the length of a string l_{str} connecting two neighboring beads at polymer concentration $c \approx c_b$ (see eq 27). At this polymer concentration the system crosses over into the so-called bead-controlled regime in which there is one bead per every correlation volume ξ^3 and polyelectrolyte solution can be viewed as a strongly correlated charged colloidal liquid of beads (regime III). If the polymer concentration increases further, the size of the beads increases due to counterion condensation. For the effective temperature $\tau < f^{1/3}u^{-1/3}$, the correlation length ξ becomes on the order of the size of a bead D_b at polymer concentration $c \approx \tau b^{-3}$. At higher polymer concentrations the system crosses over into concentrated polyelectrolyte solution (regime IV). However, if the value of the parameter τ is larger than $f^{1/3}u^{-1/3}$ the system will phase separate into concentrated polymer solution and colloidal liquid of globules.

The phase separation in the solution of hydrophobic polyelectrolytes was investigated by Dormidontova et al.[40] Using the weak-crystallization theory, the authors have calculated a phase diagram of hydrophobic polyelectrolytes. They found that the regions of stable spherical microdomains organized into body-cubic-centered lattice, cylindrical microdomains forming a triangular lattice and lamellar microdomains. These microdomain structures can also coexist with each other as well as with the homogeneous concentrated and dilute polymer phases. The specific feature of the phase diagram in ref 40 is the domain of stability of the cylindrical microdomains that separates the phase coexistence region into two parts. Our phase diagram is qualitatively different from the diagram calculated in ref 40.

It should be pointed out that the weak crystallization theory[40] is only correct close to the spinodal line of the homogeneous state where the relative amplitude of the density waves, corresponding to the formation of the microdomain structure, are smaller than unity. However, one can expect that in the strong segregation limit with a well-defined interface between the concentrated polymer and pure solvent regions, the cylindrical microdomains are unstable with respect to capillary waves that forces formation of the necklacelike structure of spherical microdomains connected by narrow string of chains. Similar effect causes cylindrical polyelectrolyte globules[5] to transform into necklacelike structures.[11,21] This instability may qualitatively alter the low-temperature region of the phase diagram of hydrophobic polyelectrolytes calculated in ref 40.

VI. Conclusion

We have presented a theory of phase separation and counterion condensation in solutions of hydrophobic polyelectrolytes. In dilute and semidilute solutions, hydrophobic polyelectrolytes form necklace globules consisting of beads connected by strings. With increasing polymer concentration, the solutions of hydrophobic polyelectrolytes may phase separate into concentrated and dilute phases or stay homogeneous depending on the value of the parameter $\epsilon_c \approx (u/f)^{1/3}\tau$—the strength of the electrostatic interaction in units of the thermal energy kT between a bead and a counterion at its surface. Hydrophobic polyelectrolytes with large values of the parameter $\epsilon_c \gg 1$ phase separate into concentrated and dilute phases. The polymer concentration in a dilute phase is exponentially low $c_{dil} \approx \tau b^{-3} \exp(-\epsilon_c)$ for large values of the counterion condensation parameter ϵ_c. This phase separation is triggered by the counterion condensation inside beads. However, hydrophobic polyelectrolytes for which the value of the parameter ϵ_c is smaller than unity are stable with respect to phase separation throughout the entire concentration interval.

The correlation length ξ of the semidilute polyelectrolyte solution of necklaces decreases with polymer concentration in both string-controlled and bead-controlled regimes. The correlation length ξ demonstrates weaker concentration dependence in comparison with that without counterion condensation.[17] This correlation length ξ corresponds to the peak in the scattering function at wavenumber $q_{peak_1} \approx \xi(c)^{-1}$ in solution of necklaces below beads overlap. Above the beads overlap concentration, there are no necklaces, and the concentrated polyelectrolyte solution may exhibit a qualitatively different peak in the scattering function at higher wavenumbers q_{peak_2}.

The size R of polyelectrolyte chain decreases throughout the semidilute solution of necklaces. In the bead-controlled regime, it becomes smaller than the Gaussian size of the chain $b\sqrt{N}$. At bead overlap concentration $c \approx \tau b^{-3}$, we expect the sharp increase of the polymer size back to the Gaussian value $b\sqrt{N}$ at which it saturates throughout the concentrated regime $c > \tau b^{-3}$.

Computer simulations of the solution of polyelectrolytes in poor solvent were performed by Kremer's group.[22,25] At low polymer concentrations, the polyelectrolyte chains were observed to form necklaces of beads connected by strings. As polymer concentration increases, the fraction of the condensed counterions on the chain increases and chains shrink by decreasing the length of strings and the number of beads on the chain. Eventually, at higher polymer concentrations, a polyelectrolyte chain forms one globule with the finite fraction of counterions inside it. However, it is possible that at high polymer concentrations the system is kinetically trapped in a metastable state,[25] and much longer simulations are required to reach the true thermodynamic equilibrium and to test the stability of these globules. At the highest polymer concentration reported in refs 22 and 25, polymer chains interpenetrate, leading to a concentrated polyelectrolyte solution. The chain size is observed to increase back toward its Gaussian value. The nonmonotonic dependence of the chain size with polymer concentration is in qualitative agrement with our predictions (see Figure 5).

The evolution of the polyelectrolyte solution with increasing polymer concentration was monitored in small-angle X-ray (SAXS) scattering experiments by Waigh et al. for solutions of poly[2-(methacryloyloxy)-ethyltrimethylammonium 1,1,2,3,3,-pentacyanopropenide] (MPCP) in acetonitrile. In the low concentration range, the peak position q_{peak} of the scattering function increases as $c^{0.45}$ with exponent close to the ordinary polyelectrolyte exponent 0.5. It is however possible that the weaker concentration dependence of q_{peak} is due to a counterion condensation effect. At the intermediate concentrations, the peak position has a much weaker concentration dependence $q_{peak} \sim c^{0.137}$ which can be attributed to the predicted behavior of the correlation length near $c \approx \tau b^{-3}$ (see Figure 6). The polyelectrolyte peak disappears in the polymer concentration range 235−404 g/L and reappears again above 422 g/L at high q values. The disappearance and reappearance of the peak in the scattering function may be related with the crossover to concentrated polyelectrolyte solutions. The scattering in the concentrated regime is expected to be qualitatively different from that in semidilute solution of necklaces. Concentration dependence of scattering intensity is qualitatively different at low (c < 235 g/L) and at high (c > 422 g/L) polymer concentrations. The scattering intensity increases at low polymer concentration and decreases at high polymer concentrations, as predicted in section IV. This difference is due to qualitative difference between the two regimes. The growth of the intensity at low concentrations is due to increased mass of the beads caused by counterion condensation. The decrease of scattering intensity at high concentrations is due to suppression of the polymer density fluctuations in this concentration range. Another important observation is the high viscosity of the samples with polymer concentrations c > 422 g/L in the so-called "gel phase". It may be related to our prediction of dramatic viscosity increase at bead overlap concentration caused by strong increase in chain size. Our simple scaling model is unable to describe the details of the transition at bead overlap concentration. More sophisticated theory, more extensive computer simulations, and experiments are needed to reveal the unique features of this interesting transition.

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